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“Guide to the expression of uncertainty in measurements”

Kattathu J Mathew

Team Lead (Mass Spectrometry / Plasma Spectrometry)

Actinide Analytical Chemistry

This publication has been assigned

LA-UR-

October 2017



Enabling Objectives

- **Provide a working knowledge of the ISO GUM method to estimation of uncertainties in safeguards measurements**
- **Introduce GUM terminology**
- **Provide brief historical background of the GUM methodology**
- **Introduce GUM Workbench software**
- **Isotope ratio measurements by MS will be discussed in the next session**

Disclaimer

- Various software packages that assist in implementing the ISO GUM approach to uncertainty evaluation are available. Some examples are: DFM-GUM (tool in Excel), QMSys Uncertainty Workshop (Softguide GmbH), NPLUnc (developed at NPL), Kragten Spreadsheet (tool in Excel), Uncertainty Sidekick freeware (from Integrated Sciences Group, www.isgmax.com)
- For this workshop, we will use the GUM Workbench Software.
- LANL/DOE is not endorsing any specific software

Announcements

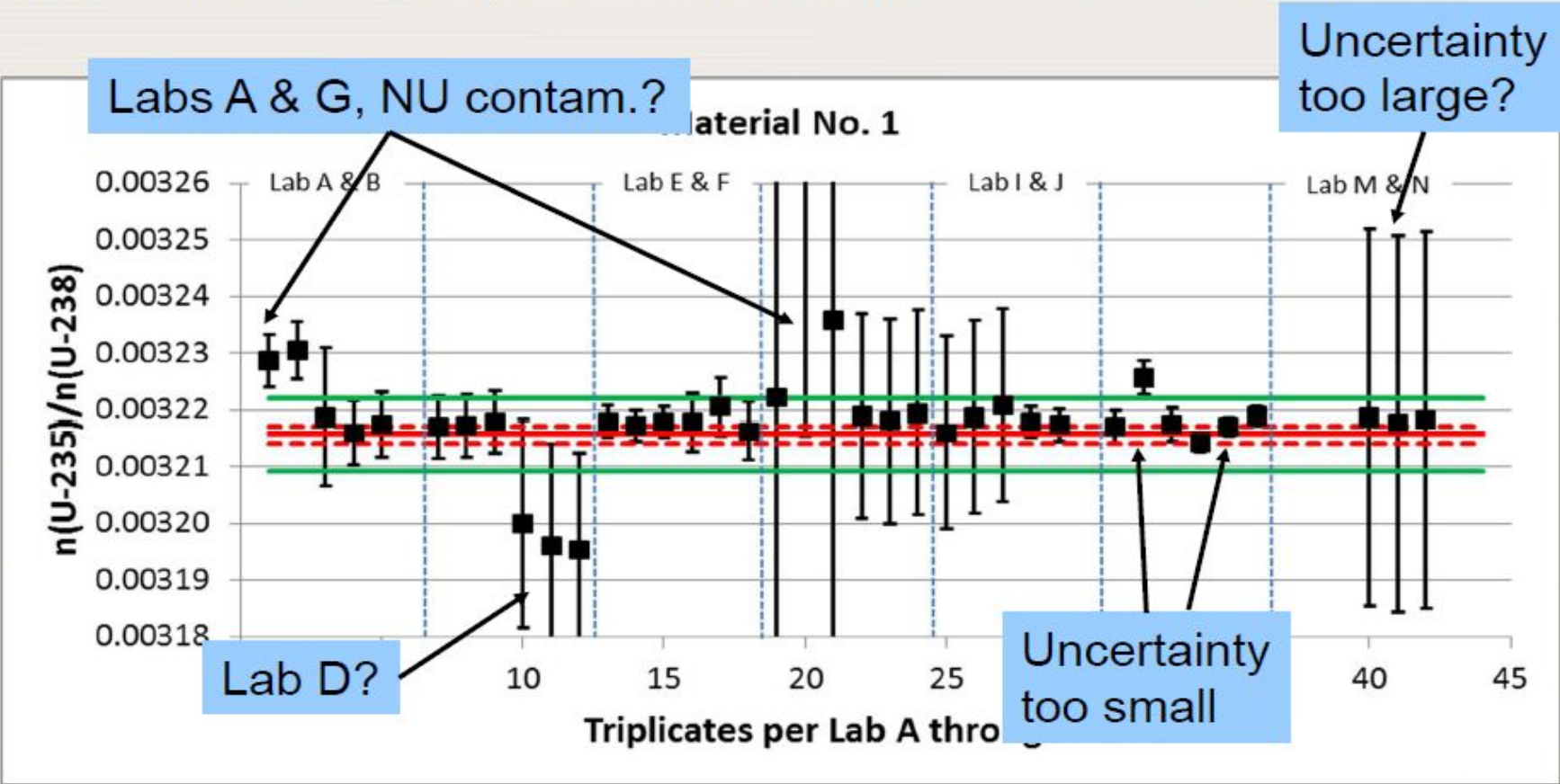
- **Logistics (lunch/coffee breaks)**
- ✓ **Questions are welcome anytime!**
 - ? Who is familiar with ISO GUM
 - ? Who uses ISO GUM on a routine basis
 - ? Who is familiar with GUM Workbench Software
 - ? Who use GUM Workbench on a routine basis
- **Emergency Evacuations / Facility Safety Related Info**
- ✓ **Exercises throughout the workshop can be completed individually or in teams**

Uncertainties in Safeguards Measurements

- **Generally assessed using Measurement Evaluation programs administered by national/International safeguards organizations**
 - ❖ IAEA NM Round Robin
 - ❖ Measurement Campaigns organized by IRMM
 - ❖ SME program administered by NBL

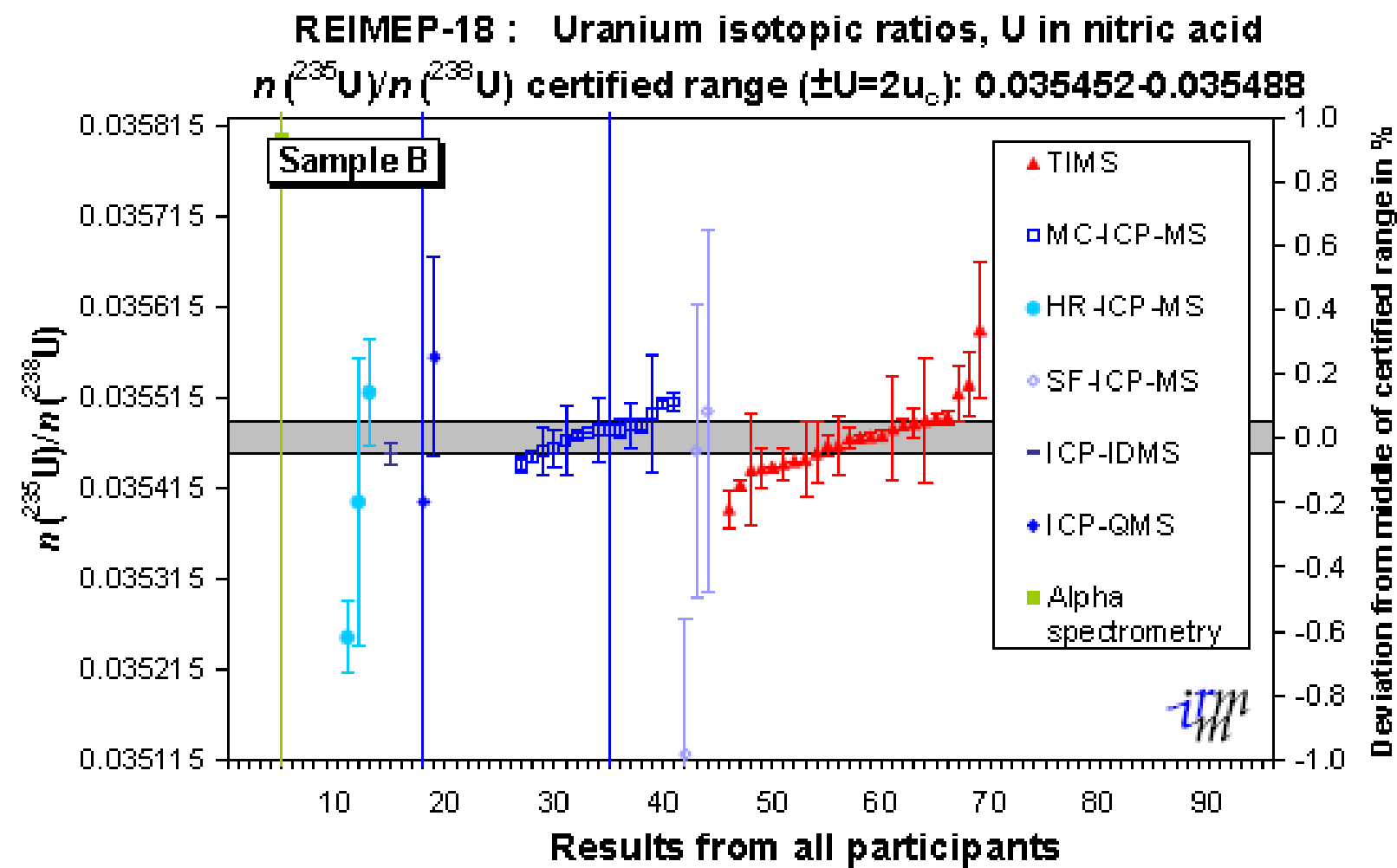
Uncertainties in Safeguards Measurements

- Material No 1, depleted uranium, 0.3 % U-235



Squares: reported data $\pm$ Uncertainty (95 %)
Green lines: ITV(sys)
Red lines: certified $\pm$ Uncertainty (95 %)

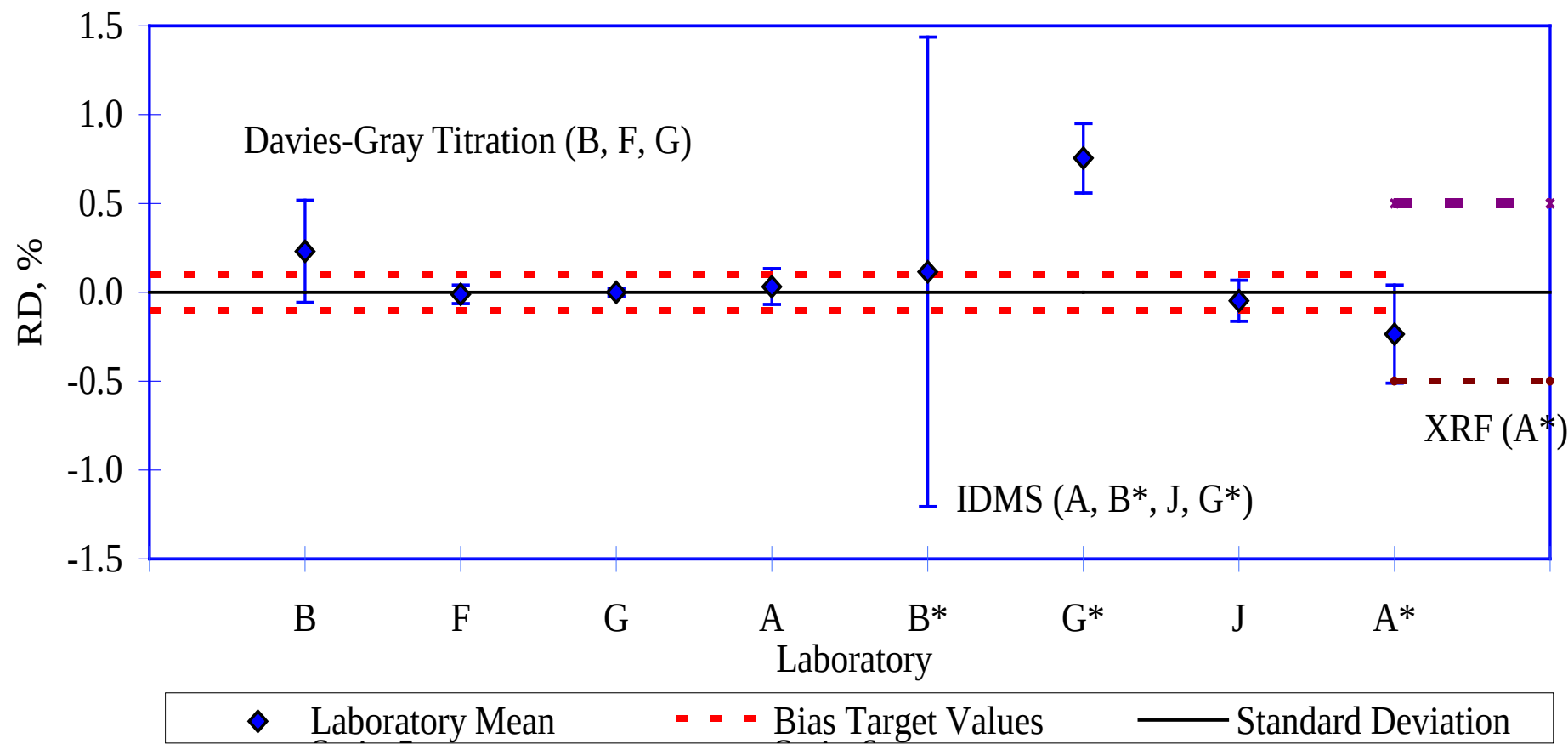
Uncertainties in Safeguards Measurements



Regular European Inter-laboratory Measurement Evaluation Program (REIMEP)
Campaign in 2006 - U in nitric acid

Uncertainties in Safeguards Measurements

New Brunswick Laboratory Safeguards Measurement Evaluation Program
UNH - Percent U



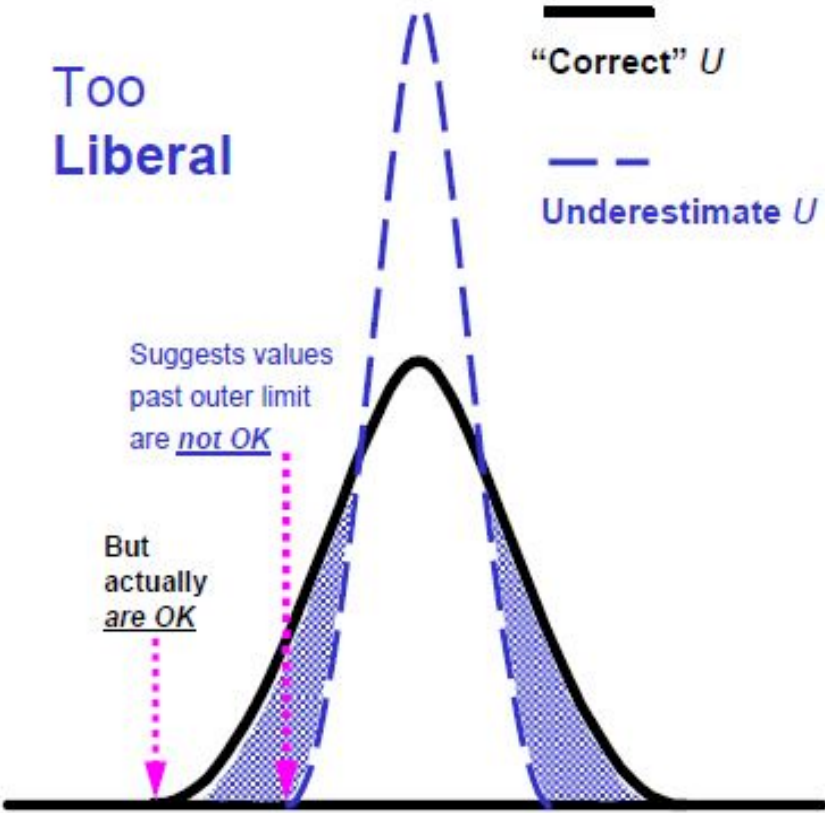
Uncertainties in Safeguards Measurements

Common Thread from Measurement Evaluation studies

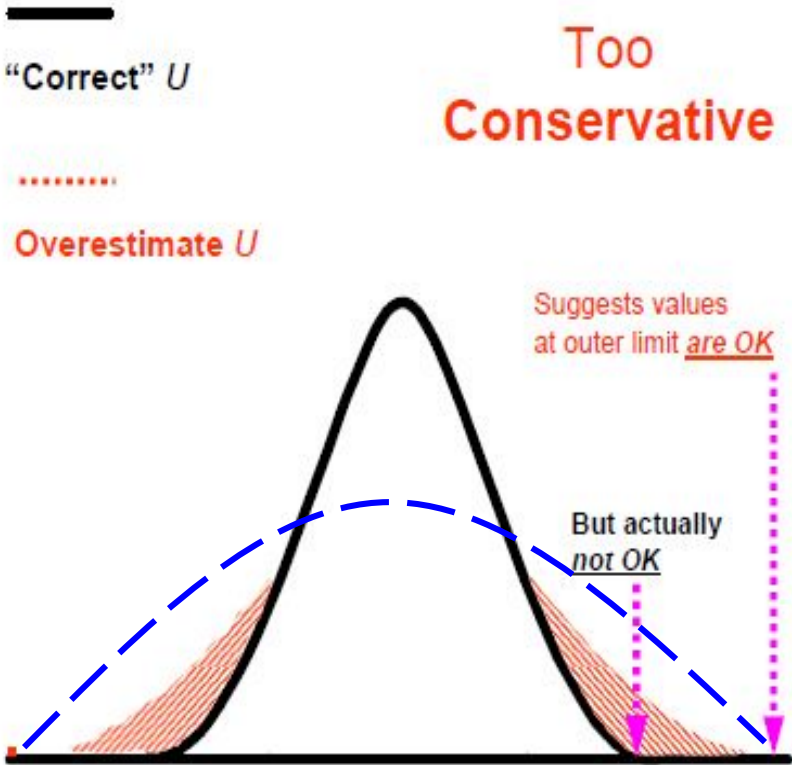
- **Measurement Uncertainties**
 - ❖ **Often underestimated**
 - ❖ **Also overestimated**
 - ❖ **Rarely – Just Right (!!!!!)**

Uncertainties in Safeguards Measurements

Effect of Underestimating
Uncertainty, U



Effect of Overestimating
Uncertainty, U



Uncertainties in Safeguards Measurements



The Goldilocks effect –
Just the right size bed

Measurements need “Just the Right Size Uncertainties”

Guide to the Expression of Uncertainty in Measurement (GUM)

GUM – An Introduction

Module 1

**Authors: K. J. Mathew (LANL)
&
S. Bürger (IAEA)**

GUM – An Introduction

➤ Enabling Objectives

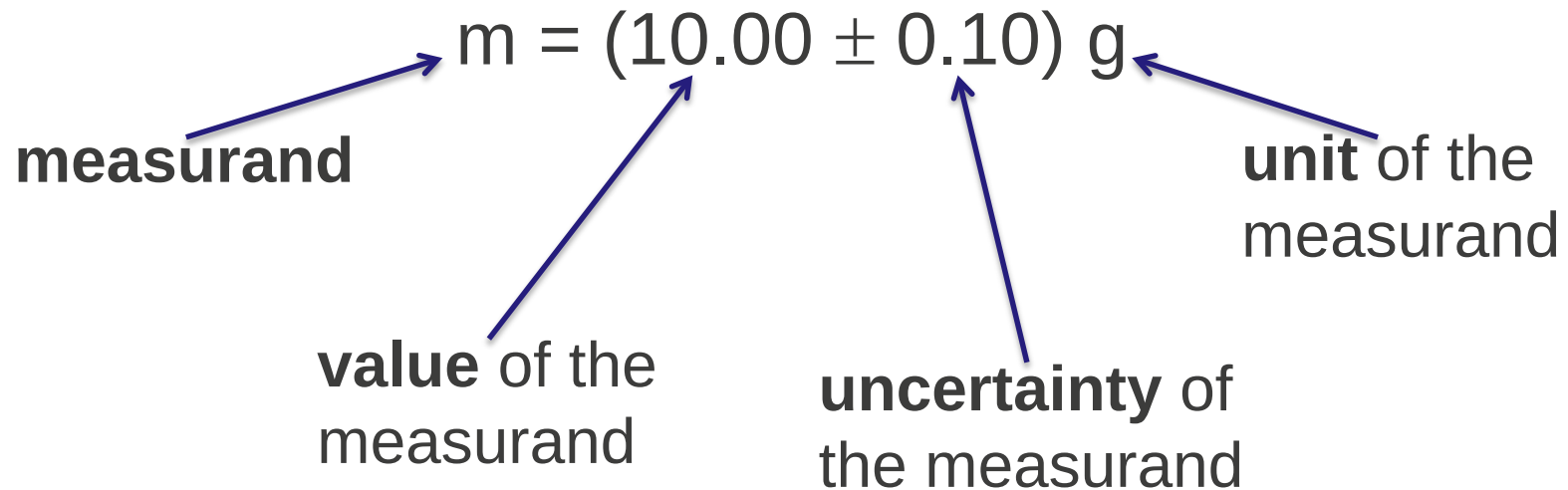
- ❑ What is GUM and the ‘GUM Guide’
- ❑ What is the GUM approach and what are its merits
- ❑ Introduce GUM terminology
- ❑ Statistical principles as applicable to GUM

GUM – An Introduction

- Part 1: General remarks, motivation, references
- Part 2: GUM as a step-by-step approach to quantification of uncertainty
- Part 3: Definition of terms & terminology
- Part 4: The role of the “GUM Workbench” software program in this workshop
- Part 5: Review of statistical principles

GUM – An Introduction

- A quantity subject to measurement (called **measurand**) is stated with its **value**, **unit**, and **uncertainty**

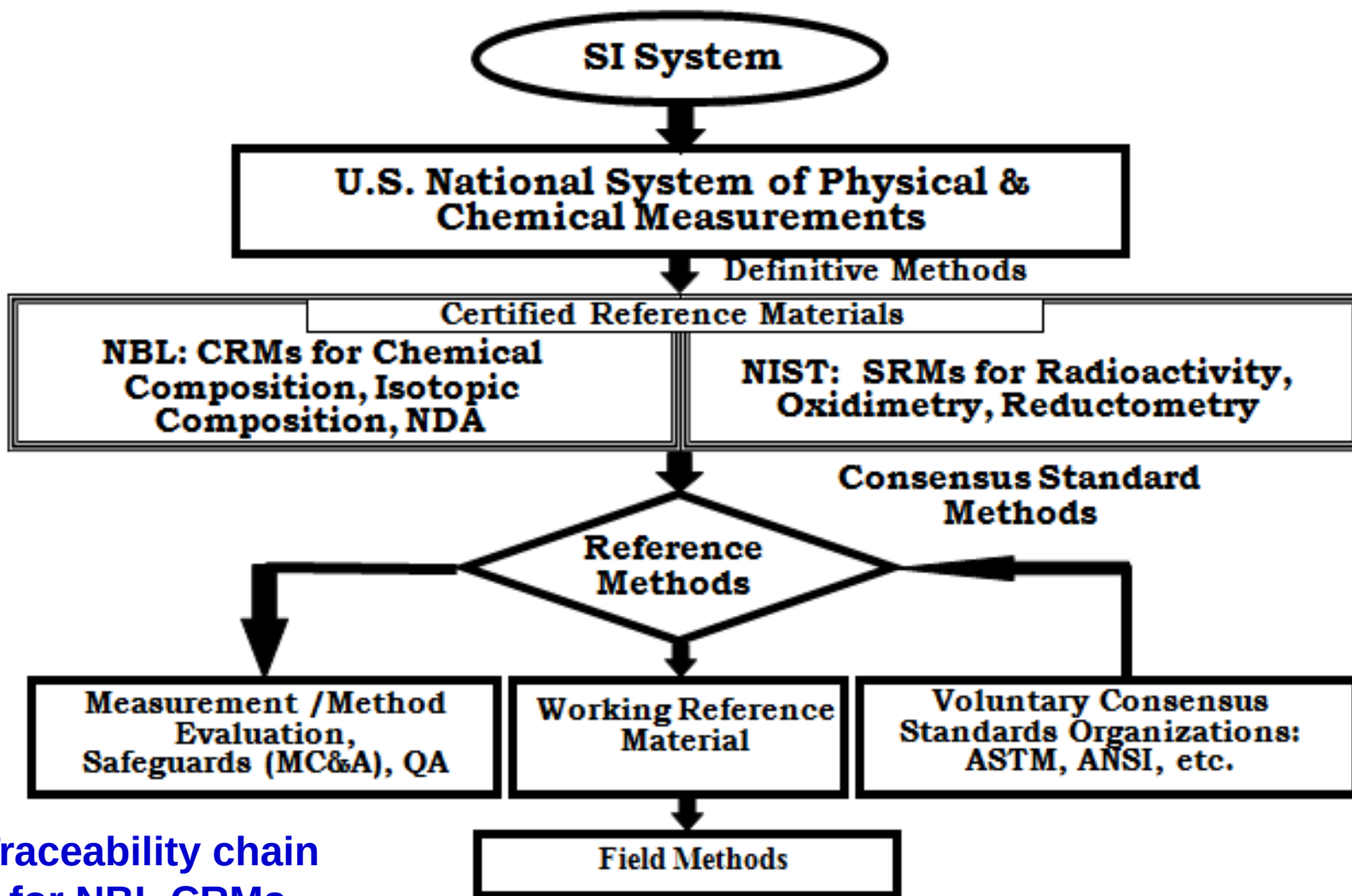


GUM – An Introduction

- A statement of the associated measurement uncertainty is an integral part of the measurement (“no measurement is exact”!) and provides, for example:
 - ❖ Confidence in the value of the measurand
 - ❖ Judgement on significance of differences between measurement results
 - ❖ Quality Assurance
 - ❖ Capability of the measurement procedure
 - ❖ Integral part of metrological traceability

GUM – An Introduction

United States Nuclear Measurement System



Traceability chain
for NBL CRMs

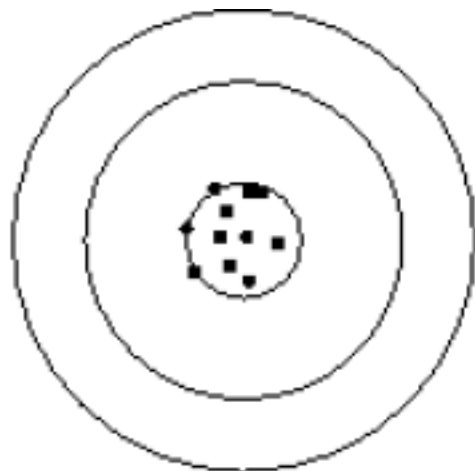
GUM – An Introduction



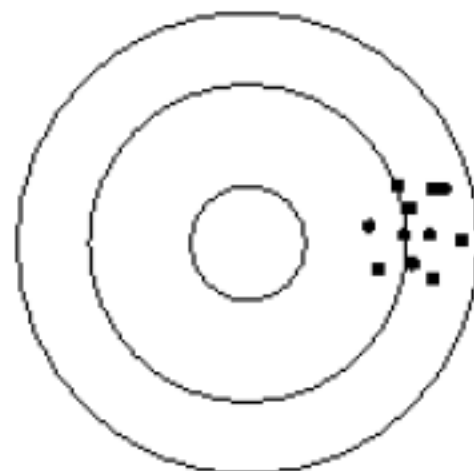
Traceability – It is all about the nail (courtesy of K. Inn)

GUM – An Introduction

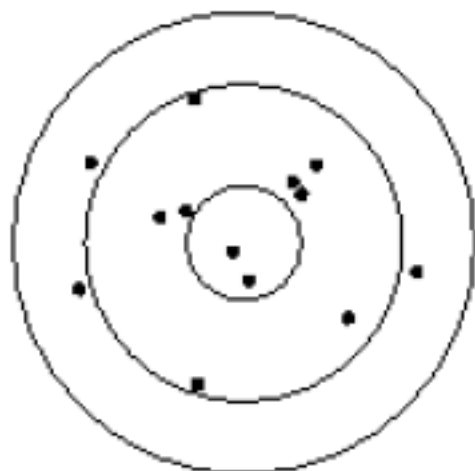
- Measurement reliability is fundamentally related to the metrology skill and craftsmanship of the practitioner.
- CRMs and metrology are parts of the tool kit of the practitioner demonstrate measurement traceability.
- Measurement traceability is the transfer of accuracy through linked calibrations to the SI unit, Bq, with stated uncertainties.
- Traceability is demonstrated through documented highly reliable procedures, and validated through verification measurements with stated uncertainties.
- Measurement uncertainty is the quantitative expression of estimated confidence in a result.
- The fundamental basis for estimating measurement uncertainty is metrology (knowledge of measurement system).



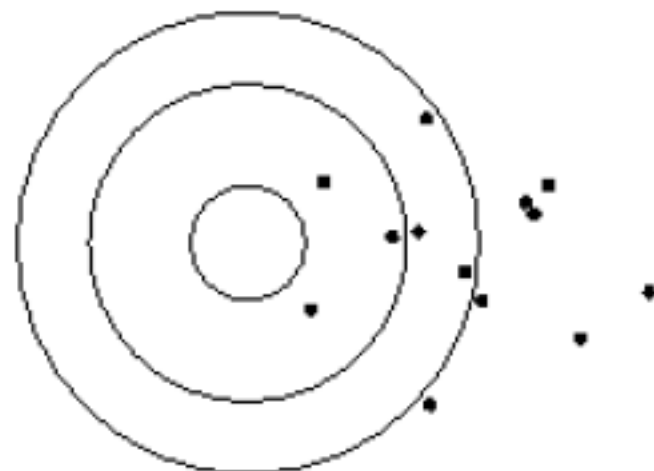
Precise and accurate



Precise, but not accurate

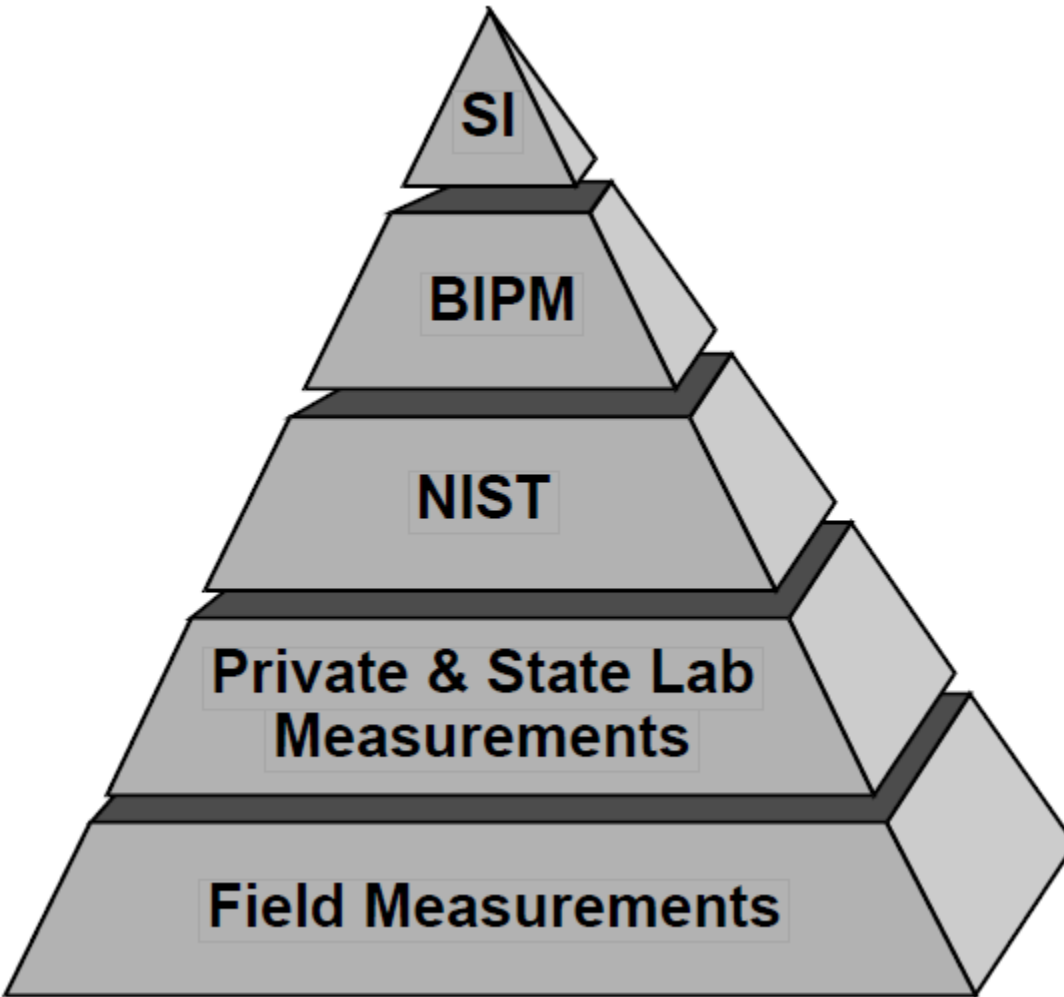


Accurate, but not precise



Neither precise nor accurate

GUM – An Introduction



Traceability: “property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty.” [NIST, VIM]

GUM – An Introduction

- Reliable measurement uncertainty will improve our understanding in the following areas:
 - ❖ Research and development, engineering
 - ❖ International comparison of measurement standards
 - ❖ Calibration, quality assurance, accreditation, and certification
 - ❖ Generating reference data
 - ❖ Enforcing laws and regulations
 - ❖ Trade
 - ❖ Judgment of safety risks

GUM – An Introduction

- Just as the use of the International System of Units (SI) brings coherence to measurements ...
- ... the Guide to the Expression of Uncertainty in Measurement (GUM) provides a consistent and standardized way of expressing uncertainty in measurements

GUM – An Introduction

- The GUM approach was developed by seven international scientific organizations (1970's to present)
 - ❖ International Bureau of Weights and Measures (BIPM)
 - ❖ International Electro-technical Commission
 - ❖ International Federation of Clinical Chemistry
 - ❖ International Organization for Standardization (ISO)
 - ❖ International Union of Pure and Applied Chemistry (IUPAC)
 - ❖ International Union of Pure and Applied Physics
 - ❖ International Organization of Legal Metrology

GUM – An Introduction

- In 1977 the CIPM asked BIPM to, in collaboration with national metrology institutes:
 - ❖ Address the problem of the lack of international agreement on expressing uncertainties, and
 - ❖ Propose a specific recommendation for a solution to the problem.
- BIPM convened a Working Group on the Statement of Uncertainties.
- The Working Group issued Recommendation INC-1 (1980) as an overview of the agreed-upon approach to measurement uncertainty evaluation.

The Origin of GUM



GUM – An Introduction

- CIPM approved INC-1 in 1981 and reaffirmed it in 1986 via its own recommendations.
- Because INC-1 was a rather broad outline, the CIPM asked the International Organization for Standardization (ISO) to develop a detailed guide.
- ISO was chosen because it represents the broad interests of industry and commerce.
- ISO Technical Advisory Group on Metrology (TAG 4) was given the responsibility.

History of the GUM

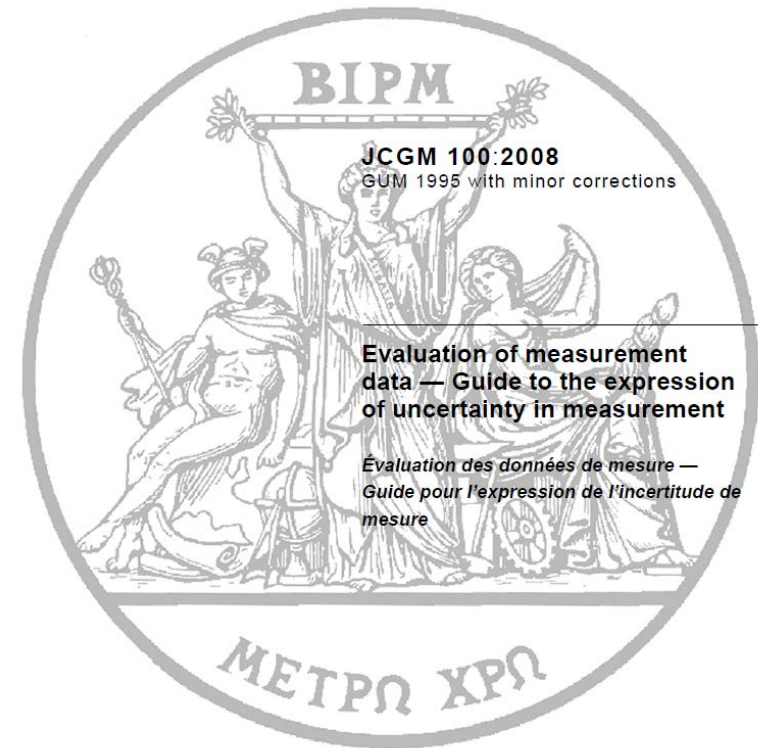
GUM – An Introduction

- ISO TAG4 established Working Group 3 in the late '80's to develop a guidance document based on the recommendation of the BIPM WG to:
 - ❖ Promote full information on how uncertainty statements are arrived at
 - ❖ Provide a basis for the international comparison of measurement results
- The “Guide to the Expression of Uncertainty in Measurement” (GUM) was published in 1993 by ISO, corrected in 1995.
- Additional revisions continue
 - ❖ JCGM 100:2008 is current GUM Guide
 - ❖ JCGM 104:2009 is an intro to the GUM Guide

History of the GUM

GUM – An Introduction

- The GUM approach has been evolving over time ...
- ... and it is published as 'GUM Guide' (i.e., the official GUM document) by ISO and BIPM
- The latest version of the GUM Guide is free for download from <http://www.bipm.org>



Title page of the GUM Guide

GUM – An Introduction

- Today, the GUM approach is regarded as **state-of-the-art** approach to estimation of uncertainty in measurement
- The GUM approach has been adopted by most national metrology institutes in the world
- There is an increasing demand to report GUM compliant uncertainties
- But why GUM instead of, for example, classical error analysis? What are the merits of GUM?

GUM – An Introduction

➤ Merits of GUM

- ❖ It improves the transparency of the uncertainty calculation, i.e., the calculation can be reproduced by others
- ❖ GUM does not separate between random component and systematic component (as classical error analysis does).
- ❖ Instead, they are treated in a more consistent way as the measurand (quantity of interest) is corrected for all recognized significant systematic effects
- ❖ This results in a single combined uncertainty value

GUM – An Introduction

➤ Merits of GUM (contd.)

- ❖ It gives an uncertainty budget which provides a feedback to the analyst and allows to better understand and improve the measurement process
- ❖ Implementing the GUM approach to a specific analytical procedure helps/demands to organize (and reflect upon) the analytical procedure
- ❖ (By now, there are commercial software programs available that assist in performing most or all of the mathematical calculations needed to perform a GUM evaluation)

GUM – An Introduction

➤ References

- ❖ The GUM Guide is published by ISO and BIPM:
 - BIPM JCGM 100:2008; free download including supplementary documents:
www.bipm.org/en/publications/guides/gum.html
 - International Organization for Standardization (ISO), Guide to the Expression of Uncertainty in Measurement, 1995
- ❖ Definitions pertaining to uncertainties are detailed in the BIPM's International Vocabulary of Metrology (VIM); www.bipm.org

GUM – An Introduction

➤ References (contd.)

❖ Additional resources are:

- NIST Technical Note 1297, Guidelines for the Evaluation and Expressing Uncertainties of NIST Measurement Results, 1994 (B. N. Taylor & C. E. Kuyatt)
- European Co-Operation for Accreditation (EA), Expression of the Uncertainty of Measurement in Calibration, EA-4/02, 1999

GUM – An Introduction

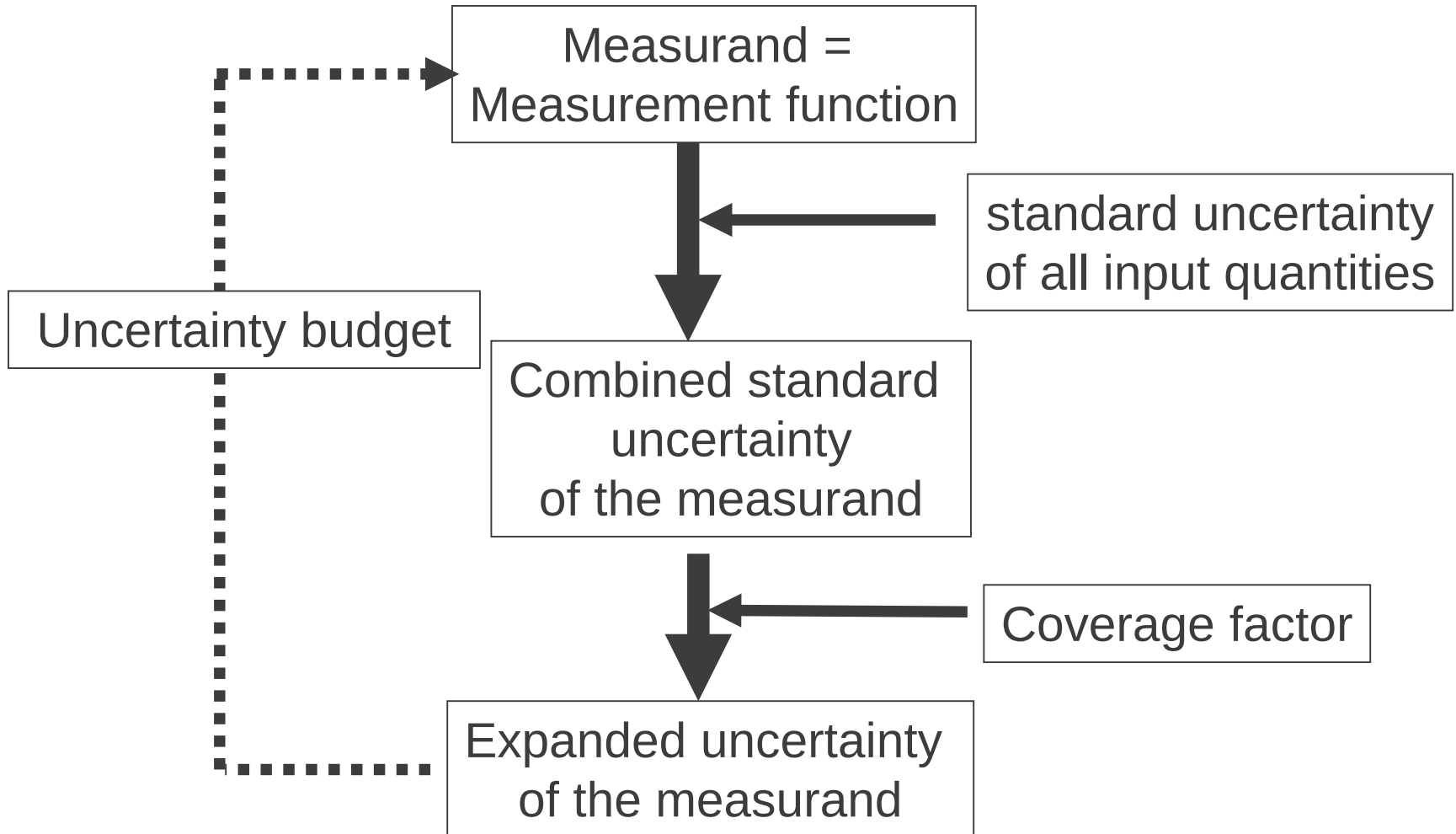
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- Part 5: Review of basic statistical principles

GUM – An Introduction

GUM is a step-by-step approach:

- Define the measurand (i.e., what is the quantity of interest?)
- Derive the measurement function from the measurement procedure (i.e., understand your analytical procedure); identify all input quantities
- Evaluate the uncertainties of the input quantities
- Calculate the combined standard uncertainty
- Using a (selected) coverage factor, calculate the expanded uncertainty of the measurand
- Document all steps in a report; review the uncertainty budget

GUM – An Introduction



GUM – An Introduction

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GUM – An Introduction

Definition of terms according to the GUM Guide:

- **Measurand (symbol “Y”):** quantity intended to be measured

- *Examples:*
 - ❖ *Mass of a sample (measured using a lab balance)*
 - ❖ *Isotope ratio $n(\text{U-235})/n(\text{U-238})$ of a uranium sample (measured using a mass spectrometer)*

GUM – An Introduction

- **Measurement:** set of operations with the objective of determining the value of a quantity (measurand)

- *Examples:*
 - ❖ *Weighing to determine the mass of a sample*
 - ❖ *Mass spectrometry to determine the isotope ratio $n(\text{U-235})/n(\text{U-238})$ of a uranium sample*

GUM – An Introduction

➤ **Measurement function (model equation)**

(symbol “f”): Often, the measurand is not measured directly, but is determined from several **input quantities (symbols “ $X_1, X_2, \dots, X_N$ ”)** using a mathematical relationship

$$Y = f(X_1, \dots, X_N)$$

➤ *Example: weighing of a sample*

$$m_{\text{sample}} = m_{\text{boat+sample}} - m_{\text{boat}}$$

where $m_{\text{boat+sample}}$ and m_{boat} are input quantities;
there might be additional input quantities

GUM – An Introduction

- **Measurement function (model equation) (contd.):** In simple terms, the measurement function shows how all the necessary input quantities are combined to obtain the desired measurement result. A good starting point is the mathematical formula(s) that are used in the Excel data crunching!

GUM – An Introduction

➤ **Measurement function (model equation) (contd.):**

GUM requires that the measurement should be corrected for all recognized significant systematic effects

- ❖ All corrections should be quantified and included (with their standard uncertainties) in the measurement function
- ❖ *Example: The mass spectrometry measurement results need to be corrected for significant atomic and molecular interferences, chemical blank, detector non-linearity, mass fractionation, etc.*

GUM – An Introduction

- **Uncertainty:** Parameter, associated with the results of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand
- ❖ “uncertainty” means doubt, and thus in its broadest sense “uncertainty of measurement” means doubt about the validity of the results of a measurement
- ❖ The old term “error” should NOT be used when referring to “uncertainty”

GUM – An Introduction

- **Uncertainty (contd.):** In practice, there are many possible sources of uncertainty. All significant sources of uncertainties should be accounted
- **Sources of Uncertainties include (among others):**
 - ❖ Variations in repeat observations of the measurand under apparently identical conditions
 - ❖ Approximations and assumptions incorporated in the measurement method / procedure
 - ❖ Inexact values of constants and other parameters obtained from external sources and used in the measurement function

GUM – An Introduction

➤ Sources of Uncertainties (contd.):

- ❖ *Example: When performing mass spectrometry measurements, (significant) sources of uncertainties may include: chemical blank, atomic and molecular interferences, detector calibration, measurement repeatability, mass fractionation, etc.*
- ❖ *“Often, measuring instruments and systems are adjusted or calibrated using measurement standards and reference materials to eliminate systematic effects; however, the uncertainties associated with these standards and materials must still be taken into account” [GUM Guide]*

GUM – An Introduction

- **Standard uncertainty (symbol “u”):** measurement uncertainty expressed as a standard deviation (of the mean)
- Within GUM, a standard uncertainty needs to be estimated for each significant source of uncertainty. This can be done using Type A and/or Type B evaluation:
- **Type A evaluation of uncertainty:** method of evaluation of uncertainty by statistical analysis of a **series of observations**
- **Type B evaluation of uncertainty:** method of evaluation of uncertainty by means **other than Type A**

GUM – An Introduction

- **Standard uncertainty (contd.):** i.e., a standard uncertainty can be estimated either as a Type A evaluation or Type B evaluation.
- ❖ To calculate the uncertainty of the measurand, standard uncertainties for all input quantities (i.e., significant source of uncertainty) are needed
- ❖ Usually, some of the standard uncertainties (of the input quantities) are evaluated as Type A and some are evaluated as Type B

GUM – An Introduction

➤ Type A evaluation of uncertainty (contd.):

- ❖ *Examples for Type A evaluation: Standard deviation (of the mean) of replicate measurements; Standard deviation from the fit of a calibration curve; Characteristic standard deviation derived from a control chart*
- ❖ Remark: a Type A uncertainty is NOT synonymous to a random uncertainty or the old term “random error”

GUM – An Introduction

- **Type B evaluation of uncertainty (contd.):**
- *Examples for Type B evaluation: Manufacturer's quoted uncertainty bounds for a measuring instrument; historical agreement among independent laboratories; non-statistical uncertainty bound for a calibration standard; result of theoretical computations; scientific judgment*
- Remark: a Type B uncertainty is NOT synonymous to a systematic uncertainty or the old term “systematic error”

GUM – An Introduction

- Why is Type B evaluation needed? Why is scientific judgment an option?

Because “[...] *the cost of collecting statistical data may be too high; the particular factor in question was not known to affect the measurement process until after the measurements were made; other indirectly-related or incompletely-specified information*”

GUM – An Introduction

- **Standard uncertainty (contd.):** One is tempted to see some overlap between the terms “Type A evaluation” $\leftrightarrow$ “random uncertainty”, as well as “Type B evaluation” $\leftrightarrow$ “systematic uncertainty”, but they are not the same and must not be confused!
- The terms “Type A evaluation” and “Type B evaluation” refer to the methods of evaluation

GUM – An Introduction

- “random” component can be “Type A” or “Type B”
- “systematic” component can be “Type A” or “Type B”
- Type A and Type B refer to the methods of evaluation

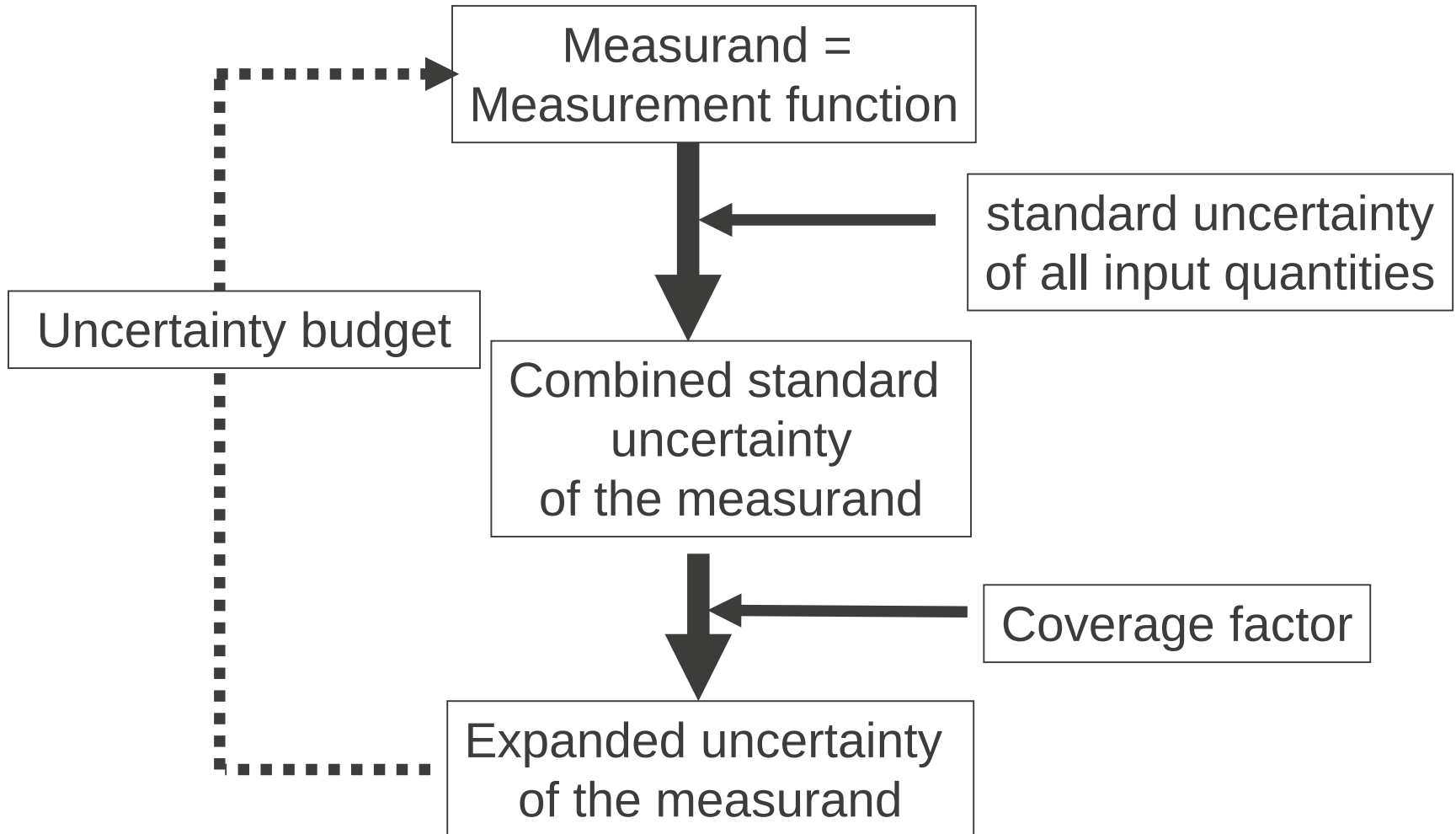
GUM – An Introduction

- **Combined standard uncertainty (symbol “ u_c ”):** standard uncertainty of the result of a measurement (measurand).
- It is obtained by the law of propagation of uncertainty using the measurement function and the standard uncertainties of all input quantities. The law of propagation of uncertainty is similar to the formula for propagation of error, traditionally called law of error propagation, in classical error analysis.

GUM – An Introduction

- **Combined standard uncertainty (contd.):** All uncertainties that contribute to the final uncertainty of the measurand are combined, i.e. Type A and Type B uncertainties are combined to one final value. The GUM approach assumes that all significant systematic effects are corrected for in the measurement function and uncertainties are assigned to the correction factors.

GUM – An Introduction



GUM – An Introduction

- **Coverage factor (symbol “k”):** numerical factor used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty
- This allows to assign a level of confidence to the uncertainty of the measurand, for example 95 % or 99 % or as needed

GUM – An Introduction

- **Expanded uncertainty (symbol “U”):** quantity defining an interval about the measurand that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand:

$$U = k \cdot u_c$$

- The result of the measurement is then conveniently expressed as: $Y = y \pm U$
- *Example:*

$$m_{\text{sample}} = 0.8225 \text{ g} \pm 0.0010 \text{ g}$$

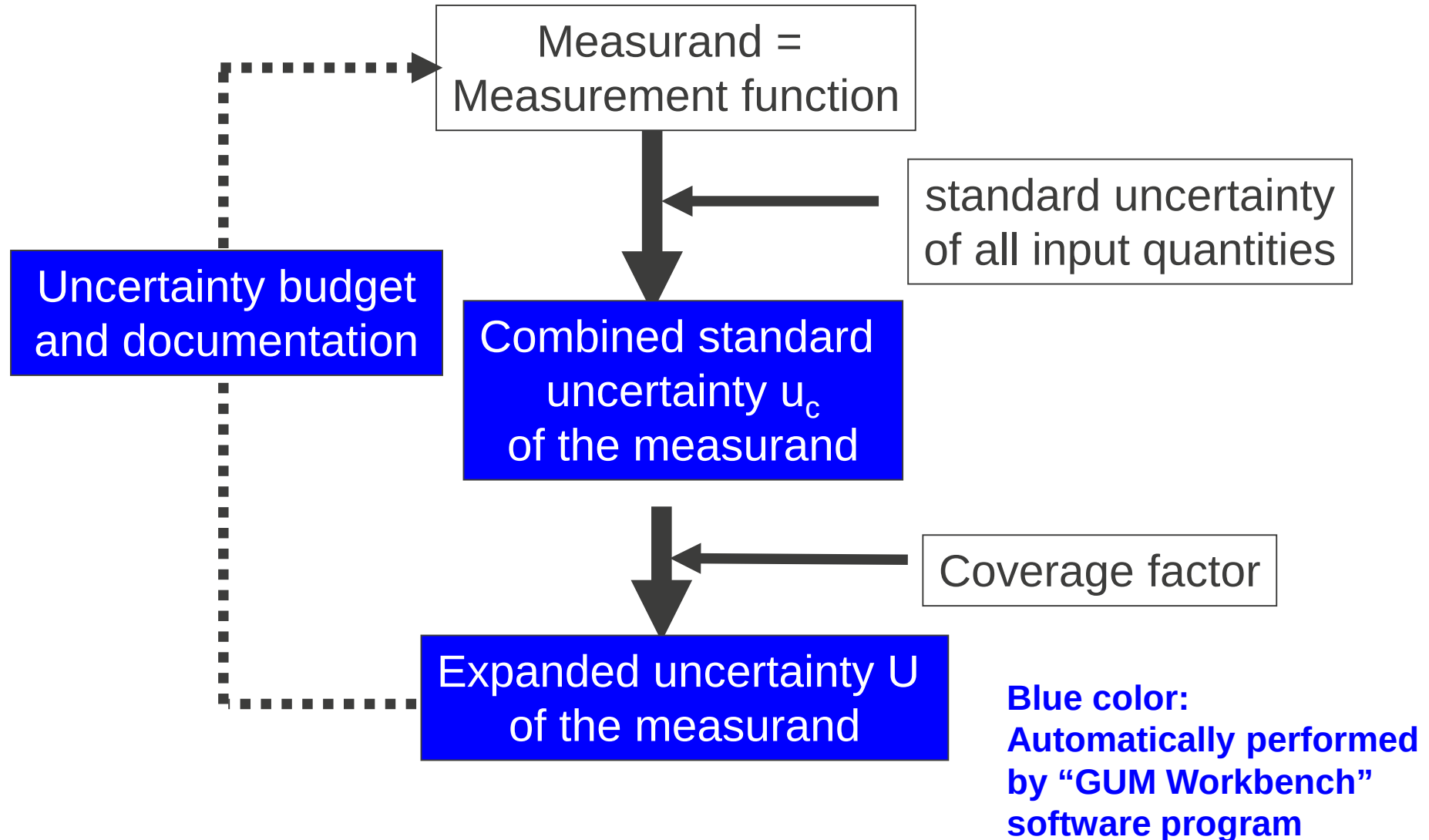
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GUM – An Introduction

- “GUM Workbench” software (commercially available) program helps implementing the GUM Guide
- Workbench performs automatically:
 - ❖ Propagate the uncertainties using the model function and calculate the combined standard uncertainty
 - ❖ Calculate expanded uncertainty and uncertainty budget
 - ❖ Provide an uncertainty evaluation report
 - ❖ (Normalizes probability distributions of input quantities, calculates correlations, and tests model function for linearity)

GUM – An Introduction



GUM – An Introduction

- Software tools like the “GUM Workbench” free the user from many of the mathematical operations required to perform a GUM uncertainty evaluation.

However:

GUM – An Introduction

- *“The evaluation of uncertainty is neither a routine task nor a purely mathematical one; it depends on detailed knowledge of the nature of the measurand and of the measurement. The quality and utility of the uncertainty quoted for the result of a measurement therefore ultimately depend on the understanding, critical analysis, and integrity of those who contribute to the assignment of its value.” [GUM Guide]*

GUM – An Introduction

- Of course, using a (commercial) software tool to guide the user through the implementation of the GUM Guide is not the only way how GUM can be done
- It is possible to set up your own Excel spreadsheet; but certain mathematical operations like partial derivatives need to be made by the user
- It is even possible to do all calculations just using pen and paper and a pocket calculator, but would be extremely cumbersome and a lot of mathematical operations need to be performed manually (easy to make mistakes!)

GUM – An Introduction

A final remark:

- The GUM approach is universal, i.e. “the method [GUM] should be applicable to all kinds of measurements and to all types of input data used in the measurements” [GUM Guide]
- Hence, GUM is not restricted to evaluating uncertainty in measurements in radioanalytical & nuclear chemistry, but all other fields involving measurements, e.g., physics, engineering, space science, etc.

GUM – An Introduction

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GUM – An Introduction

- Only those statistical terms relevant to the GUM discussions here:
 - ❖ Arithmetic mean
 - ❖ Standard deviation
 - ❖ Standard deviation of the mean
 - ❖ Repeatability
 - ❖ Reproducibility
 - ❖ “uncertainty interval” and level of confidence

GUM – An Introduction

- Arithmetic mean (also called “average”): Is the sum of values (e.g., repeat measurements $x_1, x_2, \dots, x_n$) divided by the number of values (i.e., n)

$$\bar{x} = \frac{1}{n}(x_1 + x_2 + \dots + x_n)$$

- In GUM, the result of the measurement is calculated as the arithmetic mean of the replicate measurements
- Other mathematical formulas such as the geometric mean or harmonic mean or median are sometimes used; but within GUM usually the arithmetic mean is used.

GUM Workbench Pro

File Edit View Picture Diagram Option Tools Help

Model

Observation

Correlation

Budget

Last

Result

Diagram

?

m_{measured}

Observation:

No.	Observation
1	12.00010
2	12.00035
3	12.00023
4	12.00015
5	12.00025

Method:

Direct

Unit:

GUM Workbench does
calculate the arithmetic
mean automatically

Arithmetic Mean:

12.0002160

Experimental
Standard Deviation:

96·10⁻⁶

Standard Uncertainty

43.1·10⁻⁶

changed



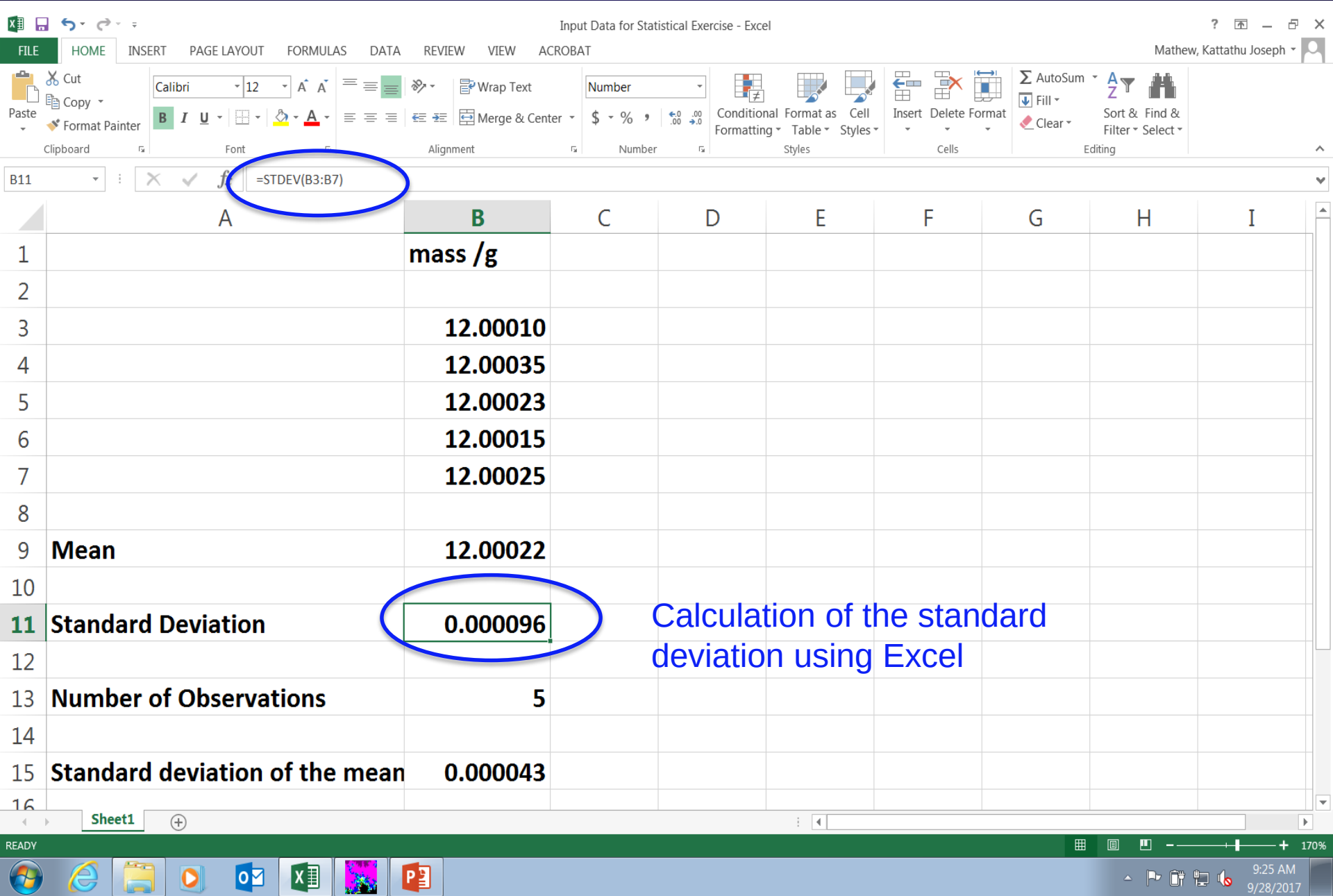
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9/28/2017

GUM – An Introduction

- Standard deviation (“s”): The positive square root of the sum of the squared deviations of observations (e.g., repeat measurements $x_1, x_2, \dots, x_n$) from their average divided by the **degrees of freedom** (= number of observations - 1)

$$s = \sqrt{\frac{1}{n-1} [(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + \dots + (x_n - \bar{x})^2]}$$

- The standard deviation is a measure of the dispersion of the data (i.e., measurement precision)



GUM Workbench Pro

File Edit View Picture Diagram Option Tools Help

Model Observation Correlation Budget Last Result Diagram

m_{measured}

Observation:

No.	Observation
1	12.00010
2	12.00035
3	12.00023
4	12.00015
5	12.00025

Method: Direct

Unit:

Arithmetic Mean: 12.0002160

Experimental Standard Deviation: $96 \cdot 10^{-6}$

Standard Uncertainty: $43.1 \cdot 10^{-6}$

changed

9:32 AM 9/28/2017

GUM Workbench does calculate the standard deviation automatically

GUM – An Introduction

- Standard deviation of the mean (“ s_{mean} ”): standard deviation (“ s ”) divided by the square root of the number of observations (“ n ”)

$$s_{\text{mean}} = s / \sqrt{n}$$

Note: Standard deviation of the mean (“ s_{mean} ”) becomes smaller as the number of observations “ n ” increases

- This is because the mean value becomes increasingly better established with increasing “ n ”
- In GUM, the standard deviation of the mean is used to calculate the standard uncertainty in Type A evaluation

Input Data for Statistical Exercise - Excel

Mathew, Kattathu Joseph

FILE HOME INSERT PAGE LAYOUT FORMULAS DATA REVIEW VIEW ACROBAT

Clipboard Font Alignment Number Styles Cells Editing

Calibri 12 A A Wrap Text Number \$ % , .00 .00 Conditional Formatting Format as Table Cell Styles Insert Delete Format AutoSum Fill Clear Sort & Find & Filter Select

B15 : X ✓ **=B11/SQRT(B13)**

	A	B	C	D	E	F	G	H	I
1		mass /g							
2									
3		12.00010							
4		12.00035							
5		12.00023							
6		12.00015							
7		12.00025							
8									
9	Mean	12.00022							
10									
11	Standard Deviation	0.000096							
12									
13	Number of Observations	5							
14									
15	Standard deviation of the mean	0.000043							
16									

Calculation of the standard deviation of the mean using Excel

GUM Workbench Pro

File Edit View Picture Diagram Option Tools Help

Model
Observation
Correlation
Budget
Last
Result
Diagram

?

m_{measured}

Observation:

No.	Observation
1	12.00010
2	12.00035
3	12.00023
4	12.00015
5	12.00025

Method:

Direct

Unit:

Arithmetic Mean:

12.0002160

Experimental Standard Deviation:

96·10⁻⁶

Standard Uncertainty

43.1·10⁻⁶

changed

GUM Workbench does calculate the standard deviation of the mean automatically

GUM – An Introduction

- (measurement) Repeatability: measurement precision (i.e., agreement between replicate measurements) under repeatability conditions of measurement (BIPM VIM)
- Repeatability conditions of measurement include:
 - ❖ same measurement procedure
 - ❖ same operator
 - ❖ same measuring instrument
 - ❖ same operating conditions and same location
 - ❖ measurements made over a short period of time

GUM – An Introduction

- Independent measurements of the same object (e.g., $n(\text{U-235})/n(\text{U-238})$ ratio measurements) using the same analytical procedure, by the same operator, using the same instrument at the same location over a short period of time can be used to calculate the standard deviation (of the mean) to express the measurement repeatability
- GUM refers to the observations made under repeatability conditions to be used in Type A evaluations: “In many cases, the result of a measurement is determined on the basis of series of observations obtained under repeatability conditions”

GUM – An Introduction

- Reproducibility conditions of measurement include:
 - ❖ different measurement procedure
 - ❖ different operator
 - ❖ different measuring instrument
 - ❖ different operating conditions and different location
 - ❖ measurements made over a longer period of time

GUM – An Introduction

- As a consequence:
 - significant differences in the measurement results between two operators should be investigated. It is another potential source of uncertainty.
 - significant differences in the measurement results between two instruments should be investigated.
 - significant differences in the measurement results after changes to the analytical procedure should be investigated.

GUM – An Introduction

- “Uncertainty interval” and level of confidence:
Usually, the uncertainty of a measured value is expressed as an interval, the “uncertainty interval”

- Example: The result of a weight measurement is
 $m = 10.0052 \pm 0.0012 \text{ g}$

This means that the uncertainty interval is $(10.0052 - 0.0012) \text{ g}$ to $(10.0052 + 0.0012) \text{ g}$

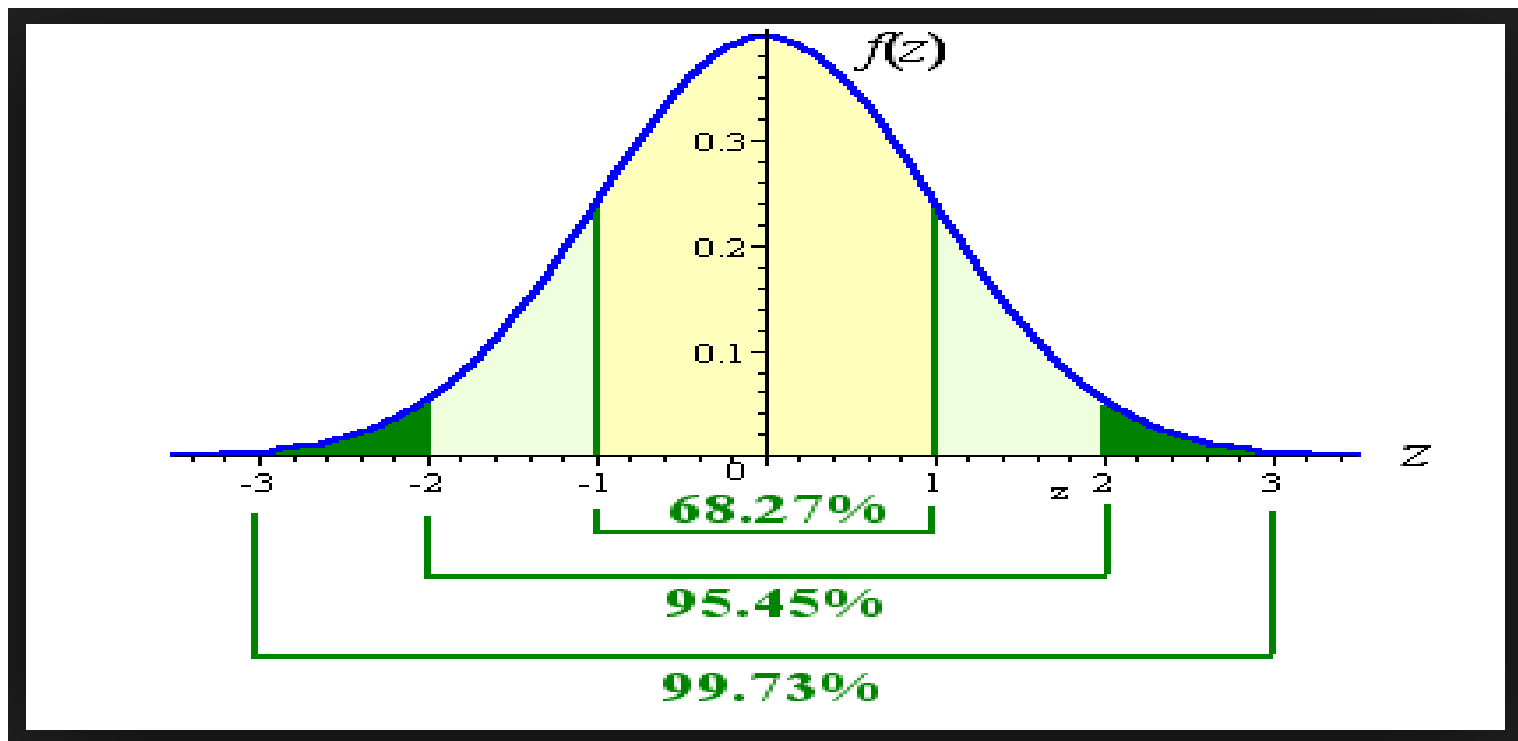
- The uncertainty interval defines a range about the measurement result within which the “true” value is expected to be with a certain level of confidence

GUM – An Introduction

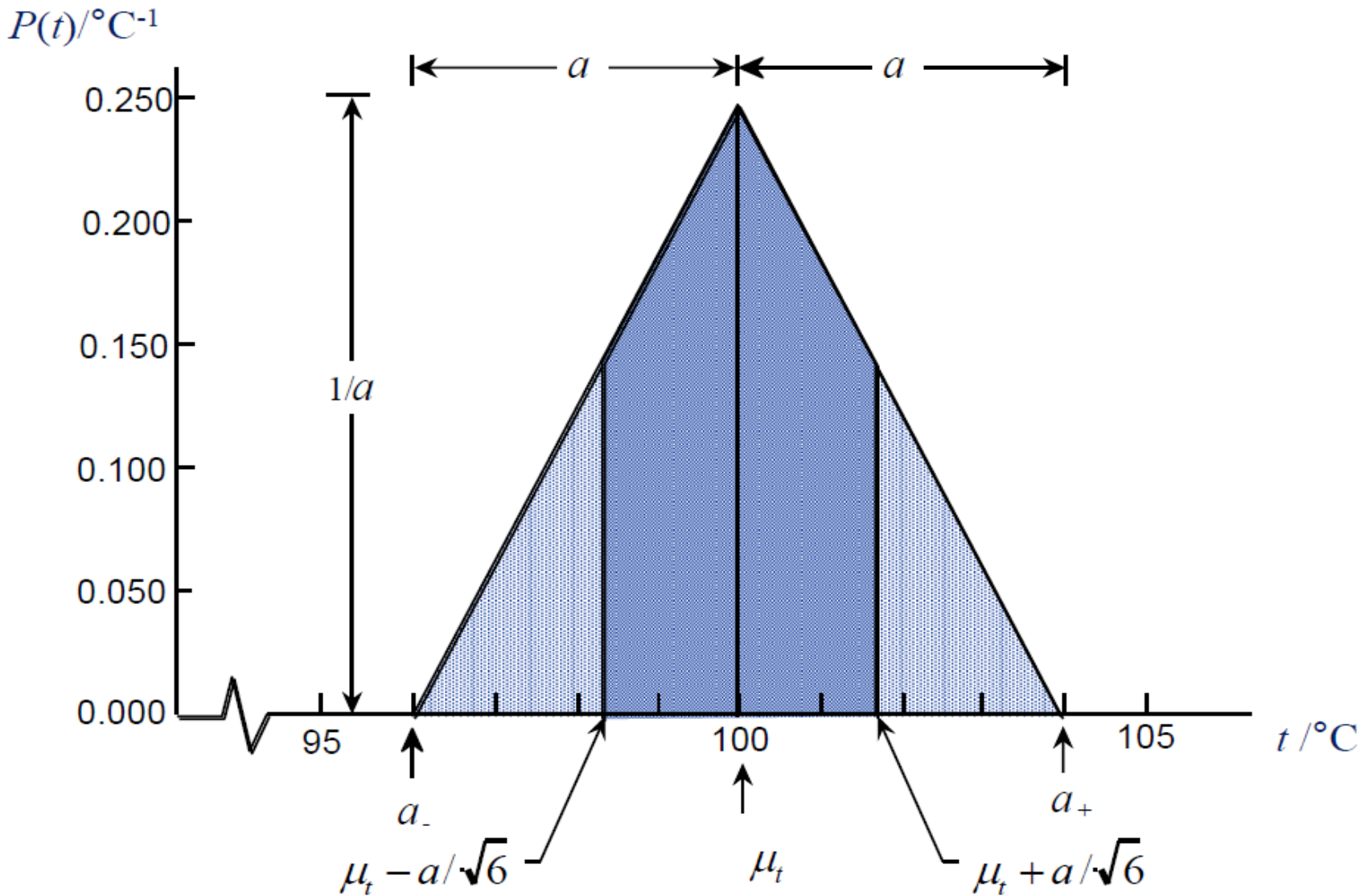
- Level of confidence: Probability that the true quantity value is contained within a specified coverage interval (here called “uncertainty interval”) (BIPM VIM)
- Levels of confidence that are typically used are 68.27 % (1-sigma, a.k.a. $1s$ or 1σ); 95.45 % (2-sigma, a.k.a. $2s$ or 2σ); or 99.73 % (3-sigma, a.k.a. $3s$ or 3σ)

GUM – An Introduction

- Levels of confidence that are typically used are 68.27 % (1-sigma, a.k.a. $1s$ or 1σ); 95.45 % (2-sigma, a.k.a. $2s$ or 2σ); or 99.73 % (3-sigma, a.k.a. $3s$ or 3σ)



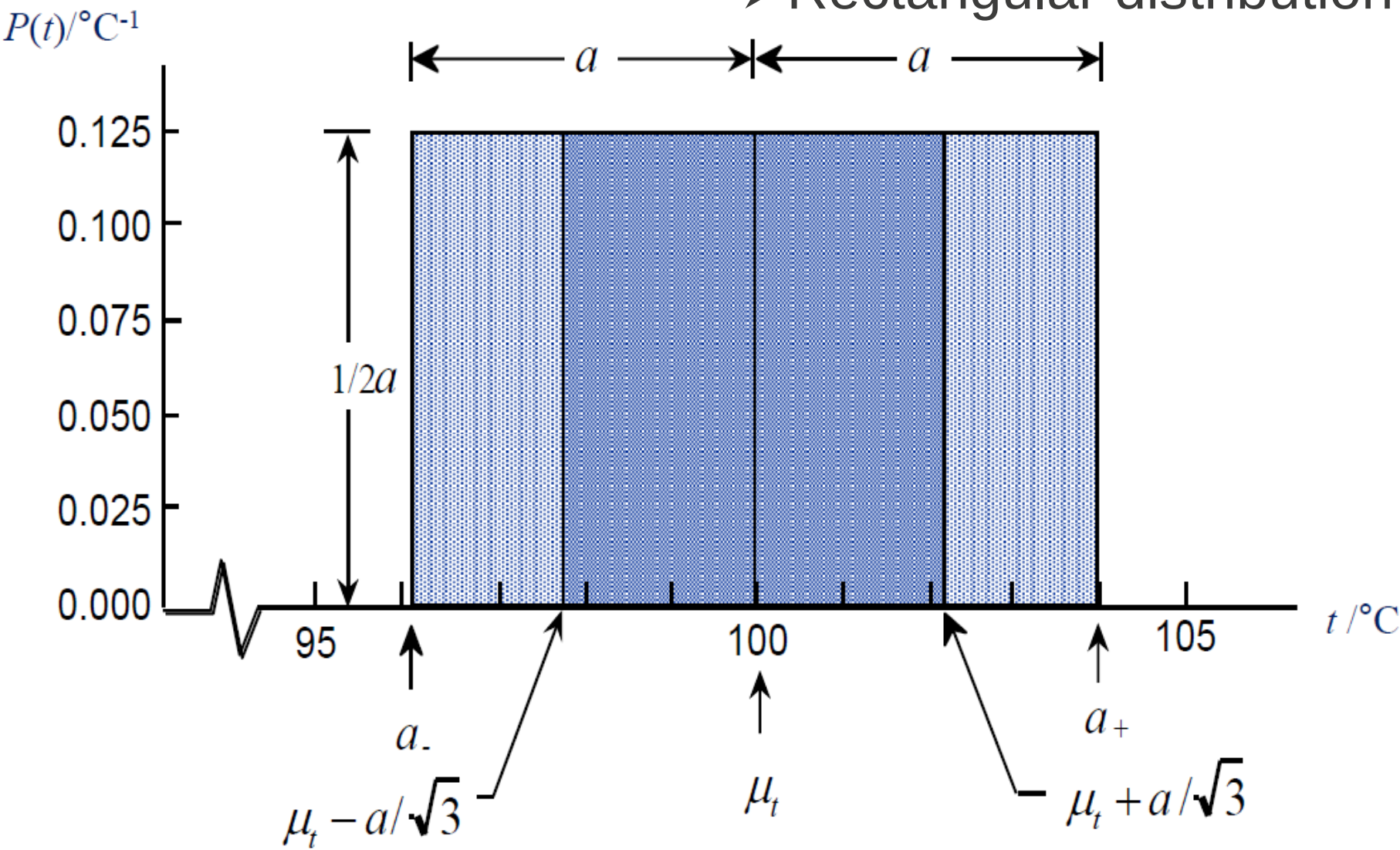
GUM – An Introduction



➤ Triangular distribution

GUM – An Introduction

➤ Rectangular distribution



GUM – An Introduction

- The uncertainty interval for a level of confidence of 99.73 % (3-sigma) and 95.45 % (2-sigma) are three and two times as large as that for a level of confidence of 68.27 % (1-sigma).
- Example: The combined standard uncertainty of 0.0012 of a weight measurement may be expanded to yield the level of confidence required
 - $m = 10.0052 \text{ g} \pm 0.0012 \text{ g}$ (68.27 % level of confidence)
 - $m = 10.0052 \text{ g} \pm 0.0024 \text{ g}$ (95.45 % level of confidence)
 - $m = 10.0052 \text{ g} \pm 0.0036 \text{ g}$ (99.73 % level of confidence)

GUM – An Introduction

- Hence, the uncertainty interval is expanded (“expanded uncertainty U ” in GUM) by a certain factor (e.g., factor of 2 or 3) depending on the desired level of confidence
- As a consequence, an uncertainty statement should always be accompanied by a statement about the level of confidence
- This factor (termed “coverage factor k ” in GUM) can be manually prescribed or it can be derived from the t-distribution (“student’s t-table) based on the effective degrees of freedom.

GUM Workbench Pro - Stat Exercises.smu

File Edit View Picture Diagram Option Tools Help

Model Observation Correlation Budget Last Result Diagram

sample_{mass}

Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
m _{measured}	12.0002160	43.1·10 ⁻⁶	normal	1.0	43·10 ⁻⁶	100.0 %

Result:

Value: 12.000216

Expanded Uncertainty Coverage Factor: ± 720·10⁻⁶ % (relativ) 2.00

sample_{mass} 12.0002160 43.1

manual
95% (t-table 95.45%)
95% (normal)
95% (rectangular)
95% (triangular)
95% (trapezoid [0.3])
95% (trapezoid [0.5])
95% (trapezoid [0.7])
95% (normal)

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GUM Workbench does expand the uncertainty interval automatically depending on the selected level of confidence or coverage factor

GUM – An Introduction

- The “GUM Workbench” software and other commercially available programs will perform all or many statistical and mathematical operations automatically, BUT ...
- The user has to apply the GUM Guide and utilize the software properly !

Guide to the Expression of Uncertainty in Measurement (GUM)

GUM – Few Examples

Module 2

Authors: K. J. Mathew (LANL)

GUM – Few Examples

- These examples are taken from EA-04

Non-Mass Spectrometry Examples

GUM Workbench Pro - Calibration of a Gauge Block.smu

File Edit View Picture Diagram Option Tools Help

Model

Observation

Correlation

Budget

Last

Result

Diagram

Title

Model Equation

Quantity Data

Partial Derivatives

Title: Calibration of a Gauge Block of Nominal Length 50 mm

Reference: Date: 09/26/2017 Version: Author: K. Mathew

General Description | Picture 1

The calibration of a Gauge Block is carried out by comparison to a comparator and a calibrated gauge block of the same nominal length and same material as reference standard. The difference in central length is determined in vertical position of the two gauge blocks using two length indicators contacting the upper and lower measuring faces.

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Non-Mass Spectrometry Examples

GUM Workbench Pro - Calibration of a Gauge Block.smu

File Edit View Picture Diagram Option Tools Help

Model Observation Correlation Budget Last Result Diagram

Title Model Equation Quantity Data Partial Derivatives

Equation: Σδ... f(x)... Rename Order Experts

{The actual length l_x of the gauge block to be calibrated is related to the actual length l_s of the reference standard by the equation}

$$L_X = L_S + \delta l_D + \delta l + \delta l_C - L * (\alpha * \delta t + \delta \alpha * \Delta t) - \delta l_v;$$

$$\alpha = (\alpha_x + \alpha_s) / 2;$$

$$\delta t = t_x - t_s ;$$

$$\delta \alpha = \alpha_x - \alpha_s ;$$

$$\Delta t = ((t_x + t_s) / 2) - t_0 ;$$

Quantity	Unit	Definition
L_X	mm	length of the unknown gauge block at the reference temp
L_S	mm	length of the reference gauge block at the reference temp $t_0 = 20^\circ\text{C}$
δl_D	mm	change in length of the reference block since its last calibration due to drift
δl	mm	observed difference in length between unknown and the reference gauge block
δl_C	mm	correction for non-linearity and offset of the comparator
L	mm	nominal length of the gauge blocks considered
α		average of the thermal expansion coefficients of the unknown and reference gauge blocks
δt		temperature difference between the unknown and reference gauge blocks
δ		difference in thermal expansion coefficients of the unknown and reference gauge blocks

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Non-Mass Spectrometry Examples

GUM Workbench Pro - Calibration of a Gauge Blocksmu

File Edit View Picture Diagram Option Tools Help

Model

Observation

Correlation

Budget

Last

Result

Diagram

Title

Model Equation

Quantity Data

Partial Derivatives

L_x

L_s

δ_b

δ_l

δ_c

L

α

δ_t

δ_α

Δ_t

δ_v

α_x

α_s

t_x

t_s

t₀

length of the unknown gauge block at the reference temp

Type:

Result

☒ in Result List

☒ Calculate Budget

☐ Calculate Correlati

Description

Picture 1

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Non-Mass Spectrometry Examples

GUM Workbench Pro - Calibration of a Gauge Block.smu

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Model Observation Correlation Budget Last Result Diagram

Title Model Equation Quantity Data Partial Derivatives

Partial Derivatives:

$$\partial L_X / \partial L_S = 1.0;$$

$$\partial L_X / \partial \delta I_D = 1.0;$$

$$\partial L_X / \partial \delta I = 1.0;$$

$$\partial L_X / \partial \delta I_C = 1.0;$$

$$\partial L_X / \partial L = -(\alpha \cdot \delta_t + \delta_\alpha \cdot \Delta_t);$$

$$\partial L_X / \partial \delta I_V = -1.0;$$

$$\partial L_X / \partial \alpha_x = -L \cdot (\delta_t \cdot \partial \alpha / \partial \alpha_x + \Delta_t \cdot \partial \delta_\alpha / \partial \alpha_x);$$

$$\partial L_X / \partial \alpha_s = -L \cdot (\delta_t \cdot \partial \alpha / \partial \alpha_s + \Delta_t \cdot \partial \delta_\alpha / \partial \alpha_s);$$

$$\partial L_X / \partial t_x = -L \cdot (\alpha \cdot \partial \delta_t / \partial t_x + \delta_\alpha \cdot \partial \Delta_t / \partial t_x);$$

$$\partial L_X / \partial t_s = -L \cdot (\alpha \cdot \partial \delta_t / \partial t_s + \delta_\alpha \cdot \partial \Delta_t / \partial t_s);$$

$$\partial L_X / \partial t_0 = -L \cdot \delta_\alpha \cdot \partial \Delta_t / \partial t_0;$$

$$\partial \alpha / \partial \alpha = 1.0 / 2.0;$$

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Non-Mass Spectrometry Examples

GUM Workbench Pro - Calibration of a Gauge Block.smu

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-

ModelObservationCorrelationBudgetLastResultDiagram?

δl

observed difference in length between unknown and the reference gauge block

Observation:

No.	Observation
1	-0.000100
2	-0.000090
3	-0.000080
4	-0.000090
5	-0.000100

Method:

Direct

Unit:

mm

Arithmetic Mean:

$-92.00 \cdot 10^{-6} \text{ mm}$

Experimental Standard Deviation:

$8.4 \cdot 10^{-6} \text{ mm}$

Standard Uncertainty

$3.74 \cdot 10^{-6} \text{ mm}$

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Non-Mass Spectrometry Examples

GUM Workbench Pro - Calibration of a Gauge Block.smu

File Edit View Picture Diagram Option Tools Help

Model

Observation

Correlation

Budget

Last

Result

Diagram

Row:

Ls

 Col:

Ls

 Coefficient:

1

Correlation Matrix:

	L_s	δl_D	δl	δl_C	δl_v	α_x	α_s	t_x	t_s	t_0
L_s	1									
δl_D		1								
δl			1							
δl_C				1						
δl_v					1					
α_x						1				
α_s							1			
t_x								1		
t_s									1	
t_0										1

Description:

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Non-Mass Spectrometry Examples

GUM Workbench Pro - Calibration of a Gauge Block.smu

File Edit View Picture Diagram Option Tools Help

L_x

length of the unknown gauge block at the reference temp

Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
L _s	50.0000200 mm	15.0·10 ⁻⁶ mm	normal	1.0	15·10 ⁻⁶ mm	30.2 %
δ _D	0.0 mm	12.2·10 ⁻⁶ mm	triangular	1.0	12·10 ⁻⁶ mm	20.1 %
δ _l	-92.00·10 ⁻⁶ mm	3.74·10 ⁻⁶ mm	normal	1.0	3.7·10 ⁻⁶ mm	1.9 %
δ _{l_C}	0.0 mm	18.5·10 ⁻⁶ mm	rectangular	1.0	18·10 ⁻⁶ mm	45.8 %
L	50.0 mm					
α	0.0	408·10 ⁻⁹				
δ _t	0.0	0.408				
δ _α	0.0	816·10 ⁻⁹				
Δ _t	0.0	0.206				
δ _{l_v}	0.0	3.87·10 ⁻⁶	rectangular	-1.0	-3.9·10 ⁻⁶ mm	2.0 %
α _x	0.0	577·10 ⁻⁹	rectangular	0.0	0.0 mm	0.0 %
α _s	0.0	577·10 ⁻⁹	rectangular	0.0	0.0 mm	0.0 %
t _x	20.000	0.289	rectangular	0.0	0.0 mm	0.0 %
t _s	20.000	0.289	rectangular	0.0	0.0 mm	0.0 %
L _x	49.9999280 mm	27.3·10 ⁻⁶ mm				

Attention: Some sensivity coefficients are zero or not valid!

Result:

Value: 49.999928 mm

Expanded Uncertainty: ± 55·10⁻⁶ mm

Coverage Factor: 2.00

Coverage: 95% (t-table 95.45)

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Non-Mass Spectrometry Examples

GUM Workbench Pro - Calibration of a Gauge Block.smu

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Model Observation Correlation Budget Last Result Diagram

?

Result

Quantity	Value	Expanded Uncertainty	Coverage-factor	Coverage
L _x	49.999928 mm	55·10 ⁻⁶ mm	2.00	95% (t-table 95.45%)

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Non-Mass Spectrometry Examples

GUM Workbench Pro - Calibration of a Gauge Block 2.smu

File Edit View Picture Diagram Option Tools Help

Model Observation Correlation Budget Last Result Diagram

Title Model Equation Quantity Data Partial Derivatives

Equation: Σδ... f(x)... Rename Order Experts

{The actual length l_x of the gauge block to be calibrated is related to the actual length l_s of the reference standard by the equation}

$$L_X = L_S + \delta l_D + \delta l + \delta l_C - L * (\alpha_{\delta t} + \delta_{\alpha t}) - \delta l_v;$$

Quantity	Unit	Definition
L_X	mm	length of the unknown gauge block at the reference temp
L_S	mm	length of the reference gauge block at the reference temp $t_0 = 20^\circ\text{C}$
δl_D	mm	change in length of the reference block since its last calibration due to drift
δl	mm	observed difference in length between unknown and the reference gauge block
δl_C	mm	correction for non-linearity and offset of the comparator
L	mm	nominal length of the gauge blocks considered
$\alpha_{\delta t}$		product of the average thermal expansion coefficient and δt
$\delta_{\alpha t}$		product of the $\delta\alpha$ and δt
δl_v		correction for non-central contacting of the measuring faces

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Non-Mass Spectrometry Examples

GUM Workbench Pro - Calibration of a Gauge Block 2.smu

File Edit View Picture Diagram Option Tools Help

ModelObservationCorrelationBudgetLastResultDiagram

L_x

length of the unknown gauge block at the reference temp

Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
L _s	50.0000200 mm	15.0·10 ⁻⁶ mm	normal	1.0	15·10 ⁻⁶ mm	16.7 %
δ _D	0.0 mm	17.1·10 ⁻⁶ mm	triangular	1.0	17·10 ⁻⁶ mm	21.9 %
δ _l	-94.00·10 ⁻⁶ mm	6.00·10 ⁻⁶ mm	normal	1.0	6.0·10 ⁻⁶ mm	2.7 %
δ _C	0.0 mm	18.5·10 ⁻⁶ mm	rectangular	1.0	18·10 ⁻⁶ mm	25.4 %
L	50.0 mm					
α _{st}	0.0	339·10 ⁻⁹	triangular	-50	-17·10 ⁻⁶ mm	21.3 %
δ _{at}	0.0	242·10 ⁻⁹	rectangular	-50	-12·10 ⁻⁶ mm	10.9 %
δ _v	0.0	3.87·10 ⁻⁶	rectangular	-1.0	-3.9·10 ⁻⁶ mm	1.1 %

L_x

49.9999260 mm

36.7·10⁻⁶ mm

Result:

Value:

Expanded Uncertainty

Coverage Factor

Coverage:

49.999926 mm

± 73·10⁻⁶ mm

2.00

95% (t-table 95.45)

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Non-Mass Spectrometry Examples

GUM Workbench Pro - Resistance Calibration.smu

File Edit View Picture Diagram Option Tools Help

Model Observation Correlation Budget Last Result Diagram

?

Title

Model Equation

Quantity Data

Partial Derivatives

Title:Standard Resistor Calibration

Reference:Date:02/12/2014Version:Author:K. Mathew

General Description

Picture 1

The resistance of a four-terminal standard resistor is determined by direct substitution using a long-scale digital multimeter (7 1/2 digit DMM) and a calibrated resistor of the same nominal value as reference standard. The resistors are immersed in a well stirred oil bath operating at a temperature of 23oC monitored by a centrally placed mercury-in-glass thermometer. The resistors are allowed to stabilize before measurement. It is determined that the measuring current on the 10 kOhm range of the DMM of 100 microA is sufficiently low not to cause any self-heating of the resistors. The measuring procedure also ensures that the effects of external leakage resistance on the result of the measurement can be considered to be insignificant.

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Non-Mass Spectrometry Examples

GUM Workbench Pro - Resistance Calibration.smu

File Edit View Picture Diagram Option Tools Help

Model Observation Correlation Budget Last Result Diagram

Title Model Equation Quantity Data Partial Derivatives

Equation: Σδ... f(x)... Rename Order Experts

{The resistance R_X of the unknown resistor is obtained from the model equation:}

$$R_X = (R_S + \delta R_D + \delta R_{TS}) * r_C * r - \delta R_{TX};$$

Quantity	Unit	Definition
R_X	Ohm	resistance of the unknown resistor
R_S	Ohm	resistance of the reference standard (nominally same as unknown)
δR_D	Ohm	drift of the resistance of the reference standard since last calibration
δR_{TS}	Ohm	temperature related resistance variation of the reference
r_C		Correction factor for parasitic voltages and instrument resolution
r		ratio of unknown/reference resistor
δR_{TX}		temperature-related resistance variation of the unknown resistor

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Non-Mass Spectrometry Examples

GUM Workbench Pro - Resistance Calibration.smu

File Edit View Picture Diagram Option Tools Help

Model Observation Correlation Budget Last Result Diagram

ratio of unknown/reference resistor

Observation:

No.	Observation
1	1.0000104
2	1.0000107
3	1.0000106
4	1.0000103
5	1.0000105

Method:
Direct

Unit:

Arithmetic Mean:
1.0000105000

Experimental
Standard Deviation:
 $160 \cdot 10^{-9}$

Standard Uncertainty
 $70.7 \cdot 10^{-9}$

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Non-Mass Spectrometry Examples

GUM Workbench Pro - Resistance Calibration.smu

File Edit View Picture Diagram Option Tools Help

ModelObservationCorrelationBudgetLastResultDiagram

R_x

resistance of the unknown resistor

Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
R _s	10000.05300 Ohm	2.50·10 ⁻³ Ohm	normal	1.0	2.5·10 ⁻³ Ohm	9.0 %
δR _D	0.02000 Ohm	5.77·10 ⁻³ Ohm	rectangular	1.0	5.8·10 ⁻³ Ohm	48.1 %
δR _{TS}	0.0 Ohm	1.59·10 ⁻³ Ohm	rectangular	1.0	1.6·10 ⁻³ Ohm	3.6 %
r _c	1.000000000	408·10 ⁻⁹	triangular	10000	4.1·10 ⁻³ Ohm	24.0 %
r	1.0000105000	70.7·10 ⁻⁹	normal	10000	710·10 ⁻⁶ Ohm	0.7 %
δR _{TX}	0.0	3.18·10 ⁻³	rectangular	-1.0	-3.2·10 ⁻³ Ohm	14.5 %

R_x

10000.17800 Ohm

8.33·10⁻³ Ohm

Result:

Value:

Expanded Uncertainty

Coverage Factor

Coverage:

10000.178 Ohm

± 0.017 Ohm

2.00

95% (t-table 95.45)

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Non-Mass Spectrometry Examples

GUM Workbench Pro - Resistance Calibration.smu

File Edit View Picture Diagram Option Tools Help

Model Observation Correlation Budget Last Result Diagram

?

Result

Quantity	Value	Expanded Uncertainty	Coverage-factor	Coverage
R_x	10000.178 Ohm	0.017 Ohm	2.00	95% (t-table 95.45%)

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Non-Mass Spectrometry Examples

GUM Workbench Pro - Weight Calibration.smu

File Edit View Picture Diagram Option Tools Help

Model Observation Correlation Budget Last Result Diagram

?

Title

Model Equation

Quantity Data

Partial Derivatives

Title:EA-4/02 Uncertainty Examples

Reference: Date:09/12/2017 Version: Author:K. Mathew

General DescriptionPicture 1

The Calibration of a weight of nominal value 10 kg is carried out by comparison to a reference standard of the same nominal value using a mass comparator whose performance characteristics have previously been determined.

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Non-Mass Spectrometry Examples

GUM Workbench Pro - Weight Calibration.smu

File Edit View Picture Diagram Option Tools Help

Model Observation Correlation Budget Last Result Diagram

Title Model Equation Quantity Data Partial Derivatives

Equation: Σδ... f(x)... Rename Order Experts

{The unknown Conventional mass m_x is obtained from}

$$m_x = m_s + \delta m_D + \delta m + \delta m_C + \delta B;$$

Quantity	Unit	Definition
m_x	g	unknown conventional mass
m_s	g	conventional mass of the standard of same nominal mass
δm_D	g	drift of value of the standard since last calibration
δm	g	observed difference in mass between unknown mass and the standard
δm_C	g	correction for eccentricity and magnetic effects
δB	g	Correction for air buoyancy

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Non-Mass Spectrometry Examples

GUM Workbench Pro - Weight Calibration.smu

File Edit View Picture Diagram Option Tools Help

ModelObservationCorrelationBudgetLastResultDiagram

?

δm

observed difference in mass between unknown mass and the standard

Observation:

No.	Hint	Reading	Observation
1	Standard	0.01	
	Unknown	0.02	
	Unknown	0.025	
2	Standard	0.015	0.0100 g
	Standard	0.025	
	Unknown	0.05	
	Unknown	0.055	
3	Standard	0.02	0.0300 g
	Standard	0.025	
	Unknown	0.045	
	Unknown	0.04	
	Standard	0.02	0.0200 g

Method:
Indirect SUUS

Unit:
g

Arithmetic Mean:
0.02000 g

Experimental
Standard Deviation:
0.010 g

Standard Uncertainty
 $5.77 \cdot 10^{-3}$ g

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Guide to the Expression of Uncertainty in Measurement (GUM)

GUM – Few Examples

Module 2

Authors: K. J. Mathew (LANL)

Guide to the Expression of Uncertainty in Measurement (GUM)

GUM – Correlation

Module 3

Authors: K. J. Mathew (LANL)

Measurand in Mass Spectrometry

- ❑ Isotopic Ratios (amount ratios a.k.a. atom ratios) are the measurands in Mass Spectrometry
- ❑ For MC&A and Criticality Safety, the mass fraction of the isotopes is often required
- ❑ Amount fractions (atom percent) and mass fractions (weight percent) are calculated from the isotope ratios – these quantities are derived quantities.

Amount Fraction and Mass Fraction Calculations

$$\text{Amount Fraction of isotope } i = 100 \bullet \frac{R_i}{\sum R_i}$$

$$\text{Mass Fraction of isotope } i = 100 \bullet \frac{R_i \bullet M_i}{\sum (R_i \bullet M_i)}$$

Where

R_i = isotope ratio

$\sum R_i$ = sum of all ratios, including reference isotope

M_i = nuclidic mass of the i^{th} isotope

What is Correlation and Why is it Important ?

According to ISO Guide to the expression of Uncertainty in Measurements (GUM), “If the same measuring instrument, physical measurement standard, or reference datum having a significant standard uncertainty is used for the determination of two input quantities, there may be significant correlation (between the input quantities)”.

Example for Correlation

- If a thermometer is used to determine a temperature correction in the estimation of the value of input quantities x_i and x_j , there could be significant correlation between the input quantities x_i and x_j
- How can the correlation be handled in uncertainty estimations?
 - Redefine x_i and x_j as uncorrelated quantities and provide the calibration curve for the thermometer as an additional input quantity with independent standard uncertainty

Are Isotope Ratios Correlated ?

Isotope ratios are highly correlated as

- i) the same instrument is used for measurement of the abundances of the different isotopes
- ii) the same standard is used for estimation of the bias corrections
- iii) the uncertainty of the standard is often the predominant component of uncertainty

The combined uncertainty for $Y = f(x_1, x_2, \dots, x_n)$ is calculated as

$$u_c = \sqrt{c_1^2 u_{(x_1)}^2 + c_2^2 u_{(x_2)}^2 + \dots + c_n^2 u_{(x_n)}^2 + C_{correlation}}$$

Where

c_i = sensitivity coefficient (partial derivative of the model function relative to x_i)

$u(x_i)$ = standard uncertainty of x_i

$C_{correlation}$ is the correlation term

Isotopic Standards (CRMs)



EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for reference materials and measurements
Isotope Measurements (Geel)

CERTIFICATE
SPIKE ISOTOPIC REFERENCE MATERIAL IRMM-3636

$2.117\,55(26) \cdot 10^{-6} \text{ mol } (^{236}\text{U}) \cdot \text{g}^{-1} \text{ (solution)}$

The Spike Isotopic Reference Material is supplied with an isotope amount content of ^{236}U certified as above.

The amounts of other uranium isotopes present are related to the ^{236}U content through the following certified amount ratios:

$n(^{233}\text{U})/n(^{236}\text{U})$	1.019 06(16)
$n(^{234}\text{U})/n(^{236}\text{U})$	0.000 366 06(48)
$n(^{235}\text{U})/n(^{236}\text{U})$	0.000 045 480(74)
$n(^{238}\text{U})/n(^{236}\text{U})$	0.000 234 81(38)

This corresponds to an isotopic composition with the following abundances:

amount fraction ($\cdot 100$)		mass fraction ($\cdot 100$)	
$n(^{233}\text{U})/n(\text{U})$	50.455 8(39)	$m(^{233}\text{U})/m(\text{U})$	50.135 5(39)
$n(^{234}\text{U})/n(\text{U})$	0.018 125(24)	$m(^{234}\text{U})/m(\text{U})$	0.018 087(24)
$n(^{235}\text{U})/n(\text{U})$	0.002 251 8(37)	$m(^{235}\text{U})/m(\text{U})$	0.002 256 8(37)
$n(^{236}\text{U})/n(\text{U})$	49.512 2(39)	$m(^{236}\text{U})/m(\text{U})$	49.832 4(39)
$n(^{238}\text{U})/n(\text{U})$	0.011 626(19)	$m(^{238}\text{U})/m(\text{U})$	0.011 801(19)



New Brunswick Laboratory
U.S. Department of Energy

Certificate of Analysis
CRM U500

Uranium Isotopic Standard
10 mg Uranium as U_3O_8

	^{234}U	^{235}U	^{236}U	^{238}U
Atom Percent:	0.5181	49.696	0.0755	49.711
Uncertainty:	± 0.0008	± 0.050	± 0.0003	± 0.050
Weight Percent:	0.5126	49.383	0.0754	50.029



New Brunswick Laboratory
U.S. Department of Energy

Certificate of Analysis
CRM U900

Uranium Isotopic Standard
10 mg Uranium as U_3O_8

	^{234}U	^{235}U	^{236}U	^{238}U
Atom Percent:	0.7777	90.196	0.3327	8.693
Uncertainty:	± 0.0015	± 0.011	± 0.0010	± 0.008
Weight Percent:	0.7735	90.098	0.3337	8.795

10/19/2017

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IRMM-3636

Calculation of the Amount Fractions and Mass Fractions from Isotopic Ratios

GUM Workbench Pro - IRMM3636 atp from ratios.SMU

File Edit View Picture Diagram Option Tools Help

Model

Observation

Correlation

Budget

Last

Result

Diagram

Title

Model Equation

Quantity Data

Partial Derivatives

Equation:

Σδ...

f(x)...

Rename

Order

Experts

{Amount Fraction Calculation with Ratios as input quantities}

$$AF_{233} = 100 * (R_{36} / (R_{36} + R_{46} + R_{56} + R_{86} + 1));$$
$$AF_{234} = 100 * (R_{46} / (R_{36} + R_{46} + R_{56} + R_{86} + 1));$$
$$AF_{235} = 100 * (R_{56} / (R_{36} + R_{46} + R_{56} + R_{86} + 1));$$
$$AF_{236} = 100 * (1 / (R_{36} + R_{46} + R_{56} + R_{86} + 1));$$
$$AF_{238} = 100 * (R_{86} / (R_{36} + R_{46} + R_{56} + R_{86} + 1));$$

{Atomic masses and uncertainties used are same as that listed in IRMM-3636 certificate dated June 2008}

$$At_{wt} = ((AF_{233} * AtM_{233}) + (AF_{234} * AtM_{234}) + (AF_{235} * AtM_{235}) + (AF_{236} * AtM_{236}) + (AF_{238} * AtM_{238})) / 100;$$

{Mass Fraction Calculation}

$$WF_{233} = (AF_{233} * AtM_{233}) / At_{wt};$$
$$WF_{234} = (AF_{234} * AtM_{234}) / At_{wt};$$
$$WF_{235} = (AF_{235} * AtM_{235}) / At_{wt};$$
$$WF_{236} = (AF_{236} * AtM_{236}) / At_{wt};$$
$$WF_{238} = (AF_{238} * AtM_{238}) / At_{wt};$$

Quantity	Unit	Definition
R ₃₆		atom/atom a.k.a. amount ratio
R ₄₆		atom/atom a.k.a. amount ratio
R ₅₆		atom/atom a.k.a. amount ratio
R ₈₆		atom/atom a.k.a. amount ratio
AF ₂₃₃		amount fraction a.k.a. atom percent
AF ₂₃₄		amount fraction a.k.a. atom percent
AF ₂₃₅		amount fraction a.k.a. atom percent
AF ₂₃₆		amount fraction a.k.a. atom percent
AF ₂₃₈		amount fraction a.k.a. atom percent
At _{wt}		g/mol
AtM ₂₃₃		g/mol
AtM ₂₃₄		g/mol
AtM ₂₃₅		g/mol
AtM ₂₃₆		g/mol
AtM ₂₃₈		g/mol
WF ₂₃₃		mass fraction a.k.a. weight percent
WF ₂₃₄		mass fraction a.k.a. weight percent
WF ₂₃₅		mass fraction a.k.a. weight percent
WF ₂₃₆		mass fraction a.k.a. weight percent

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changed

IRMM-3636

Quantity	Value	Expanded Uncertainty		Coverage- factor	Coverage
AF ₂₃₃	50.4558	0.0039	39	2.00	95% (t-table 95.45%)
AF ₂₃₄	0.018124	0.000024	24	2.00	95% (t-table 95.45%)
AF ₂₃₅	0.0022518	0.0000037	37	2.00	95% (t-table 95.45%)
AF ₂₃₆	49.5121	0.0039	39	2.00	95% (t-table 95.45%)
AF ₂₃₈	0.011626	0.000019	19	2.00	95% (t-table 95.45%)
WF ₂₃₃	50.1355	0.0039	39	2.00	95% (t-table 95.45%)
WF ₂₃₄	0.018087	0.000024	24	2.00	95% (t-table 95.45%)
WF ₂₃₅	0.0022568	0.0000037	37	2.00	95% (t-table 95.45%)
WF ₂₃₆	49.8324	0.0039	39	2.00	95% (t-table 95.45%)
WF ₂₃₈	0.011801	0.000019	19	2.00	95% (t-table 95.45%)

When amount ratios are used as input quantities and amount fractions or mass fractions are calculated – the uncertainties stated in certificate are reproduced

IRMM-3636

GUM Workbench Pro - IRMM3636ratiosfrom atp.SMU

File Edit View Picture Diagram Option Tools Help

Model Observation Correlation Budget Last Result Diagram

Title Model Equation Quantity Data Partial Derivatives

Equation: Σδ... f(x)... Rename Order Experts

{Amount Ratio Calculation with Amount Fractions as input quantities}

$$R_{36} = AF_{233} / AF_{236};$$

$$R_{46} = AF_{234} / AF_{236};$$

$$R_{56} = AF_{235} / AF_{236};$$

$$R_{86} = AF_{238} / AF_{236};$$

{Atomic masses and uncertainties used are same as that listed in IRMM-3636 certificate dated June 2008}

$$At_{wt} = ((AF_{233} * AtM_{233}) + (AF_{234} * AtM_{234}) + (AF_{235} * AtM_{235}) + (AF_{236} * AtM_{236}) + (AF_{238} * AtM_{238})) / 100;$$

{Isotopic Mass Fraction Calculation}

$$WF_{233} = (AF_{233} * AtM_{233}) / At_{wt};$$

$$WF_{234} = (AF_{234} * AtM_{234}) / At_{wt};$$

$$WF_{235} = (AF_{235} * AtM_{235}) / At_{wt};$$

$$WF_{236} = (AF_{236} * AtM_{236}) / At_{wt};$$

$$WF_{238} = (AF_{238} * AtM_{238}) / At_{wt};$$

$$u_c = \sqrt{c_1^2 u_{(x_1)}^2 + c_2^2 u_{(x_2)}^2 + ... + c_n^2 u_{(x_n)}^2 + C_{correlation}}$$

IRMM-3636

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage	
R₃₆	1.01906	0.00011	16	2.00	95% (t-table 95.45%)
R ₄₆	0.00036607	0.00000049	48	2.00	95% (t-table 95.45%)
R ₅₆	0.000045480	0.000000075	74	2.00	95% (t-table 95.45%)
R ₈₆	0.00023481	0.00000038	38	2.00	95% (t-table 95.45%)
WF₂₃₃	50.1354	0.0028	39	2.00	95% (t-table 95.45%)
WF ₂₃₄	0.018087	0.000024	24	2.00	95% (t-table 95.45%)
WF ₂₃₅	0.0022567	0.0000037	37	2.00	95% (t-table 95.45%)
WF₂₃₆	49.8324	0.0028	39	2.00	95% (t-table 95.45%)
WF ₂₃₈	0.011801	0.000019	19	2.00	95% (t-table 95.45%)



Certified Uncertainties

With amount fractions as inputs the ratio and mass fraction uncertainties are not reproduced !! – Correlation Effect

GUM Workbench Pro - IRMM3636ratiosfrom atp diff approach.smu

File Edit View Picture Diagram Option Tools Help

Model Observation Correlation Budget Last Result Diagram

Title Model Equation Quantity Data Partial Derivatives

Equation:

$$AF_{233} = 100 - (AF_{234} + AF_{235} + AF_{236} + AF_{238});$$

$$R_{36} = AF_{233} / AF_{236};$$

$$R_{46} = AF_{234} / AF_{236};$$

$$R_{56} = AF_{235} / AF_{236};$$

$$R_{86} = AF_{238} / AF_{236};$$

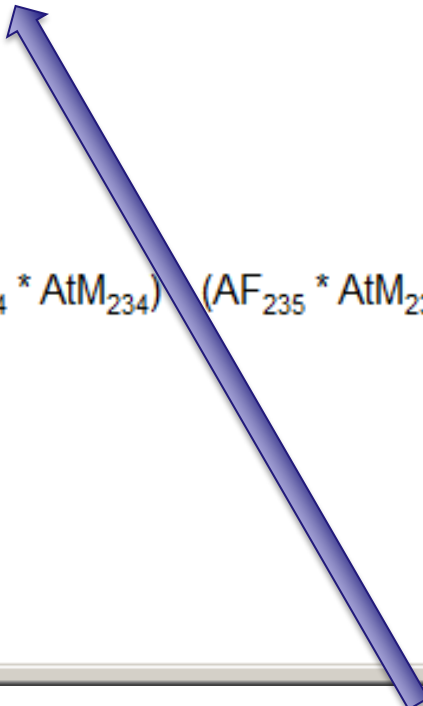
$$At_{wt} = ((AF_{233} * AtM_{233}) + (AF_{234} * AtM_{234}) + (AF_{235} * AtM_{235}) + (AF_{236} * AtM_{236}) + (AF_{238} * AtM_{238})) / 100;$$

$$WF_{233} = (AF_{233} * AtM_{233}) / At_{wt};$$

$$WF_{234} = (AF_{234} * AtM_{234}) / At_{wt};$$

$$WF_{235} = (AF_{235} * AtM_{235}) / At_{wt};$$

$$WF_{236} = (AF_{236} * AtM_{236}) / At_{wt};$$

$$WF_{238} = (AF_{238} * AtM_{238}) / At_{wt};$$


One of the major amount fraction is expressed as a function of the other amount fractions

Quantity	Value (amount fraction)	Expanded Uncertainty (amount fraction)	Coverage factor	Coverage
R₃₆	1.01906	0.00016 16	2.00	95% (t-table 95.45%)
R ₄₆	0.00036607	0.00000049 48	2.00	95% (t-table 95.45%)
R ₅₆	0.000045480	0.000000075 74	2.00	95% (t-table 95.45%)
R ₈₆	0.00023481	0.00000038 38	2.00	95% (t-table 95.45%)
WF₂₃₃	50.1354	0.0039 39	2.00	95% (t-table 95.45%)
WF ₂₃₄	0.018087	0.000024 24	2.00	95% (t-table 95.45%)
WF ₂₃₅	0.0022567	0.0000037 37	2.00	95% (t-table 95.45%)
WF₂₃₆	49.8324	0.0039 39	2.00	95% (t-table 95.45%)
WF ₂₃₈	0.011801	0.000019 19	2.00	95% (t-table 95.45%)



Certified Uncertainties

With one of the amount fractions expressed as a function of the other amount fractions the ratio and mass fraction uncertainties are reproduced.

Is IRMM-3636 a unique case ?

For several (most) NBL CRMs, only the amount fraction and mass fraction as well as the associated uncertainties are reported in the certificate of analysis.

The amount ratio and mass fractions were calculated using two different approaches:

- Approach A: ratios and mass fractions calculated from the amount fractions**
- Approach B: One of the isotopic abundances is expressed as a function of the other isotopic abundances**

The results are summarized in the following Tables

	Value	Uncertainty		Value	Uncertainty	
Ratios		Approach A	Approach B		Approach A	Approach B
$^{234}\text{U}/^{238}\text{U}$	0.010422	0.000019	0.000019	0.08946	0.000019	0.000022
$^{235}\text{U}/^{238}\text{U}$	0.9997	0.0014	0.0020	10.3757	0.0096	0.015
$^{236}\text{U}/^{238}\text{U}$	0.0015188	0.0000062	0.0000062	0.03827	0.00012	0.00013
Mass Fraction						
^{234}U	0.51264	0.00087	0.00079	0.7735	0.0015	0.0015
^{235}U	49.383	0.035	0.050 50	90.0981	0.0075	0.011 11
^{236}U	0.07534	0.00030	0.00030	0.3338	0.0010	0.0010
^{238}U	50.029	0.035	0.050 50	8.7946	0.0074	0.011
	U500			U900		

IRMM-3636 is not unique! Correlation is an issue with all isotopic standards !!
The isotope ratios are not stated in the certificates for large number of NBL CRMs.
Uncertainties can be underestimated by up to 50% due to correlation issues.

	Value	Uncertainty	
Ratios		Approach A	Approach B
$^{234}\text{U}/^{238}\text{U}$	0.20097	0.00042	0.00058
$^{235}\text{U}/^{238}\text{U}$	17.349	0.016	0.035
$^{236}\text{U}/^{238}\text{U}$	0.03768	0.00012	0.00014
Mass Fraction			
^{234}U	1.0759	0.0020	0.00020
^{235}U	93.2754	0.0051	0.010 10
^{236}U	0.20343	0.00060	0.00060
^{238}U	5.4453	0.0048	0.010
	U930		

The effect of Correlation on the different isotopic standards are different. Pu isotopic standards are also impacted by the same effect.

NBL is urged to include the isotopic ratios, amount fractions, and mass fractions in the certificate of analysis (as in 112-A, 115, 125-A, and 116-A)

Practical Implications

For isotopic abundance measurements using mass spectrometers, the correlation effects discussed imply that:

- **The practice of not reporting minor ratios, often due to poor precision (and accuracy), impacts any subsequent calculations**
- **When multiple cycles of data are collected, if any one of the individual ratio turns out to be an outlier, all ratios associated with that cycle must be discarded during the data evaluation.**

Understand the Measurement System

“The evaluation of uncertainty is neither a routine task nor a purely mathematical one; it depends on detailed knowledge of the nature of the measurand and of the measurement. The quality and utility of the uncertainty quoted for the result of a measurement therefore ultimately depend on the understanding, critical analysis, and integrity of those who contribute to the assignment of its value.”

ISO-GUM

Guide to the Expression of Uncertainty in Measurement (GUM)

TIMS Measurement Methods

Module 3

Authors: K. J. Mathew (LANL)

Why ASTM Measurement Methods?

- ASTM International, formerly known as the American Society for Testing and Materials (ASTM).
- Globally recognized leader in the development and delivery of international voluntary consensus standards.
- 12,000 ASTM standards are used around the world to improve product quality, enhance safety, facilitate market access and trade, and build consumer confidence.



ASTM standard C1672 – 07

C1672 – 17: Standard Test Method for **Determination of Uranium and Plutonium Isotopic Composition or Concentration by Total Evaporation Method Using a Thermal Ionization Mass Spectrometer**

Goal of standard:

- To determine isotopic composition and/ or concentration of U and Pu

Conditions

- U/Pu as purified nitrate solution
- Sample loaded onto degassed metal filament
- Ion beams are continually measured until sample is exhausted
- Ion currents integrated, normalized to a reference isotope ion current

ASTM standard C1672 – 07

Significance and Use

- Total evaporation method is used to measure isotopic composition of U and Pu materials and may be used to measure the elemental concentration when employing the IDMS technique.
- U and Pu as used for nuclear fuels are required to meet certain specifications.
- Size of sample loaded can vary
 - ❖ U = 10 ng to 5 µg
 - ❖ Pu = 5 ng to 250 ng
- Simultaneous measurement of both major isotopes (using Faraday cups) and minor isotopes (using ion counting detectors).

ASTM standard C1672 – 07

Interferences

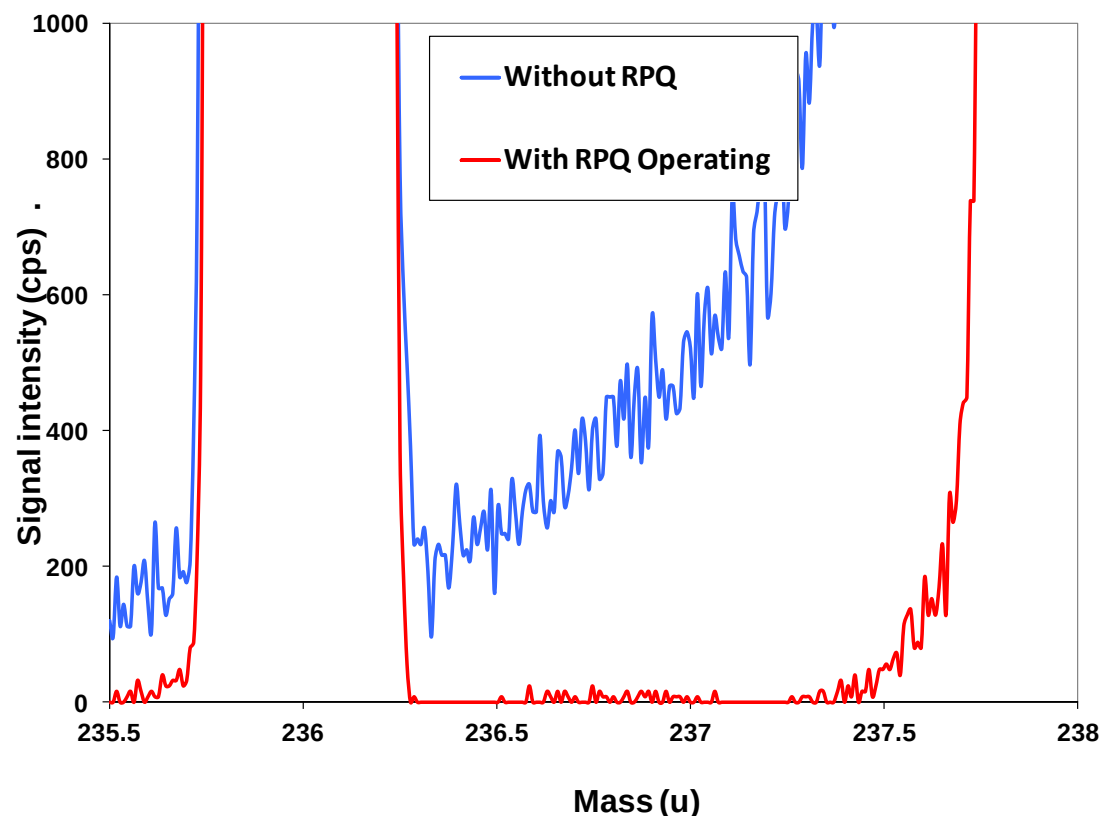
- Ions with atomic masses in the U/Pu range, may interfere with one another and require chemical separation
 - ❖ ^{238}U and ^{238}Pu
 - ❖ ^{241}Am and ^{241}Pu
- Molecular species with the same mass number
- Analysis of plutonium should occur within reasonable timeframe to reduce ^{241}Am in-growth (example: 20 days)
- Matrix matched standards and samples
- **Contamination by environmental conditions, or handling processes**
- **Measurement biases of minor isotopes from peak tailing**

ASTM standard C1672 – 07

Interferences: **minor isotope ratios are biased**

Peak tailing from major isotopes interfere with measurement of minor isotopes

- Bias correction can be applied by determining abundance sensitivity under identical experimental conditions.
- Bias can be defeated by using energy filter.
- Bias can be avoided utilizing alpha spectrometry.



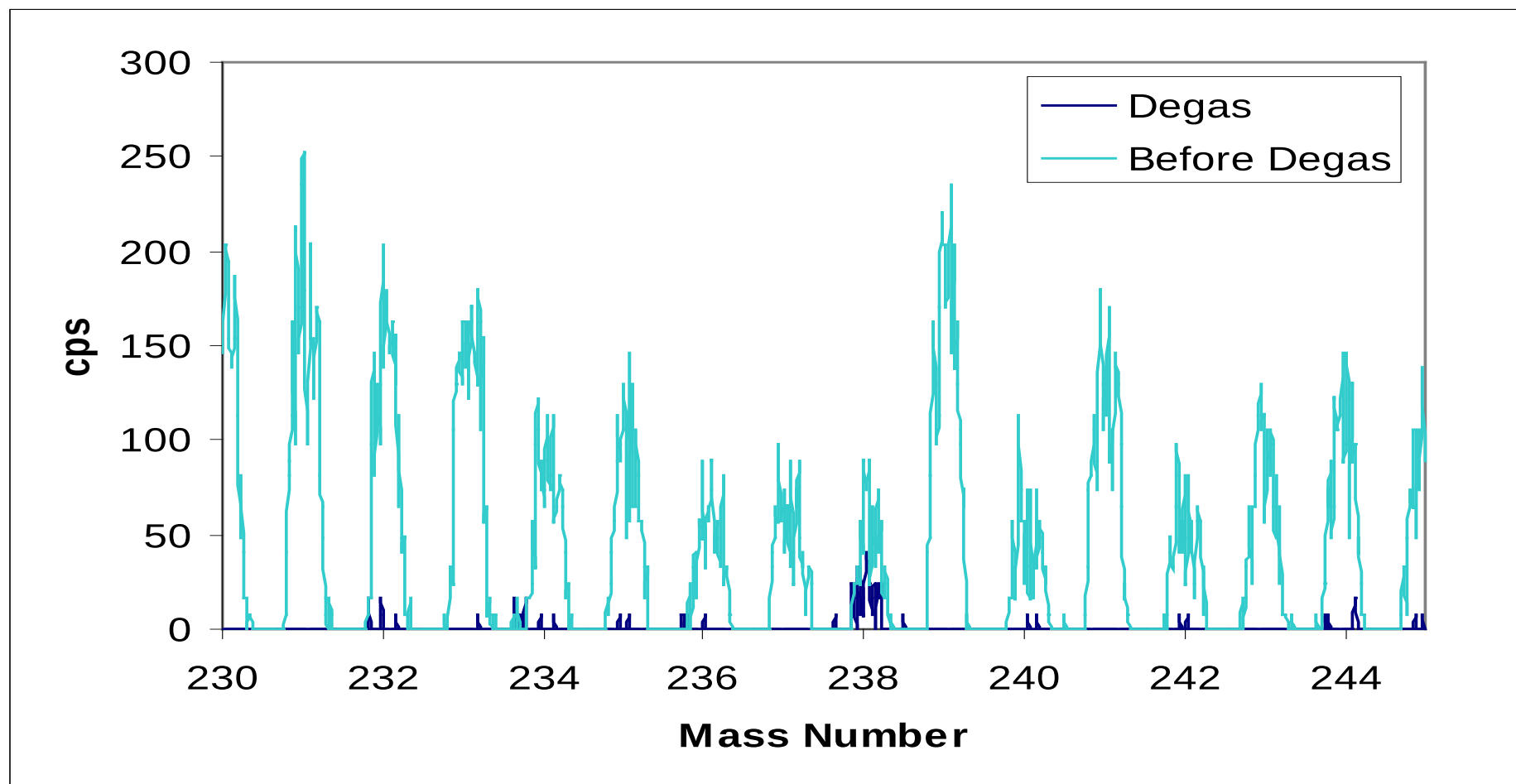
ASTM standard C1672 – 07

Instrumentation

- Mass spectrometer, evaluated by means of performance tests and should possess following characteristics:
- Thermal ionization source capable of analysis single/double filaments
- Analyzer radius sufficient to resolve adjacent, full width of peak at 1% peak height with abundance sensitivity less than 10^{-5} .
 - Abundance sensitivity is the ratio of the measured intensity of an ion beam at a mass m , to the measured intensity of the same isotope measured at one mass difference (mass m and $m \pm 1$).
- Vacuum system capable of pumping to $400\mu\text{Pa}$ (5×10^{-8} torr).
- Mechanism to scan the magnetic field.
- **Filament heating/degassing unit for cleaning filaments**

ASTM standard C1672 – 07

Filament degassing as a means of cleaning the filament



ASTM standard C1672 – 07

Calibrations and Performance Tests

- ***Electron multiplier/Faraday intercalibration*** also known as a yield calibration measures calibration factor that shall be determined when using ion counters and Faraday cups during measurement; daily when using Faraday and ion counters simultaneously
- ***Electron multiplier calibration*** determines dead time and linearity corrections that may be needed for more precise measurement of minor isotopes; as needed for better minor isotope measuring
- ***Linearity of mass spectrometer***; periodically
- ***Mass bias correction*** is not needed in theory, but is needed in practice. **Mass bias (“mass fractionation”) correction** factors can be determined by measuring a certified isotopic reference material along with the unknown samples, determining the correction factor and applying a correction to unknown samples; each time samples are analyzed

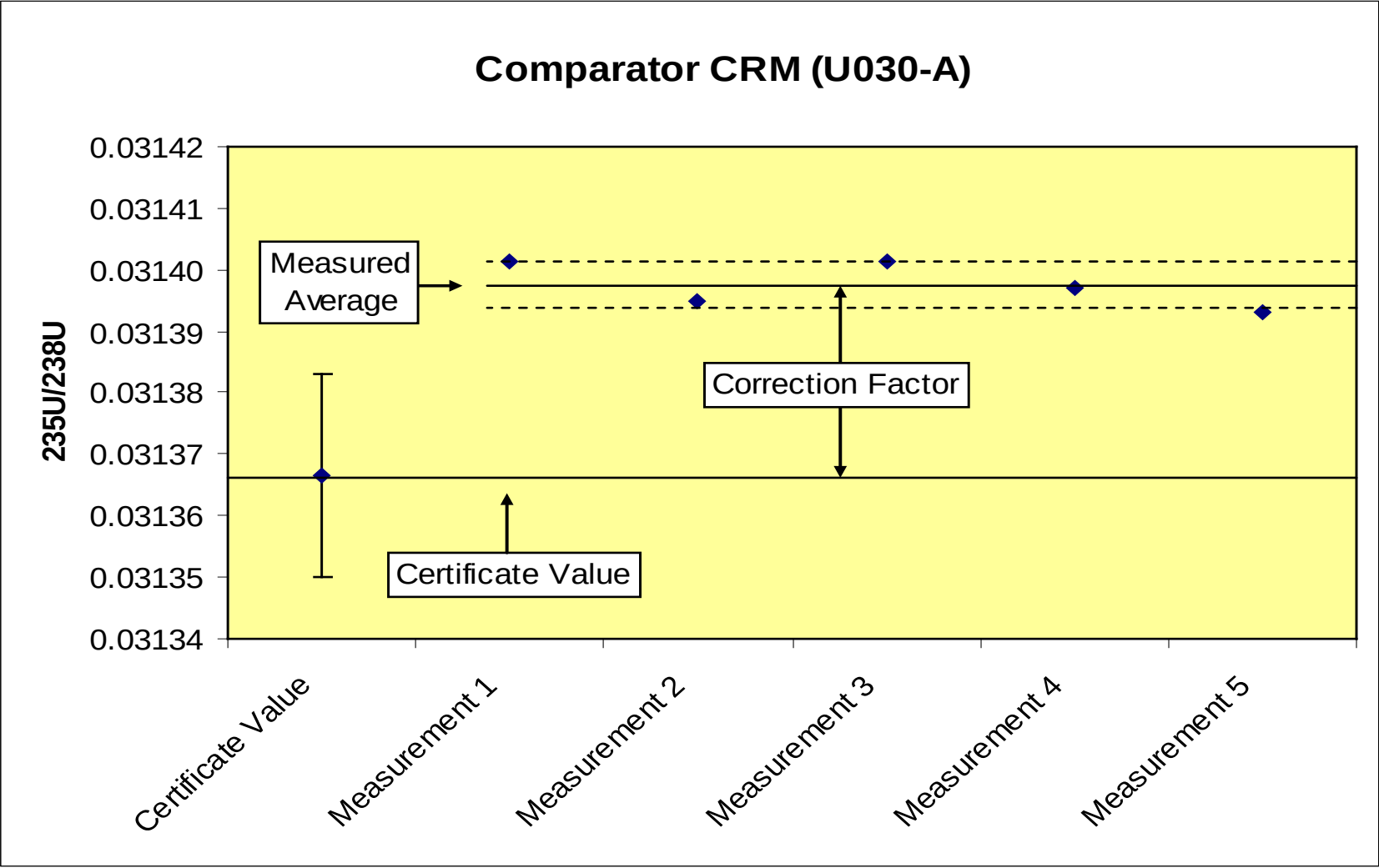
ASTM standard C1672 – 07

Mass Bias Calibration: How?

- Analyze standards, along with the samples
- Need to assume that the standards experience the same fractionation behavior as the samples.
- Load using the same methods, try to use samples and standards that have the same matrix, analyze samples and standards using the same experiments.

ASTM standard C1672 – 07

Mass Bias Calibration: How?



ASTM standard C1672 – 07

Mass fractionation correction factor (K-factor)

➤ $K = R_m / R_c$

- K = mass bias correction factor
 - R_m = averaged measured atom ratio for CRM
 - R_c = certified atom ratio value for CRM
- To correct individual measured sample ratios, calculate the appropriate mass bias correction factor based on the mass difference between isotopes (correction per mass unit), and multiply the sample ratio by the applicable mass bias correction factor

ASTM standard C1672 – 07

- Sample preparation
 - ❖ Dissolution of samples, if doing IDMS, appropriate to spike before chemical purification occurs
 - ❖ Samples and standards should undergo exact chemical preparation and handling procedures
- Sample purification as per ASTM C 1411, or similar for separating U/Pu
- Sample loading, technique should consist of a drop deposition onto a metal filament
- Sample conditioning on to filament by applying a current across filament causing evaporation of sample
 - ❖ Usually consists of ramping current on filament in increments to 2 A

ASTM standard C1672 – 07

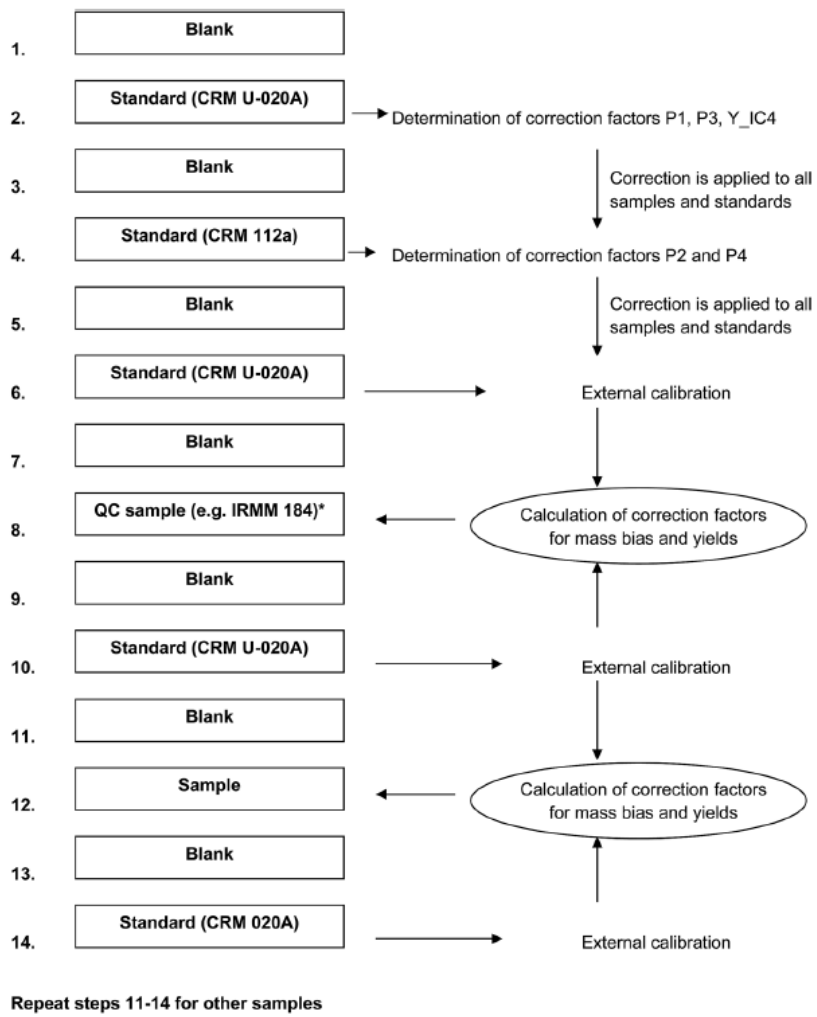
➤ Isotope ratio measurement

- ❖ Insert filament assembly into source, seal and evacuate chamber,
- ❖ Perform baseline and gain calibrations
- ❖ Heat ionization filament to sufficient heat (~1450-1850° C)
- ❖ Locate major isotope beam U/Pu, perform peak centering and focusing
- ❖ Begin data acquisition, turn filaments down when complete

ASTM standard C1672 – 07

- Three groups of samples on sample magazine:
 - ❖ Comparator
 - Always a CRM
 - Measured $^{235}\text{U}/^{238}\text{U}$ ratio used to calculate correction factor for mass fractionation
 - ❖ QC Sample
 - Another CRM or known standard (WRM)
 - Apply correction factor from comparator to this measured $^{235}\text{U}/^{238}\text{U}$ ratio for verification
 - ❖ Unknown
 - Reported result is the isotope ratio scaled using the verified correction factor from the comparator.

ASTM standard C1672 – 07



* The 1st quality control (QC) sample

Already doing an excellent job –
Boulyga et al. JAAS 2016

fig. 1 Measurement sequence.

ASTM standard C1672 – 07

Precision and Bias (^{235}U enrichments 1-90 %)

- Uranium major ratio $^{235}\text{U}/^{238}\text{U}$ varies by 0.016% to 0.028% relative standard deviation;
 - ❖ Minor isotope precision varied over a wide range depending on the abundance of the minor isotope
- Plutonium $^{240}\text{Pu}/^{241}\text{Pu}$ varies between 0.0045% and 0.0077% as percent relative standard deviation
 - ❖ Minor isotope precision varied over a wide range depending on the abundance of the minor isotope

Relative standard deviation (%RSD) is the standard deviation of a measurement set, divided by the reference value expressed as a percent.

ASTM standard C1672 – 07

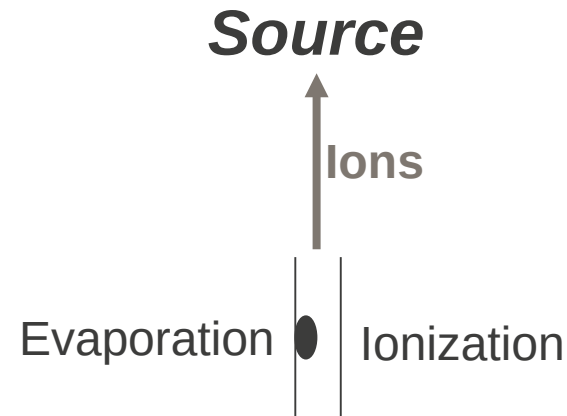
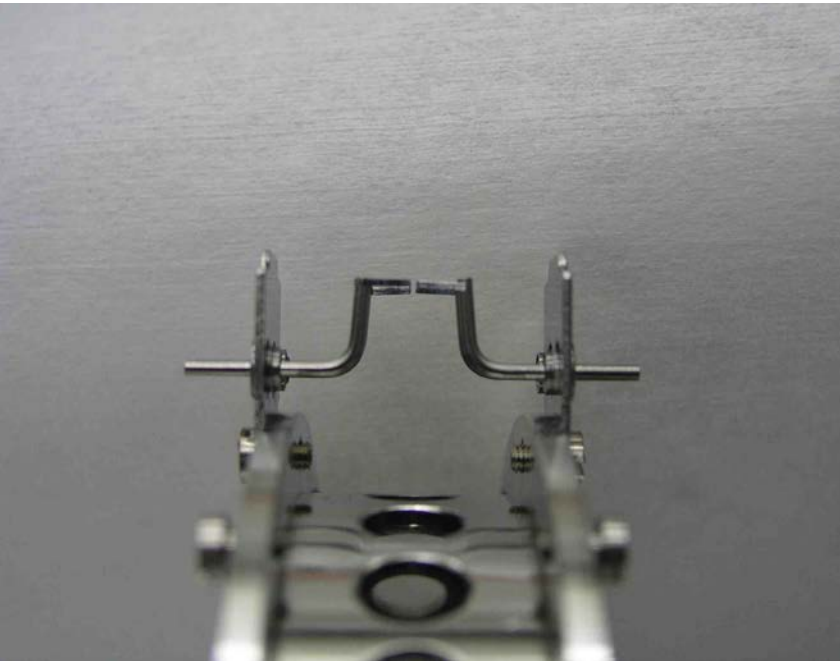
Precision and Bias (^{235}U enrichments 1-90 %)

Bias

- Prevalent bias in measuring $^{236}\text{U}/^{238}\text{U}$ most likely due to peak tailing from abundant ^{238}U isotope
- No other biases in Pu or U measurement analysis were determined

ASTM standard C1672 – 07

- Sample deposited onto a metallic filament (Re, W, Ta)
 - $\sim$ pg – μ g quantities



ASTM standard C1672 – 07

- Measurements have better precision (compared to conventional -- more consistent).
- Ion signals are continuously measured.

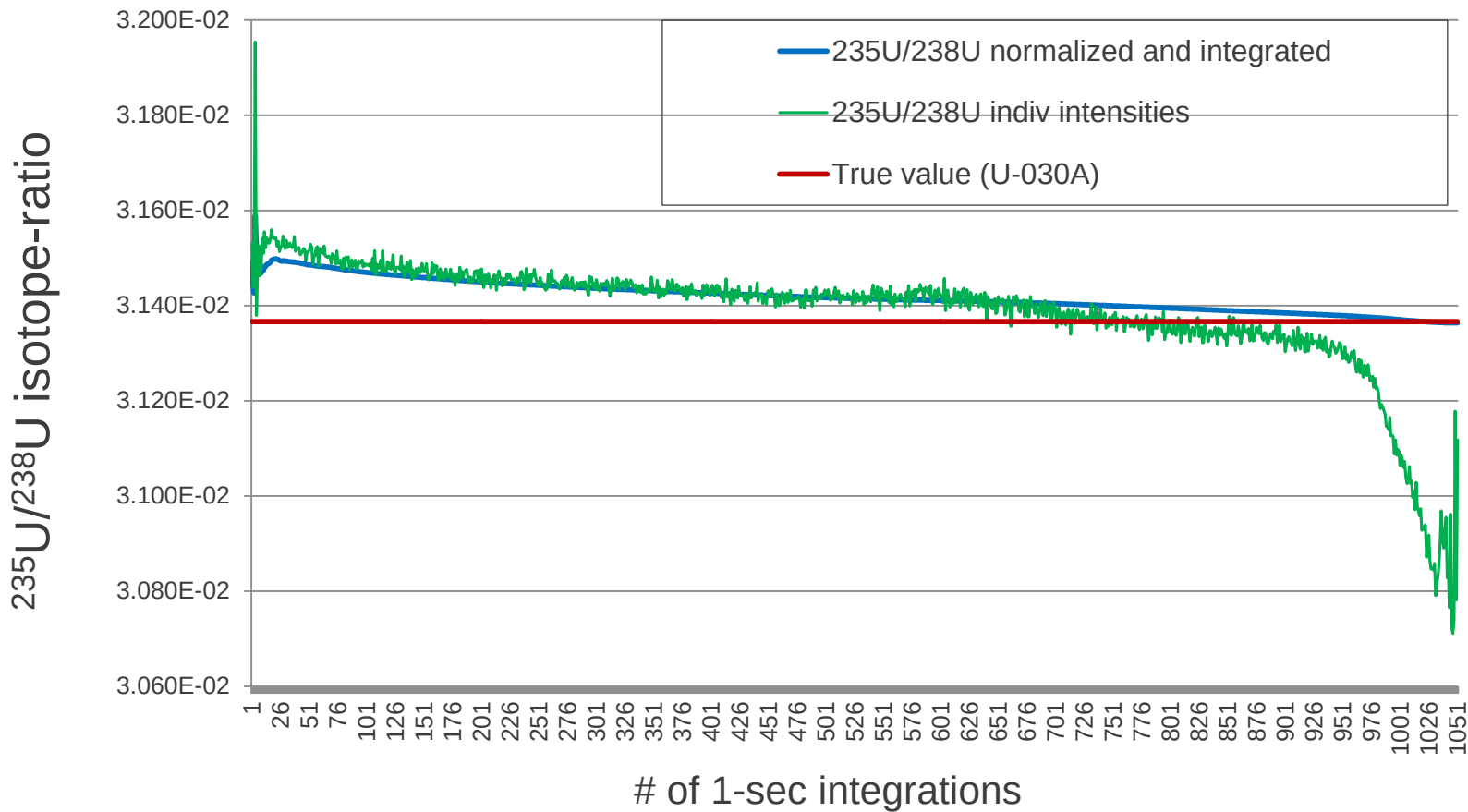
One cycle: TE

Scan	Cup L2	Cup L1	Center Cup/SEM	Cup H1	Cup H2	Cup H3	integration
1	233U	234U	235U	236U	237U	238U	1.049 s

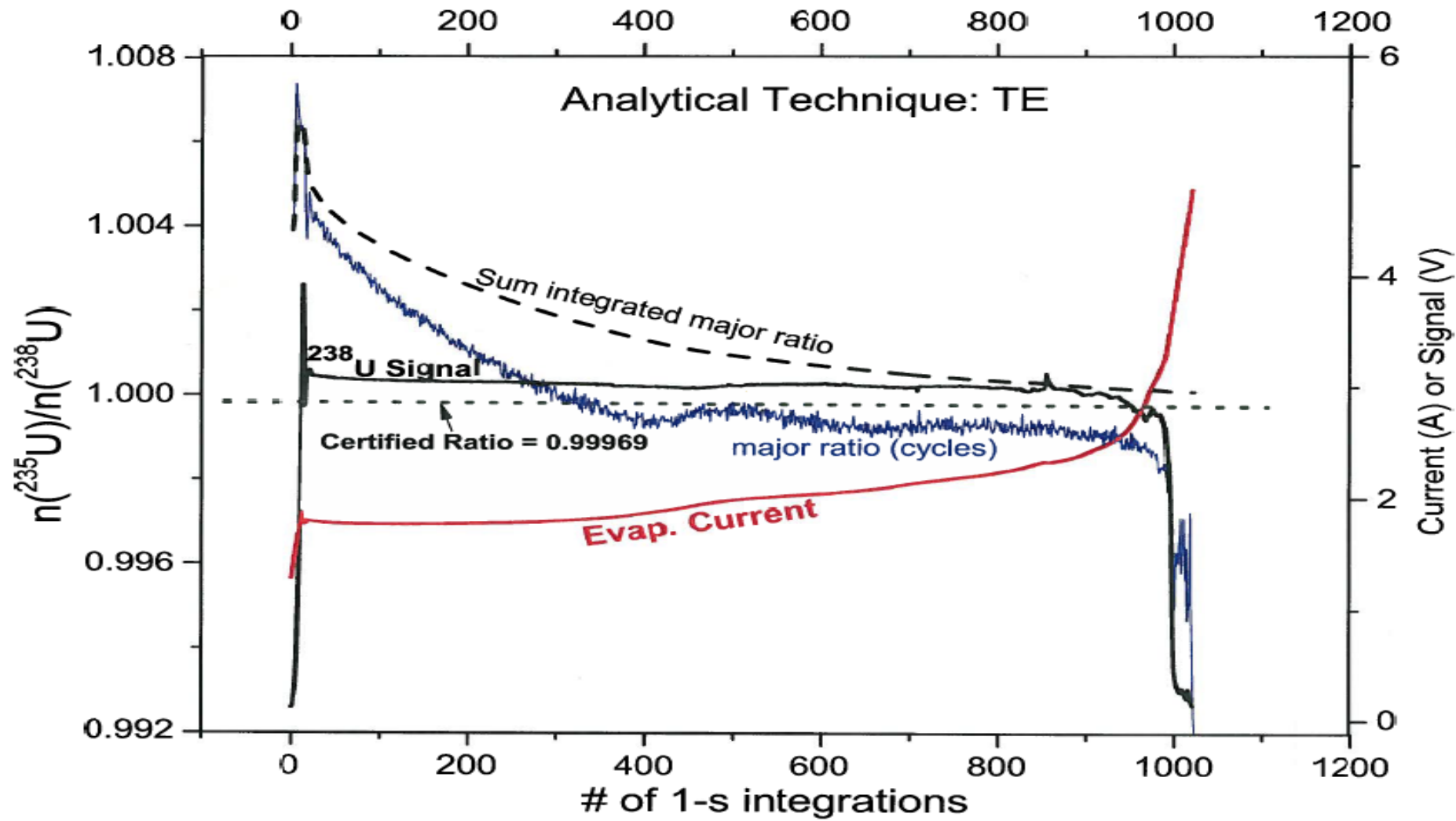
- In principle, because the entire sample is evaporated and continuously measured, a fractionation correction should not be necessary.
- However, NBL has observed that it is necessary to correct uranium isotopic ratio measurements for fractionation.

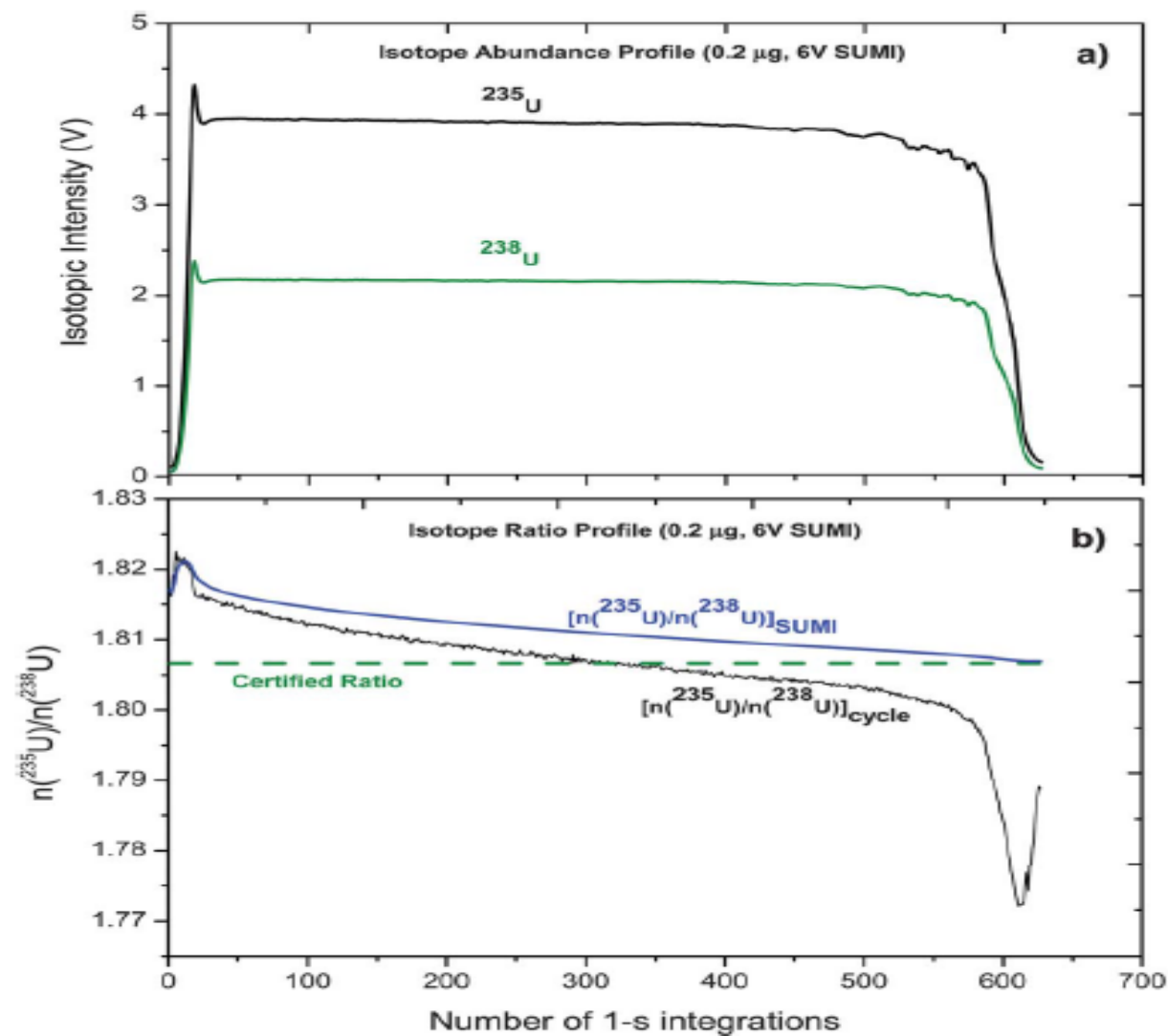
ASTM standard C1672 – 07

Total Evaporation $^{235}\text{U}/^{238}\text{U}$ ratio



ASTM standard C1672 – 07





Mathew et al., JAAS 2013

Fig. 1 The ^{235}U and ^{238}U isotope abundance profiles (a) and $n(^{235}\text{U})/n(^{238}\text{U})$ isotope-amount ratio profile (b) in TE analyses of CRM U630. Amount of U loaded is 0.2 µg and analysis intensity (sum of the ^{235}U and ^{238}U intensities) is 6 V.

V standard C1672 – 07

Mathew et al., JAAS 2013

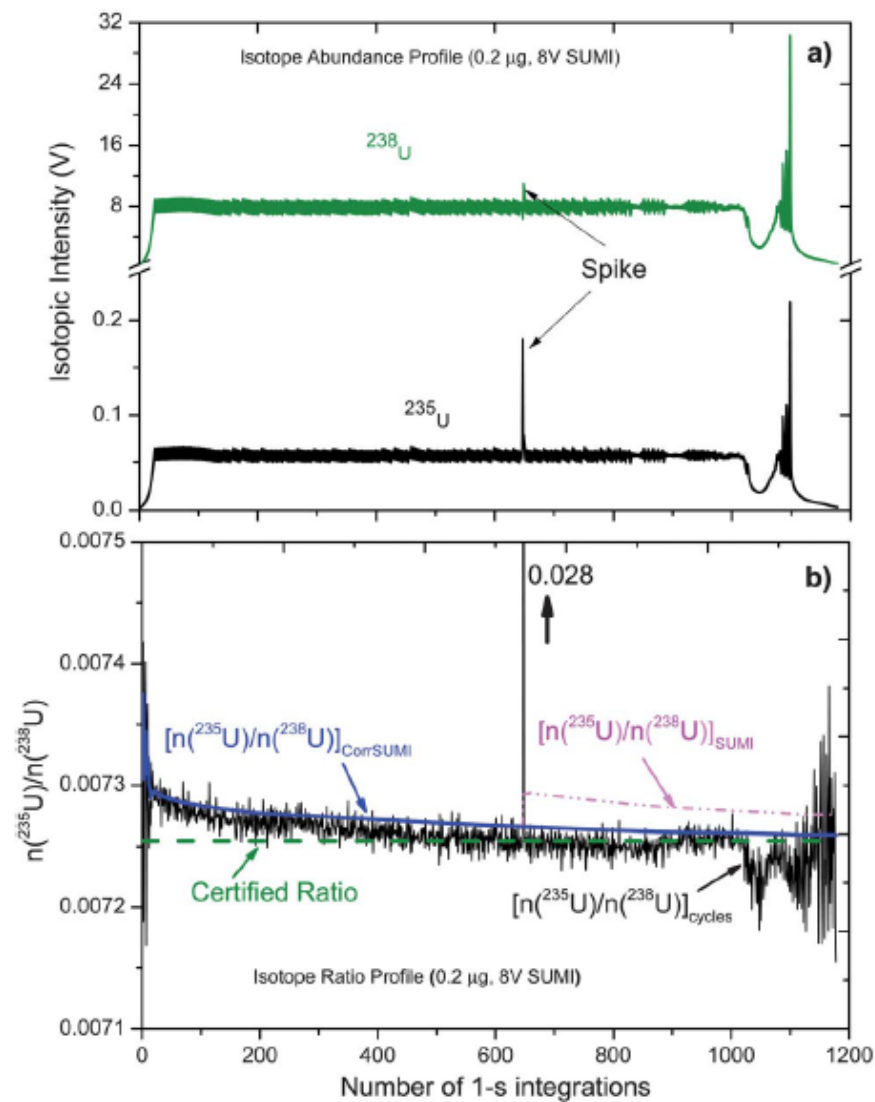
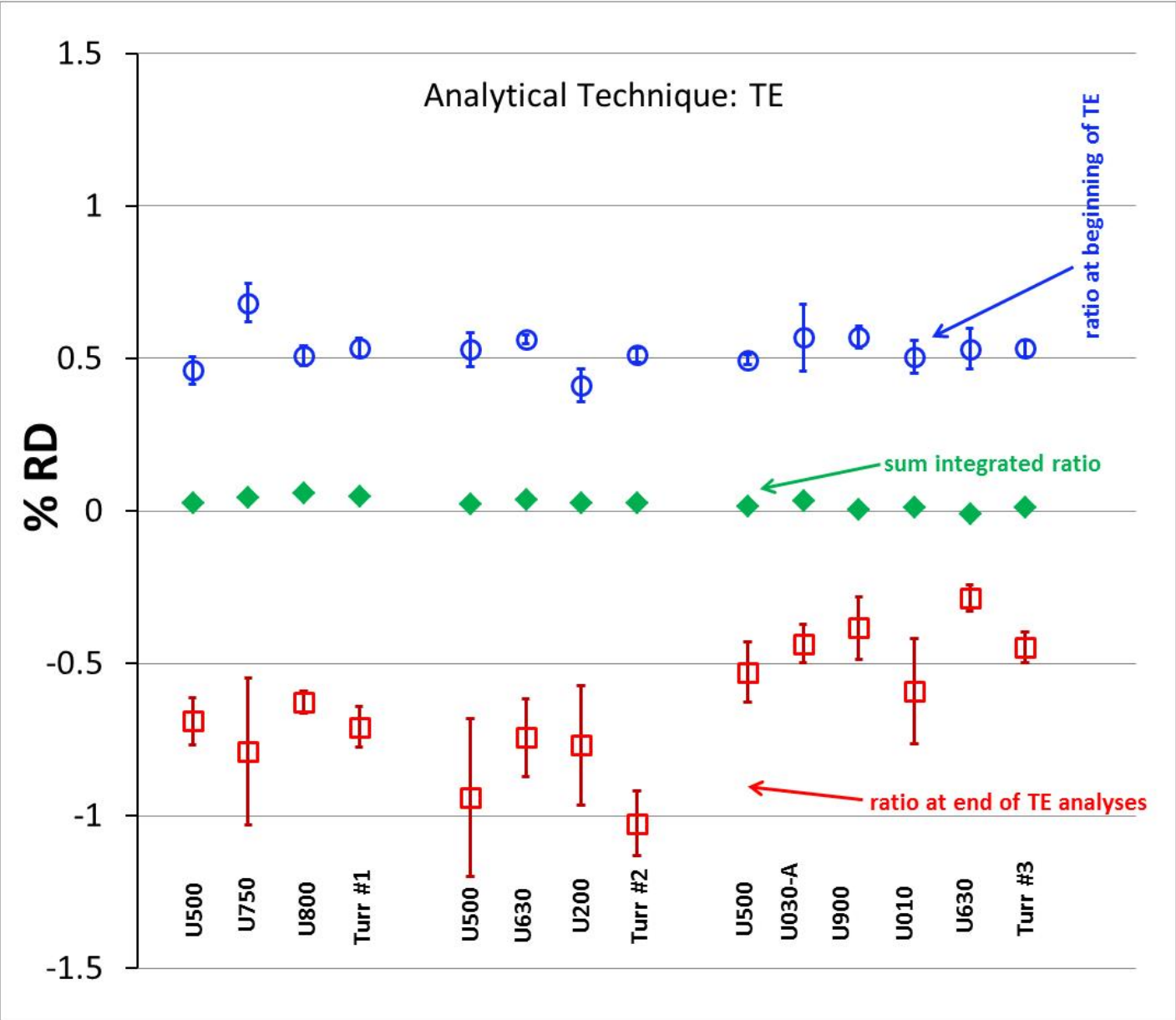


Fig. 3 The ^{235}U and ^{238}U isotope abundance profiles (a) and $n(^{235}\text{U})/n(^{238}\text{U})$ isotope-amount ratio profile (b) in TE analyses of CRM C112-A. Amount of U loaded is 0.2 µg and analysis intensity (sum of the ^{235}U and ^{238}U intensities) is 8 V. One electronic spike is present (the measured ratio in the cycle influenced by the spike is – 0.028 – indicated).

ASTM standard C1672 – 07



Disadvantages of TE Analysis

- Assume analytical conditions remain constant during analysis
 - ❖ No during-run background measurement
 - ❖ No lens-focusing
 - ❖ No peak centering
 - ❖ No gain calibration between detectors

ASTM standard C1625 – 12

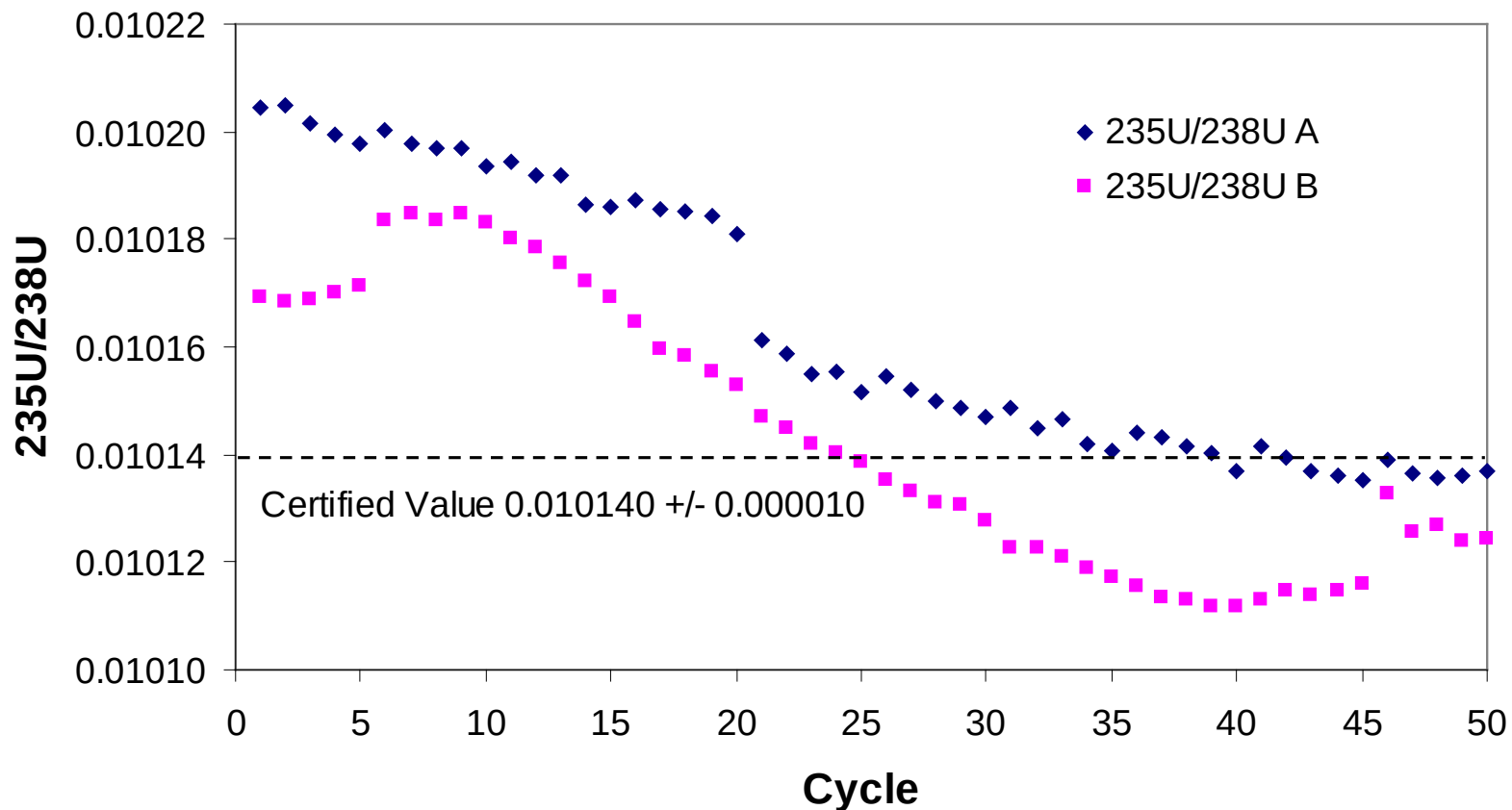
- Conventional analysis consists of repeated “Blocks” of Cycles
- Measure all isotopes of interest on Faraday/SEM
 - ^{233}U , ^{234}U , ^{235}U , ^{236}U , ^{238}U (e.g.)
- Measure minor isotopes and associated background on Faraday/SEM
 - ❖ For ^{233}U , backgrounds measured at 232.55 and 233.55

Scan	Center Cup/SEM	Cup H1	Cup H2	Cup H3	Cup H4
1	^{233}U	^{234}U	^{235}U	^{236}U	^{238}U
2	232.55	233.55	234.55	235.55	--
3	233.55	234.55	235.55	236.55	--
4	^{234}U	^{235}U	^{236}U		
5	^{233}U	^{234}U	^{235}U	^{236}U	^{238}U

One cycle of conventional analyses

ASTM standard C1625 – 12

- “ n ” (10) cycles per block
- Lens Focus and Peak Center after every “ y^{th} ” (2nd) block

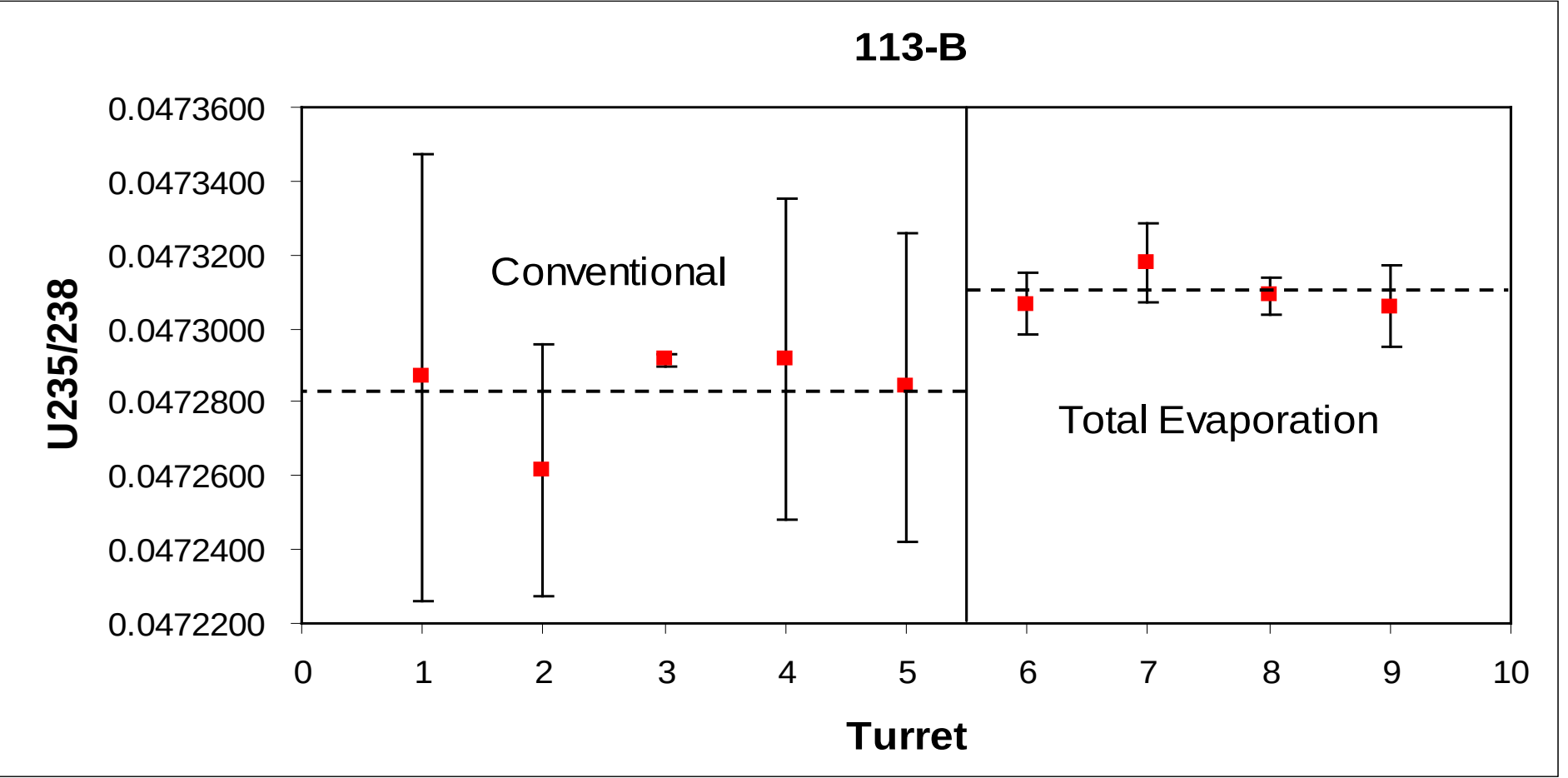


Disadvantages of “Conventional Analysis”

- Sample continuously evaporating without continuous measurement of ion currents from each isotope
- Assumes isotope ratio does not change as analysis progresses
- Ratio can vary by as much as 0.7% of actual value over the course of a run
- The point at which the data is collected can affect the measured isotopic ratio.
 - If sample is lost at the beginning of a $^{235}\text{U}/^{238}\text{U}$ analysis, the final measured ratio will be low.
 - If the analysis ends early, the final $^{235}\text{U}/^{238}\text{U}$ ratio will be biased toward higher values.

ASTM standard C1625 – 12

Repeatability: TE vs. Conventional



ASTM standard C1832-16

Modified Total Evaporation (MTE)

- Developed at NBL, perfected at IRMM/NBL
- Analysis Consists of Repeated “Blocks” of Cycles
- Measures major isotopes on Faraday cups, minor isotopes (and their backgrounds) measured on SEM

One cycle: MTE

Scan	Cup L3	Cup L2	Cup L1	Center Cup/SEM	Cup H1	Cup H2	Cup H3	Cup H4	Purpose
1	²³³ U	²³⁴ U	²³⁵ U	²³⁶ U	237	²³⁸ U	²³⁹ Pu	²⁴⁰ Pu	“dummy”
2	²³³ U	²³⁴ U	²³⁵ U	²³⁶ U	237	²³⁸ U	²³⁹ Pu	²⁴⁰ Pu	measurement
3		²³² U	²³³ U	²³⁴ U	²³⁵ U	²³⁶ U	237		measurement
4		233.7	234.7	235.7	236.7	237.7			measurement
5		234.4	235.4	236.4	237.4	238.4			measurement
6	²³³ U	²³⁴ U	²³⁵ U	²³⁶ U	237	²³⁸ U	²³⁹ Pu	²⁴⁰ Pu	measurement

ASTM standard C1832-16

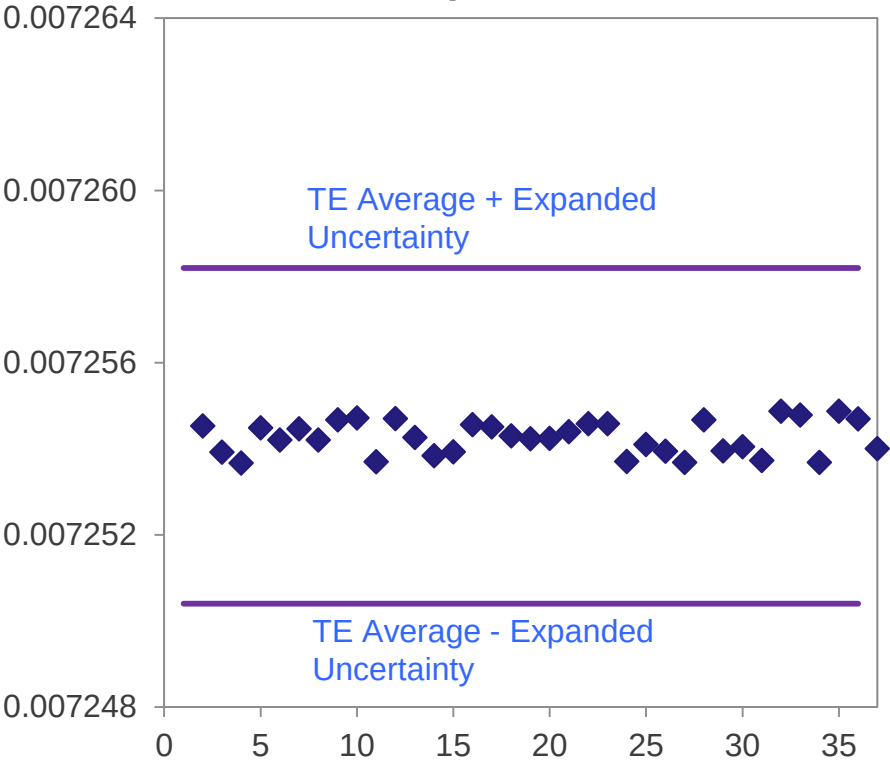
Modified Total Evaporation (MTE)

- Increased precision of minor isotope ratio measurements ($^{234}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$) by performing the following at regular intervals:
 - ❖ background measurements,
 - ❖ lens focusing
 - ❖ peak centering
 - ❖ gain calibration between detectors
- Much larger sample loads ($\sim 5\mu\text{g}$ for MTE Vs 200ng for TE)
- Much longer measurement time (~ 12 to 36 hours for MTE Vs. ~ 5 hours for TE)

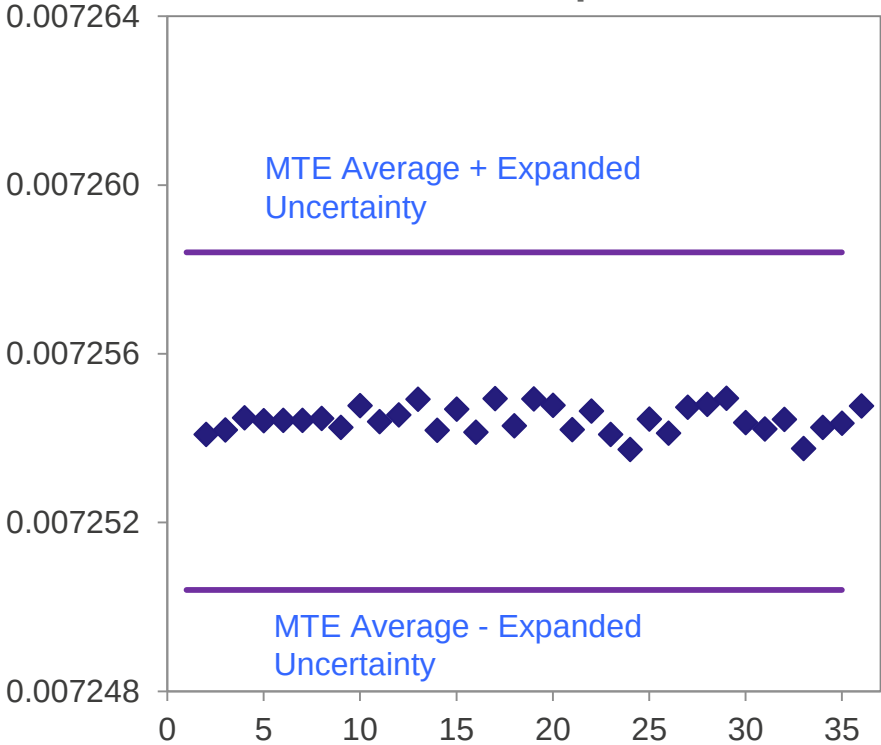
ASTM standard C1832-16

$^{235}\text{U}/^{238}\text{U}$ Ratio: TE Vs. MTE

Total Evaporation

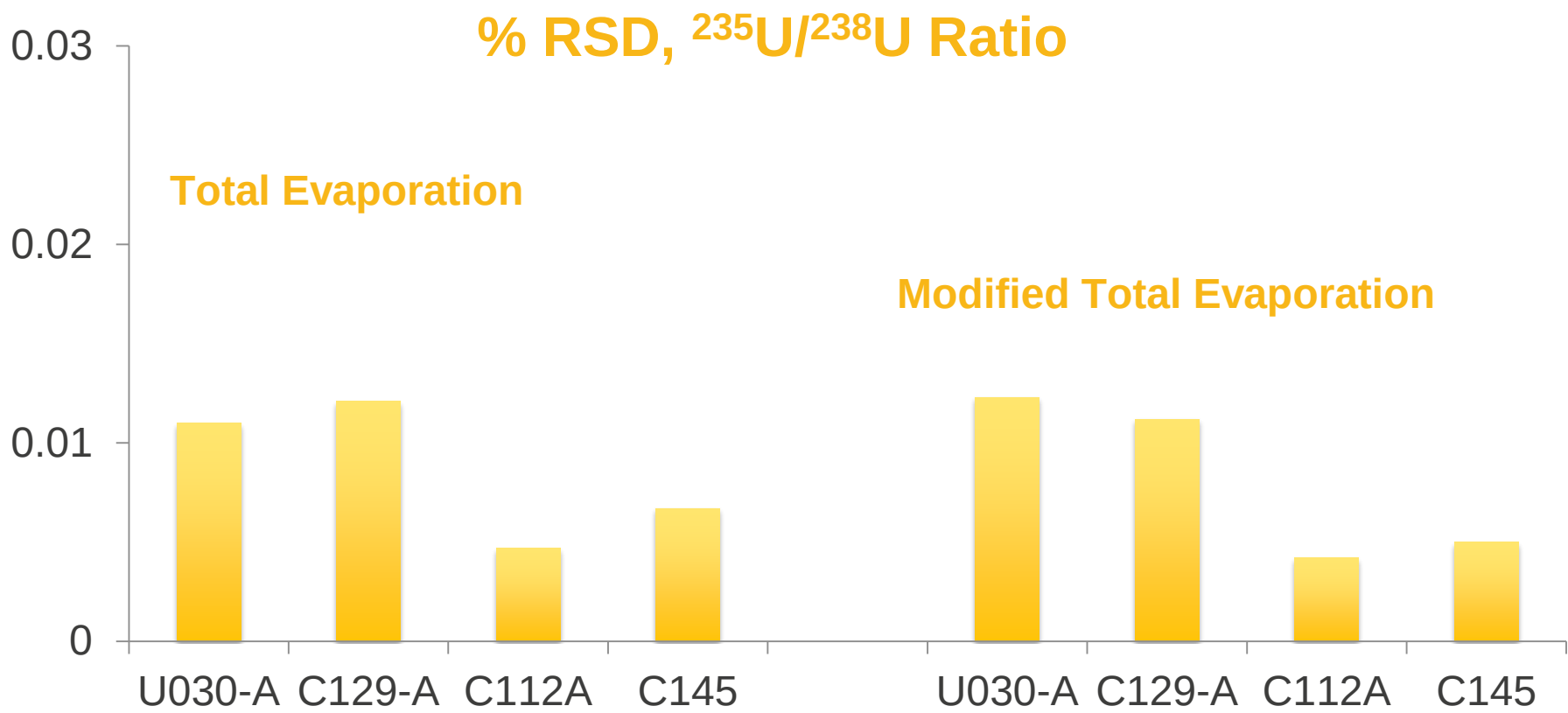


Modified Total Evaporation



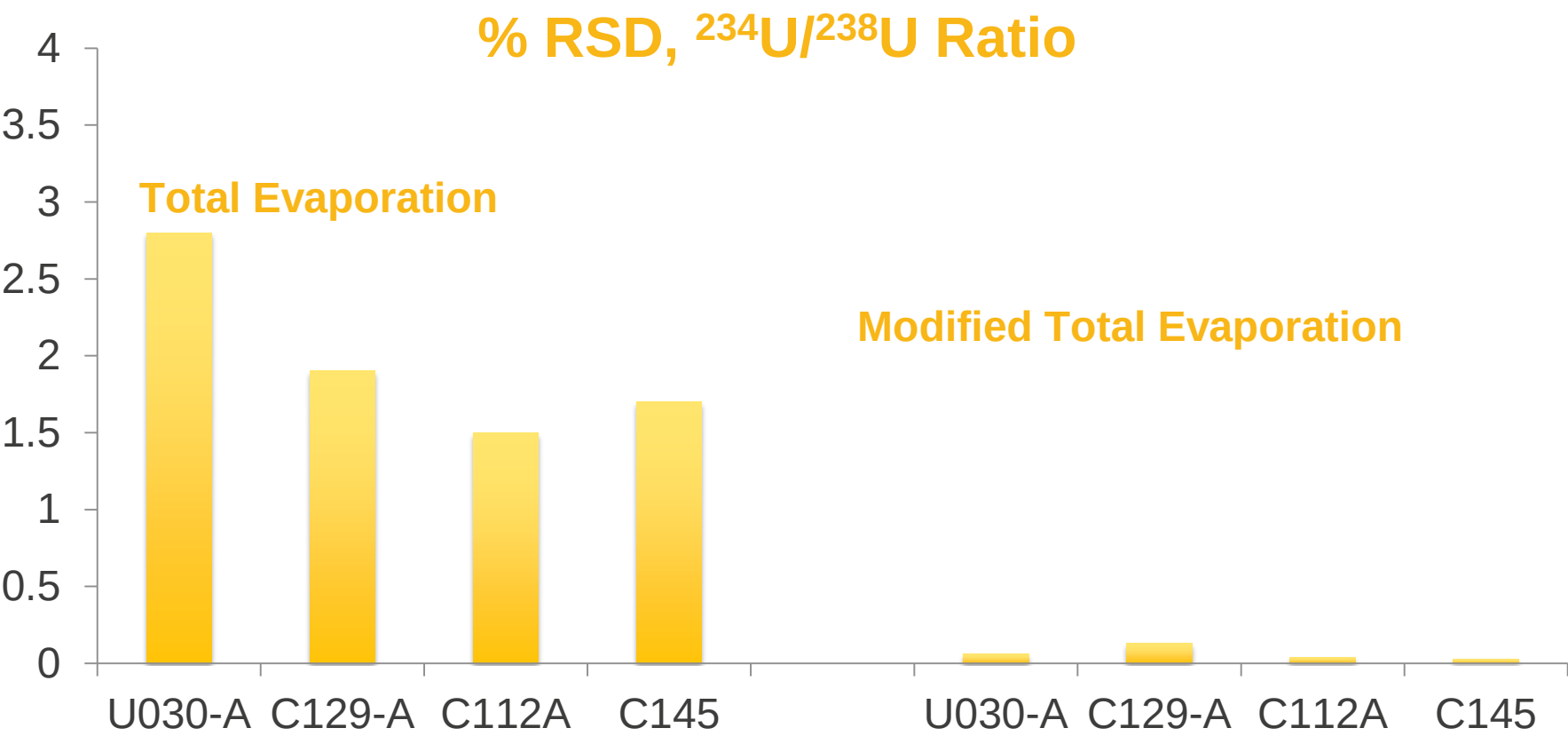
ASTM standard C1832-16

Precision of the $^{235}\text{U}/^{238}\text{U}$ Ratio: TE Vs. MTE

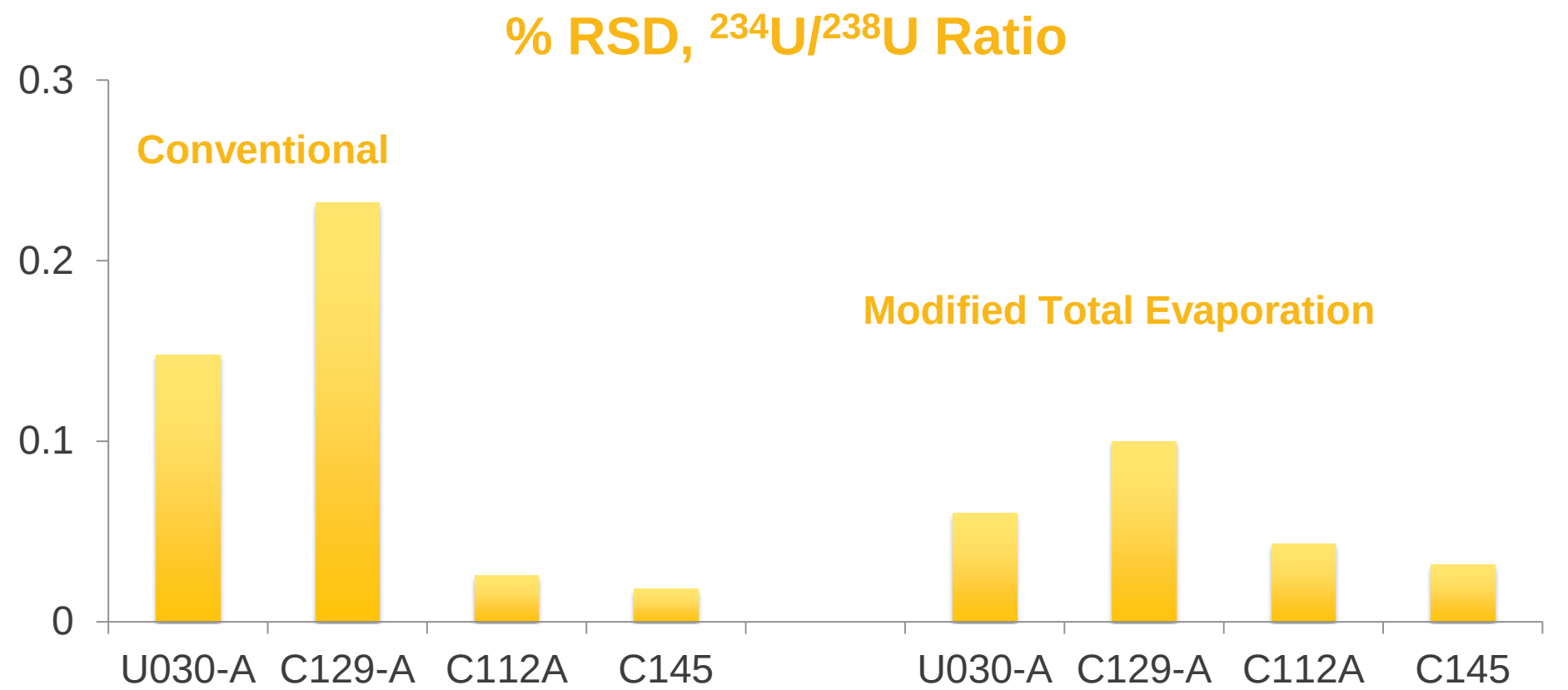


ASTM standard C1832-16

Precision of the $^{234}\text{U}/^{238}\text{U}$ Ratio: TE Vs. MTE



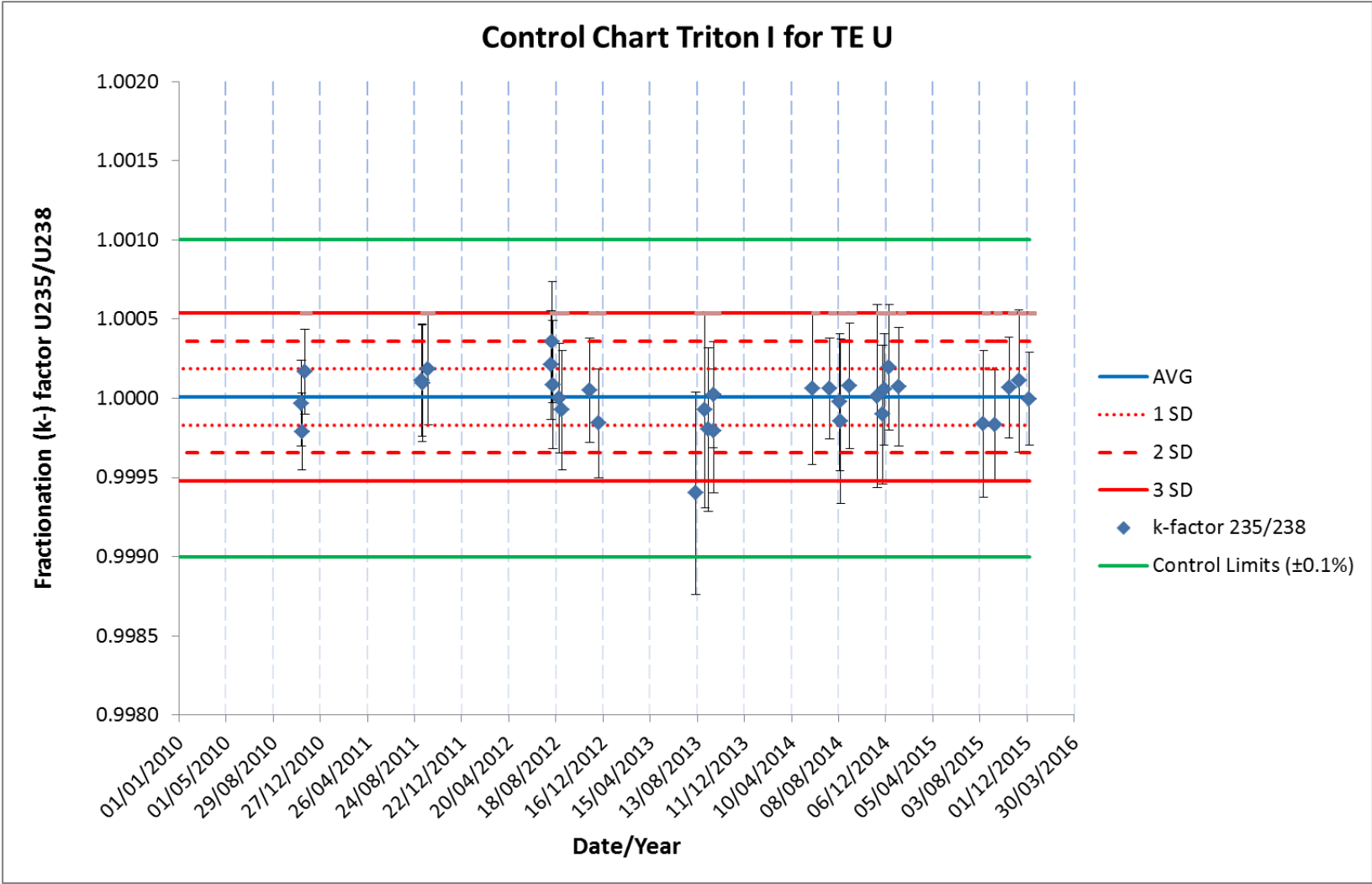
Precision of the $^{234}\text{U}/^{238}\text{U}$ Ratio: Conventional Vs. MTE



Comparator or No Comparator

- In principle, TE isotope ratio result should be free from systematic biases due to instrumental mass fractionation.
- ASTM C1672 is flexible in that use of a comparator CRM is not required.
- The TE method has been used in the recent certification of Am isotopic standard at IRMM. No isotopic standard is available for instrument calibration of the Am isotopic masses. TE method was used for isotope ratio measurements and assumption was made that the measured ratios are close to true ratio. An additional uncertainty component of 0.03 % was assigned to this assumption. But why an additional uncertainty of 0.03 % ?

Why 0.03% uncertainty for major ratio using TE

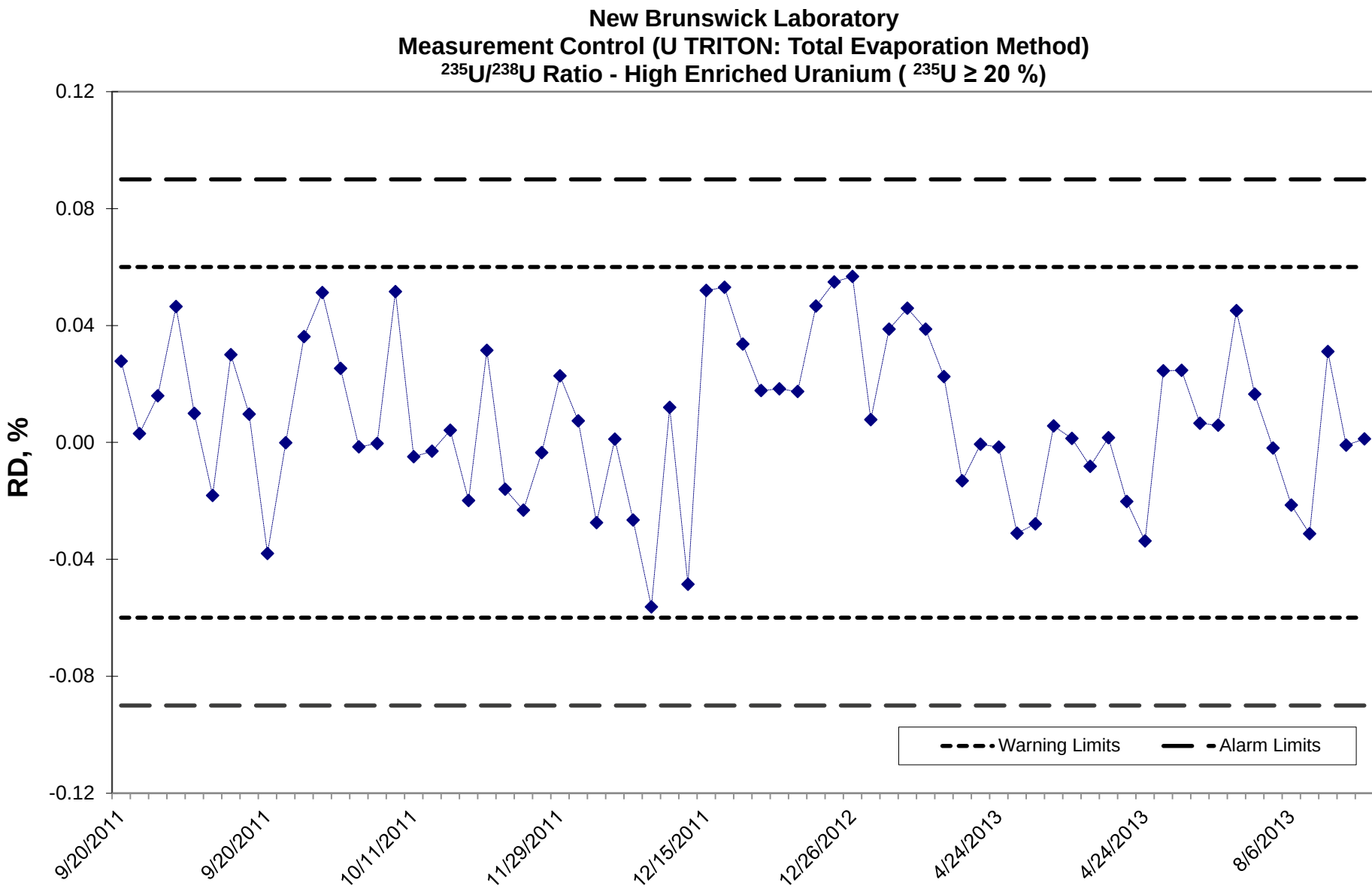


Control limits for U or Pu major ratio analyses using TE is close to 0.03 %

What if No Comparator is used ?

- An additional uncertainty component of $\sim 0.03\%$ needs to be assigned to the uncertainty of the TE measurement result.
- If a comparator is used and if the control charts are generated using the NBL methodology
- There is no need to add this additional uncertainty component.
- Why ??

If a Comparator is used ?



If a Comparator is used ?

- Uncertainty components arising from Comparator-to-Comparator, analyst-to-analyst, period-to-period, CRM-to-CRM differences are confounded into the observed variability and therefore into the control limit calculations.
- Thus there is no need to add additional uncertainty component.
- Bottom line: CRM standards provide multiple functions in measurement – calibrate the instruments, provide traceability, estimate correction factors, and serve as QC standards.
- Through the use of the comparator standard, the QC function is transferred to a different CRM.

- Uncertainties in the uranium isotope-amount ratios can be estimated from:
 - ❖ QC CRMs
 - The precision of the QC data can be combined with the accuracy to estimate typical uncertainties for the measurement method
 - As the major and minor ratios are traceable to the national/international measurement base (and to the S.I.) this can be done for both ratios
 - ❖ Following ISO GUM principles
 - Major ratio uncertainty comes from:
 - Repeatability of the major ratio measurements of the samples
 - Repeatability of the major ratio measurements of the comparator standard
 - Certified uncertainties in the major ratio of the comparator standard
 - Minor ratio uncertainties come from:
 - Repeatability of the minor ratio measurements
 - Variability in the peak-tail corrections (implemented off-line in a cycle-per-cycle basis)
 - Uncertainty in the mass bias correction (internal correction using measured value of the major ratio and its “true” value)

Table 5 Combined summary of the QC CRM data on both instruments. Relative deviation of the measured ratios from certified values and the relative standard uncertainties are shown for each CRM that was included in the present study^a

CRM	Average for CRM			%RD ± %RSE		
	$n(^{234}\text{U})/n(^{238}\text{U})$	$n(^{235}\text{U})/n(^{238}\text{U})$	$n(^{236}\text{U})/n(^{238}\text{U})$	$n(^{234}\text{U})/n(^{238}\text{U})$	$n(^{235}\text{U})/n(^{238}\text{U})$	$n(^{236}\text{U})/n(^{238}\text{U})$
U900 (<i>N</i> = 5)	0.0895869	10.3743983	0.0383095	0.1011 ± 0.0231	−0.0126 ± 0.0110	0.0975 ± 0.0431
U750 (<i>N</i> = 3)	0.0249226	3.1666920	0.0105229	0.1490 ± 0.0177	0.0178 ± 0.0152	0.2223 ± 0.0252
U630 (<i>N</i> = 3)	0.0176626	1.8062387	0.0274506	0.0815 ± 0.0647	−0.0244 ± 0.0089	0.0294 ± 0.0189
U045 (<i>N</i> = 9)	0.0004071	0.0473145	0.0002920	0.44 ± 0.25	0.0094 ± 0.0193	1.06 ± 0.62
C125-A (<i>N</i> = 1)	0.0003920	0.0422973	0.0000047	0.52 ± 0.23	−0.0218 ± 0.0081	52.6 ± 11.1
U030-A (<i>N</i> = 2)	0.0002879	0.0313720	0.0000102	0.45 ± 0.25	0.0171 ± 0.0168	64.2 ± 11.5
U010 (<i>N</i> = 5)	0.0000557	0.0101365	0.0000772	2.59 ± 1.64	−0.0362 ± 0.0112	12.6 ± 6.9
C129-A (<i>N</i> = 6)	0.0000539	0.0072618	0.0000026	1.10 ± 0.57	0.0052 ± 0.0088	—
C112-A (<i>N</i> = 6)	0.0000534	0.0072533	—	1.47 ± 0.83	−0.0141 ± 0.0226	—
U005-A (<i>N</i> = 1)	0.0000362	0.0050900	0.0000140	5.75 ± 2.31	0.0008 ± 0.0131	18.01 ± 1.85

^a *N* represents the number of turrets included in the average ratio shown (each turret had multiple replicates of the CRM).

Mathew et al., JAAS 2013
Typical precisions and accuracies of TE measurements

Guide to the Expression of Uncertainty in Measurement (GUM)

TIMS Measurement Methods

Module 3

Authors: K. J. Mathew (LANL)

Guide to the Expression of Uncertainty in Measurement (GUM)

Uncertainty Examples for TIMS Measurements

Module 4

Authors: K. J. Mathew (LANL)

- Uranium is separated from Pu and Am (four independent cuts)
- The U isotopic composition measured by Total Evaporation technique using VG-3 TIMS instrument.
- 4 V signals analyzed until the sample is totally evaporated

$$\left(\frac{{}^{235}\text{U}}{{}^{238}\text{U}}\right)_{TE} = \frac{\sum_{ALL\_INTEGRATIONS} I({}^{235}\text{U})}{\sum_{ALL\_INTEGRATIONS} I({}^{238}\text{U})} = \frac{\sum_{ALL\_INTEGRATIONS} \left[\left(\frac{I({}^{235}\text{U})}{I({}^{238}\text{U})} \right) \cdot I({}^{238}\text{U}) \right]}{\sum_{ALL\_INTEGRATIONS} I({}^{238}\text{U})}$$

Title: Uranium Isotopics on VG3

Reference: Date: 10/11/2017 Version: Author:

General Description Picture 1

This model determines the isotopic atom ratios, atom% and weight% of a sample on VG3 using TE.

A1 = Cut-41, separated on 4/19/2017 and analyzed on 5/3/2017

A2 = Cut-42, separated on 4/19/2017 and analyzed on 5/1/2017

B1 = Cut-43, separated on 4/19/2017 and analyzed on 5/1/2017

B2 = Cut-44, separated on 4/19/2017 and analyzed on 5/1/2017

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GUM Workbench Pro - U-Iso on VG3 Rev1.smu

File Edit View Picture Diagram Option Tools Help

Model

Observation

Correlation

Budget

Last

Result

Diagram

Title

Model Equation

Quantity Data

Partial Derivatives

Σδ...

f(x)...

Rename

Order

Experts

Equation:

{U Isotopic Atom Ratios on VG3 using TE}
{Standard used was U-630}
{
A1 = Cut-41, separated on 4/19/2017 and analyzed on 5/3/2017
A2 = Cut-42, separated on 4/19/2017 and analyzed on 5/1/2017
B1 = Cut-43, separated on 4/19/2017 and analyzed on 5/1/2017
B2 = Cut-44, separated on 4/19/2017 and analyzed on 5/1/2017
}
{-----}
{Calculate the fractionation per amu.}

frac_{amu} = ((knownR_{238/235,U630} - measR_{238/235,U630}) / knownR_{238/235,U630}) / (238-235);

{-----}
{Calculate the abundance correction.}

Abund_{233/235,A1} = abund_{2amu} * 1 + abund_{1amu} * measR_{234/235,A1} + abund_{3amu} * measR_{236/235,A1};
Abund_{234/235,A1} = abund_{1amu} * 1 + abund_{2amu} * measR_{236/235,A1} + abund_{4amu} * measR_{238/235,A1};
Abund_{236/235,A1} = abund_{1amu} * 1 + abund_{2amu} * measR_{234/235,A1} + abund_{2amu} * measR_{238/235,A1};
Abund_{238/235,A1} = abund_{1amu} * 1 + abund_{2amu} * measR_{234/235,A1} + abund_{2amu} * measR_{236/235,A1};
}

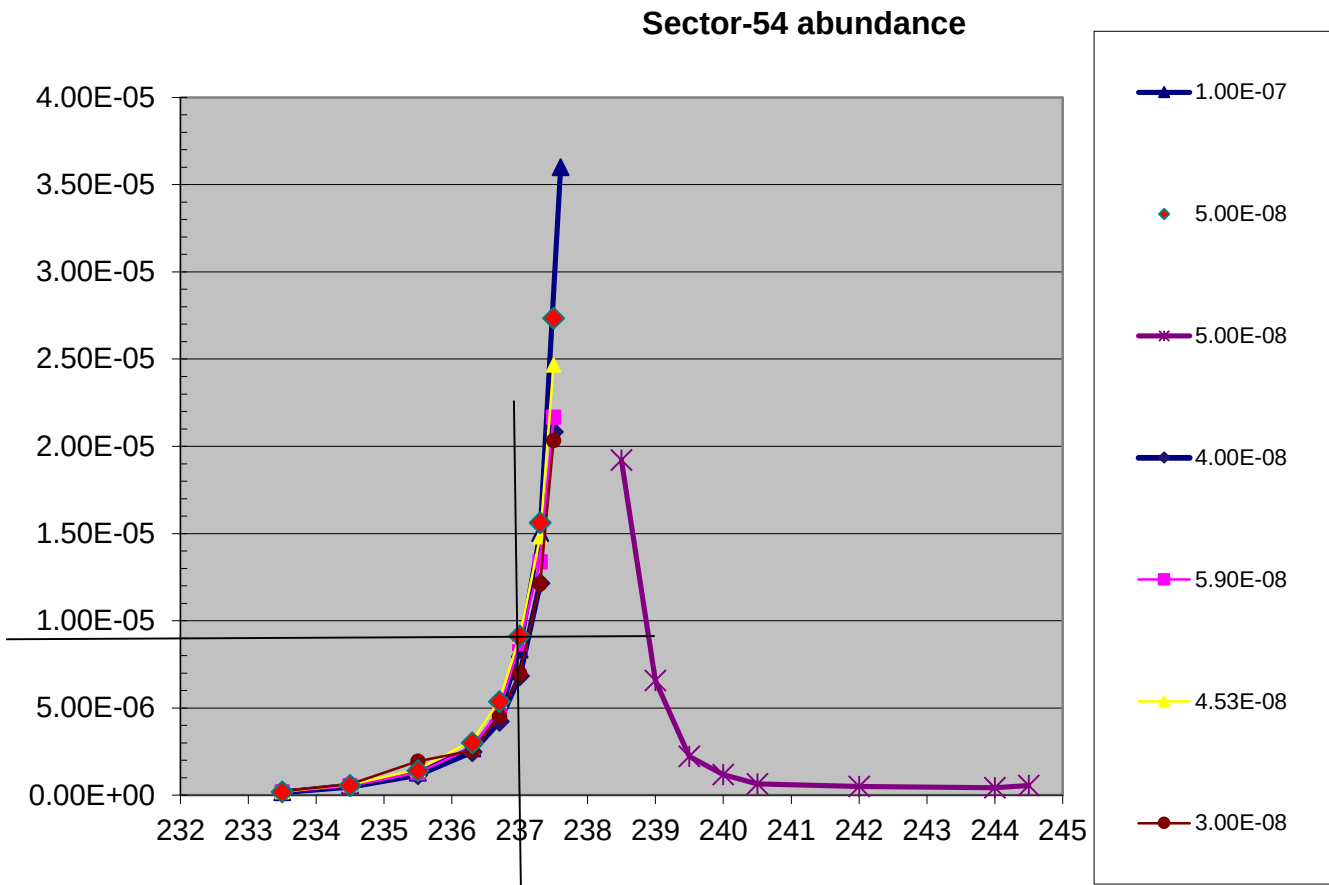
Quantity	Unit	Definition
AMU ₂₃₃		
AMU ₂₃₄		

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Abundance sensitivity curve for VG3



Absolute value of the tailing correction is critically dependent on the vacuum level and thus be different from one filament to the next

GUM Workbench Pro - U-Iso on VG3 Rev1.smu

File Edit View Picture Diagram Option Tools Help

Model

Observation

Correlation

Budget

Last

Result

Diagram

?

Title

Model Equation

Quantity Data

Partial Derivatives

AMU₂₃₃

AMU₂₃₄

AMU₂₃₅

AMU₂₃₆

AMU₂₃₈

knownR_{238/235,U63}

measR_{238/235,U630}

δ_{234/235,U630}

δ_{236/235,U630}

δ_{238/235,U630}

abund_{1amu}

abund_{2amu}

abund_{3amu}

abund_{4amu}

frac_{amu}

Bias₂₃₄

DL_{233/235}

measR_{234/235,A1}

measR_{236/235,A1}

measR_{238/235,A1}

measR_{234/235,A2}

measR_{236/235,A2}

Type: Type B

Distribution: Normal

Value: 1

Expanded Uncertainty: 0.064%

Coverage Factor: 2

Description

Picture 1

From COA

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GUM Workbench Pro - U-Iso on VG3 Rev1.smu

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ModelObservationCorrelationBudgetLastResultDiagram

?

corrR_{233/235,A1}

corrR_{234/235,A1}

corrR_{236/235,A1}

corrR_{238/235,A1}

corrR_{233/235,A2}

corrR_{234/235,A2}

corrR_{236/235,A2}

corrR_{238/235,A2}

◀▶

Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
knownR _{238/235,U630}	0.553510	0.000245	normal	0.018	4.4·10 ⁻⁶	5.8 %
measR _{238/235,U630}	0.5533424	0.0000525	normal	-0.018	-950·10 ⁻⁹	0.3 %
δ _{234/235,U630}	1.000000	0.000320	normal	0.030	9.6·10 ⁻⁶	27.3 %
abund _{1amu}	9.590·10 ⁻⁶	0.403·10 ⁻⁶	normal	-1.0	-400·10 ⁻⁹	0.0 %
abund _{2amu}	3.160·10 ⁻⁶	0.265·10 ⁻⁶	normal	-0.23	-61·10 ⁻⁹	0.0 %
abund _{4amu}	340.0·10 ⁻⁹	68.0·10 ⁻⁹	normal	-0.015	-1.0·10 ⁻⁹	0.0 %
frac _{amu}	101·10 ⁻⁶	151·10 ⁻⁶				
Bias ₂₃₄	-11.20000·10 ⁻⁶	0.00526·10 ⁻⁶	normal	-1.0	-5.3·10 ⁻⁹	0.0 %
measR _{234/235,A1}	0.0299721	0.0000150	normal	1.0	15·10 ⁻⁶	66.6 %
measR _{236/235,A1}	0.2302894	0.0000576	normal	-3.2·10 ⁻⁶	-180·10 ⁻¹²	0.0 %
measR _{238/235,A1}	0.0150700	0.0000121	normal	-340·10 ⁻⁹	-4.1·10 ⁻¹²	0.0 %
Abund _{234/235,A1}	10.323·10 ⁻⁶	0.407·10 ⁻⁶				

corrR_{234/235,A1}

0.0299760

0.0000184

Result:
Value: Expanded UncertaintyCoverage FactorCoverage:
0.029976 ± 0.12 % (relative) 2.00 95% (normal)

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ModelObservationCorrelationBudgetLastResultDiagram

?

corrR_{233/235,A1}

corrR_{234/235,A1}

corrR_{236/235,A1}

corrR_{238/235,A1}

corrR_{233/235,A2}

corrR_{234/235,A2}

corrR_{236/235,A2}

corrR_{238/235,A2}

Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
DL _{233/235}	9.00·10 ⁻⁶	5.00·10 ⁻⁶	normal	1.0	5.0·10 ⁻⁶	100.0 %

corrR_{233/235,A1}

9.00·10⁻⁶

5.00·10⁻⁶

Result:

Value:

Expanded Uncertainty

Coverage Factor

Coverage:

9·10⁻⁶

± 110 % (relative)

2.00

95% (normal)

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ModelObservationCorrelationBudgetLastResultDiagram

corrR_{233/235,A1}

corrR_{234/235,A1}

corrR_{236/235,A1}

corrR_{238/235,A1}

corrR_{233/235,A2}

corrR_{234/235,A2}

corrR_{236/235,A2}

corrR_{238/235,A2}

Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
knownR _{238/235,U630}	0.553510	0.000245	normal	-0.14	-34·10 ⁻⁶	16.0 %
measR _{238/235,U630}	0.5533424	0.0000525	normal	0.14	7.3·10 ⁻⁶	0.7 %
δ _{236/235,U630}	1.000000	0.000225	normal	0.23	52·10 ⁻⁶	37.3 %
abund _{1amu}	9.590·10 ⁻⁶	0.403·10 ⁻⁶	normal	-1.0	-400·10 ⁻⁹	0.0 %
abund _{2amu}	3.160·10 ⁻⁶	0.265·10 ⁻⁶	normal	-0.045	-12·10 ⁻⁹	0.0 %
frac _{amu}	101·10 ⁻⁶	151·10 ⁻⁶				
measR _{234/235,A1}	0.0299721	0.0000150	normal	-3.2·10 ⁻⁶	-47·10 ⁻¹²	0.0 %
measR _{236/235,A1}	0.2302894	0.0000576	normal	1.0	58·10 ⁻⁶	46.0 %
measR _{238/235,A1}	0.0150700	0.0000121	normal	-3.2·10 ⁻⁶	-38·10 ⁻¹²	0.0 %
Abund _{236/235,A1}	9.732·10 ⁻⁶	0.403·10 ⁻⁶				

corrR_{236/235,A1}

0.2302564

0.0000849

Result:

Value:

Expanded Uncertainty

Coverage Factor

Coverage:

0.23026

± 0.074 % (relative)

2.00

95% (normal)

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Model Observation Correlation **Budget** Last Result Diagram



corrR_{233/235,A1} corrR_{234/235,A1} corrR_{236/235,A1} **corrR_{238/235,A1}** corrR_{233/235,A2} corrR_{234/235,A2} corrR_{236/235,A2} corrR_{238/235,A2} ◀ ▶

Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
knownR _{238/235,U630}	0.553510	0.000245	normal	-0.027	-6.7·10 ⁻⁶	18.8 %
measR _{238/235,U630}	0.5533424	0.0000525	normal	0.027	1.4·10 ⁻⁶	0.9 %
δ _{238/235,U630}	1.000000	0.000442	normal	0.015	6.7·10 ⁻⁶	18.8 %
abund _{2amu}	3.160·10 ⁻⁶	0.265·10 ⁻⁶	normal	-0.23	-61·10 ⁻⁹	0.0 %
abund _{3amu}	1.040·10 ⁻⁶	0.125·10 ⁻⁶	normal	-1.0	-120·10 ⁻⁹	0.0 %
abund _{4amu}	340.0·10 ⁻⁹	68.0·10 ⁻⁹	normal	-0.030	-2.0·10 ⁻⁹	0.0 %
frac _{amu}	101·10 ⁻⁶	151·10 ⁻⁶				
measR _{234/235,A1}	0.0299721	0.0000150	normal	-340·10 ⁻⁹	-5.1·10 ⁻¹²	0.0 %
measR _{236/235,A1}	0.2302894	0.0000576	normal	-3.2·10 ⁻⁶	-180·10 ⁻¹²	0.0 %
measR _{238/235,A1}	0.0150700	0.0000121	normal	1.0	12·10 ⁻⁶	61.5 %
Abund _{238/235,A1}	1.778·10 ⁻⁶	0.139·10 ⁻⁶				

corrR_{238/235,A1} 0.0150637 0.0000154

Result:
 Value: 0.015064 ± 0.20 % (relative) Coverage Factor: 2.00 Coverage: 95% (normal)

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GUM Workbench Pro - U-Iso on VG3 Rev1.smu

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Model Observation Correlation Budget Last **Result** Diagram

Result

Quantity	Value	Expanded Uncertainty	Coverage-factor	Coverage
corrR _{233/235,A1}	9·10 ⁻⁶	110 % (relative)	2.00	95% (normal)
corrR _{234/235,A1}	0.029976	0.12 % (relative)	2.00	95% (normal)
corrR _{236/235,A1}	0.23026	0.074 % (relative)	2.00	95% (normal)
corrR _{238/235,A1}	0.015064	0.20 % (relative)	2.00	95% (normal)
corrR _{233/235,A2}	9·10 ⁻⁶	110 % (relative)	2.00	95% (normal)
corrR _{234/235,A2}	0.029976	0.12 % (relative)	2.00	95% (normal)
corrR _{236/235,A2}	0.23024	0.074 % (relative)	2.00	95% (normal)
corrR _{238/235,A2}	0.015058	0.20 % (relative)	2.00	95% (normal)
corrR _{233/235,B1}	9·10 ⁻⁶	110 % (relative)	2.00	95% (normal)
corrR _{234/235,B1}	0.029977	0.12 % (relative)	2.00	95% (normal)
corrR _{236/235,B1}	0.23021	0.074 % (relative)	2.00	95% (normal)
corrR _{238/235,B1}	0.015049	0.20 % (relative)	2.00	95% (normal)
corrR _{233/235,B2}	9·10 ⁻⁶	110 % (relative)	2.00	95% (normal)
corrR _{234/235,B2}	0.029988	0.12 % (relative)	2.00	95% (normal)
corrR _{236/235,B2}	0.23020	0.074 % (relative)	2.00	95% (normal)
corrR _{238/235,B2}	0.015044	0.20 % (relative)	2.00	95% (normal)
atomPercent _{233,A1}	710·10 ⁻⁶	110 % (relative)	2.00	95% (normal)
atomPercent _{234,A1}	2.3505	0.12 % (relative)	2.00	95% (normal)
atomPercent _{235,A1}	78.413	0.014 % (relative)	2.00	95% (normal)
atomPercent _{236,A1}	18.055	0.060 % (relative)	2.00	95% (normal)
atomPercent _{238,A1}	1.1812	0.20 % (relative)	2.00	95% (normal)

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changed



- Plutonium is separated from U and Am (four independent cuts)
- The Pu isotopic composition measured by Total Evaporation technique using VG-4 TIMS instrument.
- 4 V signals analyzed until the sample is totally evaporated

GUM Workbench Pro - Pu-Iso on VG4 Rev1.smu

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Model Observation Correlation Budget Last Result Diagram

?

Title

Model Equation

Quantity Data

Partial Derivatives

Σδ...

f(x)...

Rename

Order

Experts

Equation:

{-----}

{Calculate fractionation per amu for each set of replicates.}

$$\text{frac}_{\text{amu}} = (\text{knownR}_{240/239,\text{CRM126a}} - \text{measR}_{240/239,\text{CRM126a}}) / \text{knownR}_{240/239,\text{CRM126a}}$$

{-----}

{Calculate abundance corrections}

$$\text{Abund}_{238,\text{A1}} = \text{Faraday}_{1\text{AMULow}} + (\text{A1}_{240/239} * \text{Faraday}_{2\text{AMULow}});$$
$$\text{Abund}_{238,\text{A2}} = \text{Faraday}_{1\text{AMULow}} + (\text{A2}_{240/239} * \text{Faraday}_{2\text{AMULow}});$$
$$\text{Abund}_{238,\text{A3}} = \text{Faraday}_{1\text{AMULow}} + (\text{A3}_{240/239} * \text{Faraday}_{2\text{AMULow}});$$
$$\text{Abund}_{238,\text{B1}} = \text{Faraday}_{1\text{AMULow}} + (\text{B1}_{240/239} * \text{Faraday}_{2\text{AMULow}});$$
$$\text{Abund}_{238,\text{B2}} = \text{Faraday}_{1\text{AMULow}} + (\text{B2}_{240/239} * \text{Faraday}_{2\text{AMULow}});$$
$$\text{Abund}_{240,\text{A1}} = \text{Faraday}_{1\text{AMUHigh}};$$
$$\text{Abund}_{240,\text{A2}} = \text{Faraday}_{1\text{AMUHigh}};$$

Quantity	Unit	Definition
knownR _{240/239,CRM126a}		
measR _{240/239,CRM126a}		
frac _{amu}		
Faraday _{1AMUHigh}		

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known $R_{240/239,CR}$
meas $R_{240/239,CRM}$
frac _{amu}
Faraday _{1AMUHigh}
Faraday _{1AMULow}
Faraday _{2AMULow}
A ₁ _{238/239}
A ₁ _{240/239}
A ₁ _{241/239}
A ₁ _{242/239}
A ₂ _{238/239}
A ₂ _{240/239}
A ₂ _{241/239}
A ₂ _{242/239}
A ₃ _{238/239}
A ₃ _{240/239}
A ₃ _{241/239}
A ₃ _{242/239}
B ₁ _{238/239}
B ₁ _{240/239}
B ₁ _{241/239}
B ₁ _{242/239}

Coverage Factor: 2

Taken from CRM126a Certificate and decay corrected to 2/5/2016. See xxxxx-Plutonium QC Chart-VG4.xlsx

GUM Workbench Pro - Pu-Iso on VG4 Rev1.smu

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ModelObservationCorrelationBudgetLastResultDiagram

?

araday1AMUHiaraday1AMULoaraday2AMULoA1238/239A1240/239A1241/239A1242/239A2238/239A2240/239A2241/239A2242/239◀▶

Observation:

No.	Observation
1	8.5E-7

Method:

Direct

Unit:

Arithmetic Mean:

850.0·10⁻⁹

Experimental Standard Deviation:

not valid!

Standard Uncertainty

35.7·10⁻⁹

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GUM Workbench Pro - Pu-Iso on VG4 Rev1.smu

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Model Observation **Correlation** Budget Last Result Diagram

?

Row:

knownR_{240/239}

 Col:

knownR_{240/239}

 Coefficient:

1

Correlation Matrix:

	knownR _{240/239,CRM126a}	measR _{240/239,CRM126a}	Faraday _{1AMUHigh}	Faraday _{1AMULow}	Faraday _{2AMULow}	A1 _{238/239}	A1 _{240/239}	A1 _{241/239}	A1 _{242/239}
knownR _{240/239,CRM126a}	1								
measR _{240/239,CRM126a}		1							
Faraday _{1AMUHigh}			1						
Faraday _{1AMULow}				1					
Faraday _{2AMULow}					1				
A1 _{238/239}						1			
A1 _{240/239}							1		
A1 _{241/239}								1	
A1 _{242/239}									
A2 _{238/239}									
A2 _{240/239}									
A2 _{241/239}									
A2 _{242/239}									
A3.....									

Description:

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GUM Workbench Pro - Pu-Iso on VG4 Rev1.smu

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Model Observation Correlation Budget Last Result Diagram

AtomPercent_{238,A1} AtomPercent_{238,A2} AtomPercent_{238,A3} AtomPercent_{238,B1} AtomPercent_{238,B2} AtomPercent_{239,A1} AtomPercent_{239,A2} AtomPercent_{239,A3} Ator

Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
knownP _{240/239,CRM12}	0.06268370	0.00000799	normal	-0.093	-750·10 ⁻⁹	0.0 %
measP _{240/239,CRM126}	0.06269260	0.00000533	normal	0.093	500·10 ⁻⁹	0.0 %
frac _{amu}	-142·10 ⁻⁶	153·10 ⁻⁶				
Faraday _{1AMUHigh}	850.0·10 ⁻⁹	35.7·10 ⁻⁹	normal	5.6·10 ⁻³	200·10 ⁻¹²	0.0 %
Faraday _{1AMULow}	7.940·10 ⁻⁶	0.167·10 ⁻⁶	normal	-95	-16·10 ⁻⁶	0.2 %
Faraday _{2AMULow}	2.580·10 ⁻⁶	0.108·10 ⁻⁶	normal	-5.0	-550·10 ⁻⁹	0.0 %
A1 _{238/239}	66.74·10 ⁻⁶	4.20·10 ⁻⁶	normal	95	400·10 ⁻⁶	99.8 %
A1 _{240/239}	0.05314216	0.00000452	normal	-5.5·10 ⁻³	-25·10 ⁻⁹	0.0 %
A1 _{241/239}	275.024·10 ⁻⁶	0.358·10 ⁻⁶	normal	-5.3·10 ⁻³	-1.9·10 ⁻⁹	0.0 %
A1 _{242/239}	138.547·10 ⁻⁶	0.236·10 ⁻⁶	normal	-5.3·10 ⁻³	-1.2·10 ⁻⁹	0.0 %
DL _{244/239}	9.00·10 ⁻⁶	4.50·10 ⁻⁶	normal	-5.3·10 ⁻³	-24·10 ⁻⁹	0.0 %
δ _{238,CRM}	1.000000	0.00115	normal	5.6·10 ⁻³	6.4·10 ⁻⁶	0.0 %
δ _{240,CRM}	1.000000	0.000130	normal	-280·10 ⁻⁶	-37·10 ⁻⁹	0.0 %
δ _{241,CRM}	1.000000	0.000240	normal	-1.5·10 ⁻⁶	-350·10 ⁻¹²	0.0 %
AtomPercent _{238,A1}	5.569·10 ⁻³	0.399·10 ⁻³				

Result:
 Value: 5.57·10⁻³ Expanded Uncertainty: ± 14 % (relative) Coverage Factor: 2.00 Coverage: 95% (normal)

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Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
knownR _{240/239,CRM12}	0.06268370	0.00000799	normal	-78	-620·10 ⁻⁶	27.2 %
measR _{240/239,CRM126}	0.06269260	0.00000533	normal	78	410·10 ⁻⁶	12.1 %
frac _{amu}	-142·10 ⁻⁶	153·10 ⁻⁶				
Faraday _{1AMUHigh}	850.0·10 ⁻⁹	35.7·10 ⁻⁹	normal	95	3.4·10 ⁻⁶	0.0 %
Faraday _{1AMULow}	7.940·10 ⁻⁶	0.167·10 ⁻⁶	normal	90	15·10 ⁻⁶	0.0 %
Faraday _{2AMULow}	2.580·10 ⁻⁶	0.108·10 ⁻⁶	normal	4.8	520·10 ⁻⁹	0.0 %
A1 _{238/239}	66.74·10 ⁻⁶	4.20·10 ⁻⁶	normal	-90	-380·10 ⁻⁶	10.1 %
A1 _{240/239}	0.05314216	0.00000452	normal	-90	-410·10 ⁻⁶	11.7 %
A1 _{241/239}	275.024·10 ⁻⁶	0.358·10 ⁻⁶	normal	-90	-32·10 ⁻⁶	0.0 %
A1 _{242/239}	138.547·10 ⁻⁶	0.236·10 ⁻⁶	normal	-90	-21·10 ⁻⁶	0.0 %
DL _{244/239}	9.00·10 ⁻⁶	4.50·10 ⁻⁶	normal	-90	-410·10 ⁻⁶	11.6 %
δ _{238,CRM}	1.000000	0.00115	normal	-5.3·10 ⁻³	-6.1·10 ⁻⁶	0.0 %
δ _{240,CRM}	1.000000	0.000130	normal	-4.8	-620·10 ⁻⁶	27.3 %
δ _{241,CRM}	1.000000	0.000240	normal	-0.025	-5.9·10 ⁻⁶	0.0 %
AtomPercent _{239 A1}	94.91134	0.00119				

Result:			
Value:	Expanded Uncertainty	Coverage Factor	Coverage:
94.9113	$\pm 2.5 \cdot 10^{-3} \%$ (relative)	2.00	95% (normal)

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GUM Workbench Pro - Pu-Iso on VG4 Rev1.smu

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Model Observation Correlation Budget Last Result Diagram

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AtomPercent_{240,A2} AtomPercent_{240,A3} AtomPercent_{240,B1} AtomPercent_{240,B2} AtomPercent_{241,A1} AtomPercent_{241,A2} AtomPercent_{241,A3} AtomPercent_{241,B1} Ator ◀ ▶

Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
knownR _{240/239,CRM12}	0.06268370	0.00000799	normal	0.81	6.5·10 ⁻⁶	3.4 %
measR _{240/239,CRM126}	0.06269260	0.00000533	normal	-0.81	-4.3·10 ⁻⁶	1.5 %
frac _{amu}	-142·10 ⁻⁶	153·10 ⁻⁶				
Faraday _{1AMUHigh}	850.0·10 ⁻⁹	35.7·10 ⁻⁹	normal	-5.0	-180·10 ⁻⁹	0.0 %
Faraday _{1AMULow}	7.940·10 ⁻⁶	0.167·10 ⁻⁶	normal	0.025	4.1·10 ⁻⁹	0.0 %
Faraday _{2AMULow}	2.580·10 ⁻⁶	0.108·10 ⁻⁶	normal	1.3·10 ⁻³	140·10 ⁻¹²	0.0 %
A1 _{238/239}	66.74·10 ⁻⁶	4.20·10 ⁻⁶	normal	-0.025	-100·10 ⁻⁹	0.0 %
A1 _{240/239}	0.05314216	0.00000452	normal	-0.025	-110·10 ⁻⁹	0.0 %
A1 _{241/239}	275.024·10 ⁻⁶	0.358·10 ⁻⁶	normal	95	34·10 ⁻⁶	92.0 %
A1 _{242/239}	138.547·10 ⁻⁶	0.236·10 ⁻⁶	normal	-0.025	-5.8·10 ⁻⁹	0.0 %
DL _{244/239}	9.00·10 ⁻⁶	4.50·10 ⁻⁶	normal	-0.025	-110·10 ⁻⁹	0.0 %
δ _{238,CRM}	1.00000	0.00115	normal	-1.5·10 ⁻⁶	-1.7·10 ⁻⁹	0.0 %
δ _{240,CRM}	1.000000	0.000130	normal	-1.3·10 ⁻³	-170·10 ⁻⁹	0.0 %
δ _{241,CRM}	1.000000	0.000240	normal	0.026	6.3·10 ⁻⁶	3.1 %
AtomPercent _{241,A1}	0.0260912	0.0000354				

Result:
Value: Expanded Uncertainty Coverage Factor Coverage:
0.026091 ± 0.27 % (relative) 2.00 95% (normal)

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Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
knownR _{240/239,CRM12}	0.06268370	0.00000799	normal	0.61	4.9·10 ⁻⁶	4.4 %
measR _{240/239,CRM126}	0.06269260	0.00000533	normal	-0.61	-3.3·10 ⁻⁶	2.0 %
frac _{amu}	-142·10 ⁻⁶	153·10 ⁻⁶				
Faraday _{1AMUHigh}	850.0·10 ⁻⁹	35.7·10 ⁻⁹	normal	-0.013	-460·10 ⁻¹²	0.0 %
Faraday _{1AMULow}	7.940·10 ⁻⁶	0.167·10 ⁻⁶	normal	0.012	2.1·10 ⁻⁹	0.0 %
Faraday _{2AMULow}	2.580·10 ⁻⁶	0.108·10 ⁻⁶	normal	660·10 ⁻⁶	71·10 ⁻¹²	0.0 %
A _{3238/239}	70.87·10 ⁻⁶	4.20·10 ⁻⁶	normal	-0.012	-52·10 ⁻⁹	0.0 %
A _{3240/239}	0.05315412	0.00000452	normal	-0.012	-56·10 ⁻⁹	0.0 %
A _{3241/239}	273.650·10 ⁻⁶	0.356·10 ⁻⁶	normal	-0.012	-4.4·10 ⁻⁹	0.0 %
A _{3242/239}	137.552·10 ⁻⁶	0.234·10 ⁻⁶	normal	95	22·10 ⁻⁶	90.3 %
DL _{244/239}	9.00·10 ⁻⁶	4.50·10 ⁻⁶	normal	-0.012	-56·10 ⁻⁹	0.0 %
δ _{238,CRM}	1.000000	0.00115	normal	-780·10 ⁻⁹	-890·10 ⁻¹²	0.0 %
δ _{240,CRM}	1.000000	0.000130	normal	-660·10 ⁻⁶	-86·10 ⁻⁹	0.0 %
δ _{241,CRM}	1.000000	0.000240	normal	-3.4·10 ⁻⁶	-810·10 ⁻¹²	0.0 %
AtomPercent _{242A3}	0.0130495	0.0000233				

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GUM Workbench Pro - U-Iso on VG3 Rev1.smu

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Model Observation Correlation Budget Last Result Diagram

Result

Quantity	Value	Expanded Uncertainty	Coverage-factor	Coverage
corrR _{233/235,A1}	9·10 ⁻⁶	110 % (relative)	2.00	95% (normal)
corrR _{234/235,A1}	0.029976	0.12 % (relative)	2.00	95% (normal)
corrR _{236/235,A1}	0.23026	0.074 % (relative)	2.00	95% (normal)
corrR _{238/235,A1}	0.015064	0.20 % (relative)	2.00	95% (normal)
corrR _{233/235,A2}	9·10 ⁻⁶	110 % (relative)	2.00	95% (normal)
corrR _{234/235,A2}	0.029976	0.12 % (relative)	2.00	95% (normal)
corrR _{236/235,A2}	0.23024	0.074 % (relative)	2.00	95% (normal)
corrR _{238/235,A2}	0.015058	0.20 % (relative)	2.00	95% (normal)
corrR _{233/235,B1}	9·10 ⁻⁶	110 % (relative)	2.00	95% (normal)
corrR _{234/235,B1}	0.029977	0.12 % (relative)	2.00	95% (normal)
corrR _{236/235,B1}	0.23021	0.074 % (relative)	2.00	95% (normal)
corrR _{238/235,B1}	0.015049	0.20 % (relative)	2.00	95% (normal)
corrR _{233/235,B2}	9·10 ⁻⁶	110 % (relative)	2.00	95% (normal)
corrR _{234/235,B2}	0.029988	0.12 % (relative)	2.00	95% (normal)
corrR _{236/235,B2}	0.23020	0.074 % (relative)	2.00	95% (normal)
corrR _{238/235,B2}	0.015044	0.20 % (relative)	2.00	95% (normal)
atomPercent _{233,A1}	710·10 ⁻⁶	110 % (relative)	2.00	95% (normal)
atomPercent _{234,A1}	2.3505	0.12 % (relative)	2.00	95% (normal)
atomPercent _{235,A1}	78.413	0.014 % (relative)	2.00	95% (normal)
atomPercent _{236,A1}	18.055	0.060 % (relative)	2.00	95% (normal)
atomPercent _{238,A1}	1.1812	0.20 % (relative)	2.00	95% (normal)

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➤ Pu-IDMS

- Pu Assay dissolves a sample and gives 2 aliquots to MS. Pu Assay provides the amount of each cut along with their associated uncertainties. MS receives each aliquots into a bottle - Dilution 1. An aliquot of Dilution 1 is transferred into another bottle - Dilution 2. Two aliquots of Dilution 2 is added to each "5000Series" Pu244 spike vial. Each spike vial is analyzed by TIMS and the %Pu present in the sample is calculated.

Using a ²⁴²Pu enriched material as the spike, the ²³⁹Pu content in an unknown sample can be determined by isotope dilution, through a measurement of the isotope ratio $R(^{242}\text{Pu}/^{239}\text{Pu}, \text{B})$ in the blend. The plutonium amount content can be calculated using the following (full IDMS) equation:

$$c(\text{Pu}, X) = \frac{R(^{242}\text{Pu}/^{239}\text{Pu}, Y) - R(^{242}\text{Pu}/^{239}\text{Pu}, B)}{R(^{242}\text{Pu}/^{239}\text{Pu}, B) - R(^{242}\text{Pu}/^{239}\text{Pu}, X)} \cdot \frac{\sum_m R(^m\text{Pu}/^{239}\text{Pu}, X)}{\sum_m R(^m\text{Pu}/^{239}\text{Pu}, Y)} \cdot \frac{m(Y)}{m(X)} \cdot c(\text{Pu}, Y)$$

where:

$R(^m\text{Pu}/^{239}\text{Pu}, X)$	= amount ratio $^m\text{Pu}/^{239}\text{Pu}$ in the unknown sample material X
$R(^m\text{Pu}/^{239}\text{Pu}, Y)$	= amount ratio $^m\text{Pu}/^{239}\text{Pu}$ in the known spike material Y
$R(^m\text{Pu}/^{239}\text{Pu}, B)$	= amount ratio $^m\text{Pu}/^{239}\text{Pu}$ in the measured blend material B
$m(X)$	= mass of the unknown sample used in the measurement
$m(Y)$	= mass of the spike solution used in the measurement
$c(^{239}\text{Pu}, X)$	= amount content (moles) of ²³⁹ Pu / g sample material
$c(^{242}\text{Pu}, Y)$	= amount content (moles) of ²⁴² Pu / g spike solution
$c(\text{Pu}, X)$	= amount content of Pu / kg sample material
$c(\text{Pu}, Y)$	= amount content of Pu / kg spike solution

The equation is valid even when ²⁴²Pu is present in the sample

GUM Workbench Pro - Pu-IDMS with a Double Dilution Rev1.smu

File Edit View Picture Diagram Option Tools Help

Model Observation Correlation Budget Last Result Diagram ?

Title Model Equation Quantity Data Partial Derivatives

Title: Pu-IDMS in a Solution

Reference: Date: 10/11/2017 Version: Author:

General Description Picture 1

This model calculates the uncertainty of the Pu-IDMS results.

Pu Assay dissolves a sample and gives 2 aliquots to MS. Pu Assay provides the amount of each cut along with their associated uncertainties. MS receives each aliquots into a bottle - Dilution 1. An aliquot of Dilution 1 is transferred into another bottle - Dilution 2. Two aliquots of Dilution 2 is added to each "5000Series" Pu244 spike vial. Each spike vial is analyzed by TIMS and the %Pu present in the sample is calculated.

A1 = Cut-9 which was separated on 10/01/2014 and analyzed on 10/22/2014.

A2 = Cut-10 which was separated on 10/01/2014 and analyzed on 10/22/2014.

B1 = Cut-26 which was separated on 11/04/2014 and analyzed on 11/10/2014.

B2 = Cut-17 which was separated on 10/01/2014 and analyzed on 10/22/2014.

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GUM Workbench Pro - Pu-IDMS with a Double Dilution Rev1.smu

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Model Observation Correlation Budget Last Result Diagram

?

Title

Model Equation

Quantity Data

Partial Derivatives

Σδ...

f(x)...

Rename

Order

Experts

Equation:

{Pu-Assay weighs a sample, dissolves it and then transfer it to a bottle.}

{An aliquot of this solution is transferred to a dilution bottle.}

{-----}

{MS obtains 2 aliquots from Pu Assay which are placed into a pre-weighed bottle that contains 7M HNO3 - Dilution1}

{Calculate the concentration in the bottle - Dilution1.}

conc1stDilution_A = (Wt_{aliquotA}) / (wtBottle1_{A,total} - wtBottle1_{A,empty});

conc1stDilution_B = (Wt_{aliquotB}) / (wtBottle1_{B,total} - wtBottle1_{B,empty});

{-----}

{MS takes an aliquot from Dilution 1 bottle and places it into a bottle containing 7M HNO3 - Dilution2}

{Calculate the concentration in the bottle - Dilution2.}

conc2ndDilution_A = conc1stDilution_A * ((wtBottle2_{A,total} - wtBottle2_{A,Diluent}) / (wtBottle2_{A,total} - wtBottle2_{A,empty}));

conc2ndDilution_B = conc1stDilution_B * ((wtBottle2_{B,total} - wtBottle2_{B,Diluent}) / (wtBottle2_{B,total} - wtBottle2_{B,empty}));

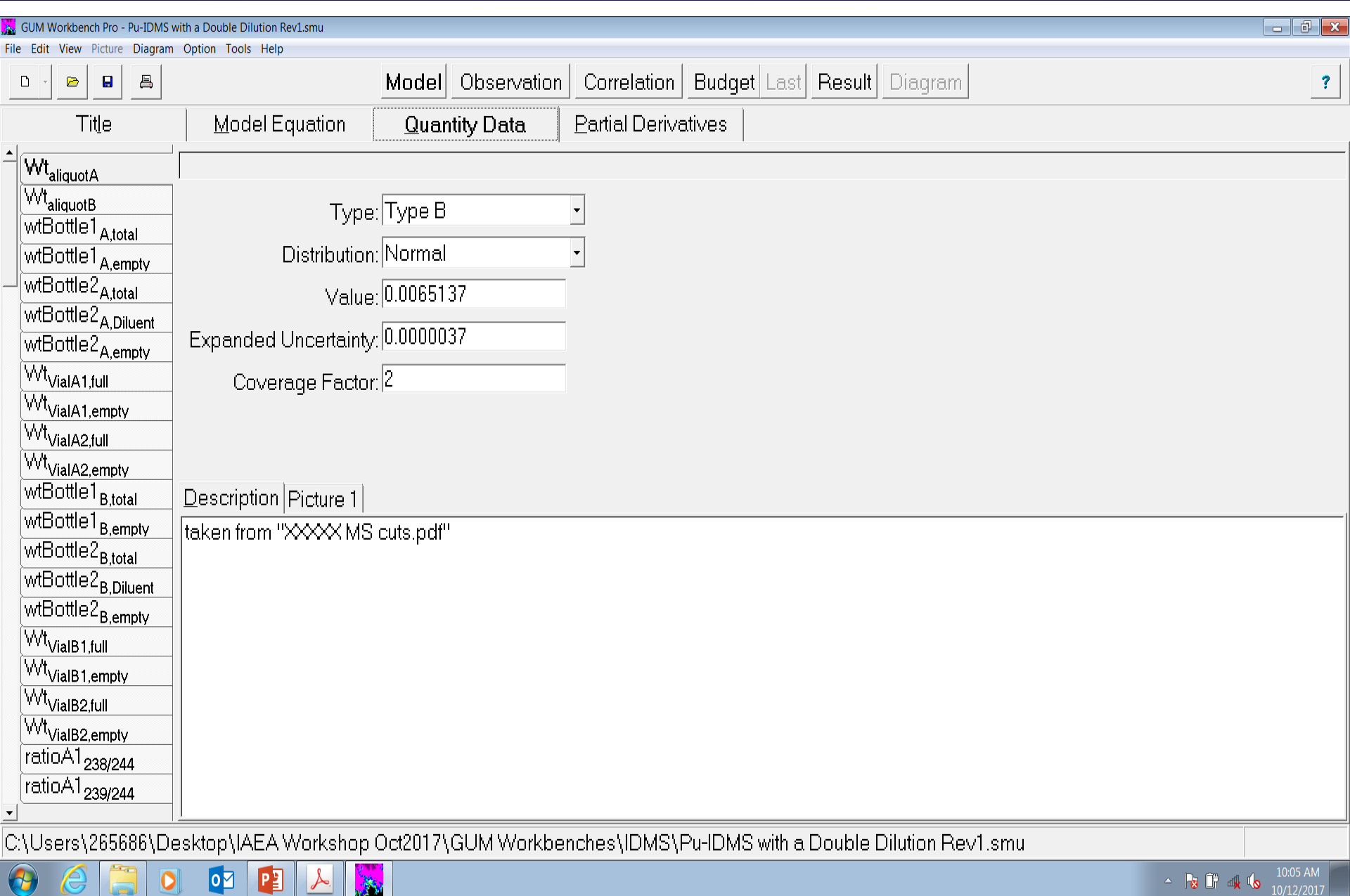
CF_B = (Wt_{before} - Wt_{bottle}) / (Wt_{now} - Wt_{bottle});

{note. CF_B is an evaporation correction for a sample done after the first three, i.e., a re-do}

Quantity	Unit	Definition
Wt _{aliquotA}		
Wt ...		

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GUM Workbench Pro - Pu-IDMS with a Double Dilution Rev1.smu

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?

wtBottle1A,totalwtBottle1A,emptywtBottle2A,totalwtBottle2A,DiluerwtBottle2A,emptyWtVialA1,fullWtVialA1,emptyWtVialA2,fullWtVialA2,emptywtBottle1B,totalwtBottle1B,t

Observation:

No.	Observation
1	33.48282

Method:

Direct

Unit:

Arithmetic Mean:

33.4828200

Experimental Standard Deviation:

not valid!

Standard Uncertainty

26.0·10⁻⁶

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Row: Wt_{aliquotA} Col: Wt_{aliquotA} Coefficient: 1

Correlation Matrix:

	Wt _{aliquotA}	Wt _{aliquotB}	wtBottle1 _{A,total}	wtBottle1 _{A,empty}	wtBottle2 _{A,total}	wtBottle2 _{A,Diluent}	wtBottle2 _{A,empty}	Wt _{VialA1,full}	Wt _{VialA1,empty}	Wt _{VialA2,full}	Wt _{VialA2,empty}
Wt _{aliquotA}	1										
Wt _{aliquotB}		1									
wtBottle1 _{A,total}			1								
wtBottle1 _{A,empty}				1							
wtBottle2 _{A,total}					1						
wtBottle2 _{A,Diluent}						1					
wtBottle2 _{A,empty}							1				
Wt _{VialA1,full}								1			
Wt _{VialA1,empty}									1		
Wt _{VialA2,full}										1	
Wt _{VialA2,empty}											1
wtBottle1 _{B,total}											
wtBottle1 _{B,empty}											
wtBottle2 _{B,total}											

Description:

ASTM C1672 states that “In case that the ratios from the unknown sample material X, the known spike material Y, or the blend material B have been obtained by an isotope ratio measurement using the same reference material for the mass bias correction factor (that is K-factor, see Eq 1) or even within the same measurement sequence, the corrected ratios cannot be considered truly independent. In this case, it is recommended that the uncorrected ratios multiplied by the (common) K-factor be entered into Eq 6 to Eq 13 instead of the corrected ratios.”

GUM Workbench Pro - Pu-IDMS with a Double Dilution Rev1.smu

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percentPu_{A1}

percentPu_{A2}

percentPu_{B1}

percentPu_{B2}

percentPu_{avg}

Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
Wt _{aliquotA}	6.51370·10 ⁻³	1.85·10 ⁻⁶	normal	-15000	-0.028	18.5 %
wtBottle1 _{A,total}	33.4828200	26.0·10 ⁻⁶	normal	3.9	100·10 ⁻⁶	0.0 %
wtBottle1 _{A,empty}	8.1529300	26.0·10 ⁻⁶	normal	-3.9	-100·10 ⁻⁶	0.0 %
wtBottle2 _{A,total}	141.9489000	92.0·10 ⁻⁶	normal	-80	-7.4·10 ⁻³	1.3 %
wtBottle2 _{A,Diluent}	140.7401000	92.0·10 ⁻⁶	normal	81	7.5·10 ⁻³	1.3 %
wtBottle2 _{A,empty}	19.4305200	26.0·10 ⁻⁶	normal	-0.80	-21·10 ⁻⁶	0.0 %
Wt _{VialA1,full}	14.6367200	26.0·10 ⁻⁶	normal	-80	-2.1·10 ⁻³	0.1 %
Wt _{VialA1,empty}	13.4184700 grams	26.0·10 ⁻⁶ grams	normal	80	2.1·10 ⁻³	0.1 %
ratioA1 _{238/244}	108.30·10 ⁻⁶	9.75·10 ⁻⁶	normal	31	300·10 ⁻⁶	0.0 %
ratioA1 _{239/244}	3.12076	1.40·10 ⁻³	normal	31	0.043	45.0 %
ratioA1 _{240/244}	0.0570762	57.1·10 ⁻⁶	normal	31	1.8·10 ⁻³	0.0 %
ratioA1 _{241/244}	255.600·10 ⁻⁶	537·10 ⁻⁹	normal	31	17·10 ⁻⁶	0.0 %
ratioA1 _{242/244}	0.0135828	21.7·10 ⁻⁶	normal	31	680·10 ⁻⁶	0.0 %
AMU ₂₃₉	239.05216340	1.00·10 ⁻⁶	normal	0.40	400·10 ⁻⁹	0.0 %
percentPu _{A1}	98.0170	0.0647				

Result:

Value: 98.02

Expanded Uncertainty: ± 0.13 % (relative)

Coverage Factor: 2.00

Coverage: 95% (normal)

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percentPu_{A1} percentPu_{A2} percentPu_{B1} percentPu_{B2} percentPu_{avg}

Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
Wt _{aliquotA}	6.51370·10 ⁻³	1.85·10 ⁻⁶	normal	-7500	-0.014	8.3 %
Wt _{aliquotB}	6.18590·10 ⁻³	1.80·10 ⁻⁶	normal	-7900	-0.014	8.7 %
wtBottle1 _{A,total}	33.4828200	26.0·10 ⁻⁶	normal	1.9	50·10 ⁻⁶	0.0 %
wtBottle1 _{A,empty}	8.1529300	26.0·10 ⁻⁶	normal	-1.9	-50·10 ⁻⁶	0.0 %
wtBottle2 _{A,total}	141.9489000	92.0·10 ⁻⁶	normal	-40	-3.7·10 ⁻³	0.6 %
wtBottle2 _{A,Diluent}	140.7401000	92.0·10 ⁻⁶	normal	41	3.7·10 ⁻³	0.6 %
wtBottle2 _{A,empty}	19.4305200	26.0·10 ⁻⁶	normal	-0.40	-10·10 ⁻⁶	0.0 %
Wt _{VialA1,full}	14.6367200	26.0·10 ⁻⁶	normal	-20	-520·10 ⁻⁶	0.0 %
Wt _{VialA1,empty}	13.4184700 grams	26.0·10 ⁻⁶ grams	normal	20	520·10 ⁻⁶	0.0 %
Wt _{VialA2,full}	14.5421600	26.0·10 ⁻⁶	normal	-20	-520·10 ⁻⁶	0.0 %
Wt _{VialA2,empty}	13.3242700	26.0·10 ⁻⁶	normal	20	520·10 ⁻⁶	0.0 %
wtBottle1 _{B,total}	33.2430700	26.0·10 ⁻⁶	normal	2.0	51·10 ⁻⁶	0.0 %
wtBottle1 _{B,empty}	8.1212200	26.0·10 ⁻⁶	normal	-2.0	-51·10 ⁻⁶	0.0 %
wtBottle2 _{B,total}	142.6506000	92.0·10 ⁻⁶	normal	-40	-3.7·10 ⁻³	0.6 %
percentPu _{avg}	98.0850	0.0483				

Result:
Value: 98.085 Expanded Uncertainty Coverage Factor Coverage:
± 0.099 % (relative) 2.00 95% (normal)

GUM Workbench Pro - Pu-IDMS with a Double Dilution Rev1.smu

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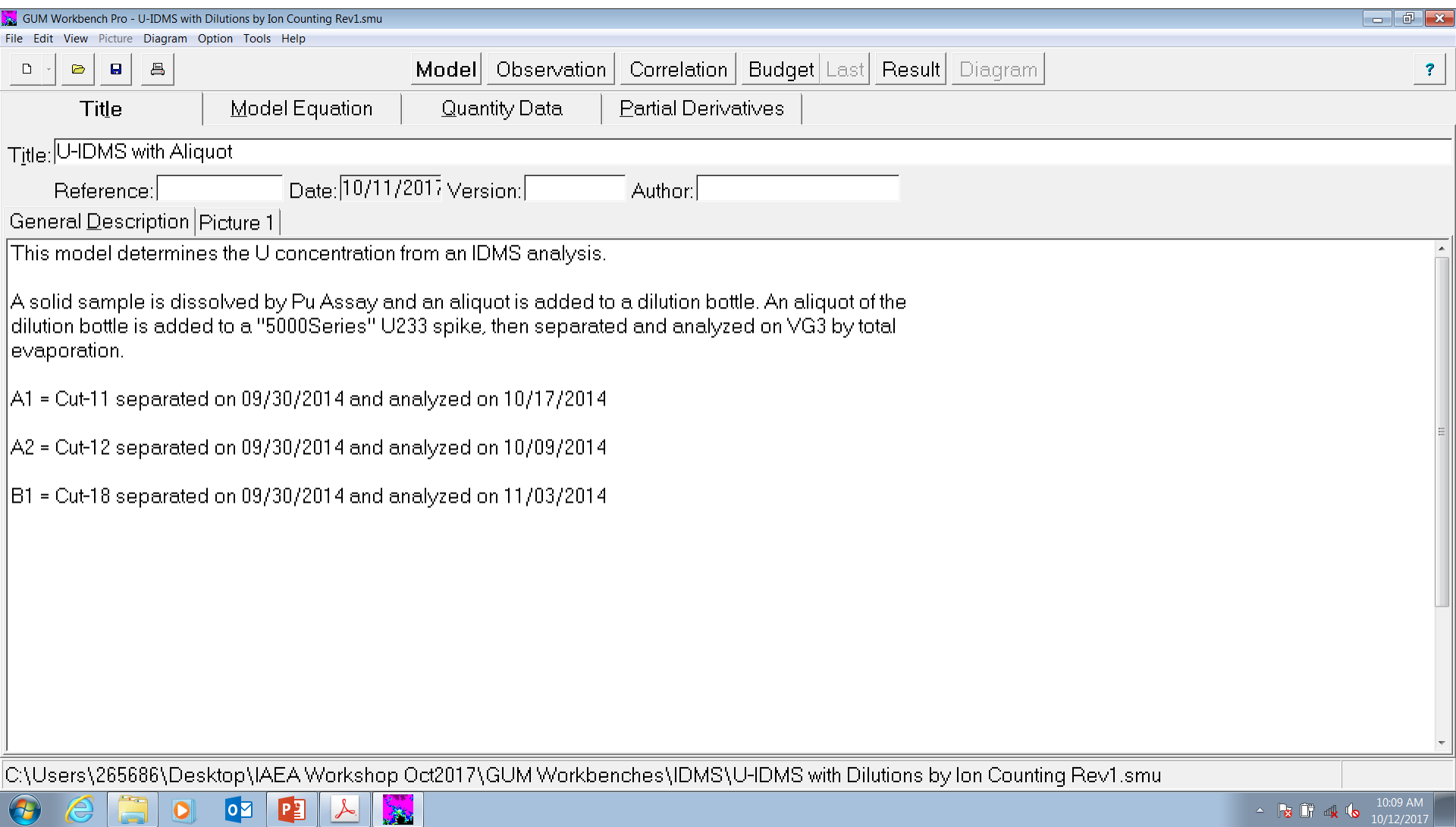
Result

Quantity	Value	Expanded Uncertainty	Coverage- factor	Coverage
percentPu _{A1}	98.02	0.13 % (relative)	2.00	95% (normal)
percentPu _{A2}	98.04	0.13 % (relative)	2.00	95% (normal)
percentPu _{B1}	98.18	0.13 % (relative)	2.00	95% (normal)
percentPu _{B2}	98.11	0.13 % (relative)	2.00	95% (normal)
percentPu _{avg}	98.085	0.099 % (relative)	2.00	95% (normal)

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- A solid sample is dissolved by Pu Assay and an aliquot is added to a dilution bottle. An aliquot of the dilution bottle is added to a "5000Series" U233 spike, then separated and analyzed on VG3 by total evaporation.



GUM Workbench Pro - U-IDMS with Dilutions by Ion Counting Rev1.smu

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Model Observation Correlation Budget Last Result Diagram

?

Title

Model Equation

Quantity Data

Partial Derivatives

Σδ...

f(x)...

Rename

Order

Experts

Equation:

{Pu-Assay weighs a sample, dissolves it and then transfer it to a bottle. An aliquot of this solution is transferred to a dilution bottle.}

{ Pu Assay provides the GUM uncertainty on the weight of the aliquots.}

{An aliquot, obtained from Pu Assay, is diluted by MS.}

$$\text{Conc}_{\text{dilution,A}} = \text{Wt}_A / (\text{wtBottle1}_{\text{A,total}} - \text{wtBottle1}_{\text{A,empty}});$$

$$\text{Conc}_{\text{dilution,B}} = \text{Wt}_B / (\text{wtBottle1}_{\text{B,total}} - \text{wtBottle1}_{\text{B,empty}});$$

{An aliquot from each dilution bottle is placed in two spike vials.}

$$\text{Wt}_{\text{CutA1}} = \text{Conc}_{\text{dilution,A}} * (\text{Wt}_{\text{vialA1,full}} - \text{Wt}_{\text{vialA1,empty}});$$

$$\text{Wt}_{\text{CutA2}} = \text{Conc}_{\text{dilution,A}} * (\text{Wt}_{\text{vialA2,full}} - \text{Wt}_{\text{vialA2,empty}});$$

$$\text{Wt}_{\text{CutB1}} = \text{Conc}_{\text{dilution,B}} * (\text{Wt}_{\text{vialB1,full}} - \text{Wt}_{\text{vialB1,empty}});$$

$$\text{Wt}_{\text{CutB2}} = \text{Conc}_{\text{dilution,B}} * (\text{Wt}_{\text{vialB2,full}} - \text{Wt}_{\text{vialB2,empty}});$$

{correct 238/233 ratio}

$$\text{Rcorr}_{\text{cutA1,238/233}} = \text{R}_{\text{cutA1,238/233}} - (\text{R}_{\text{cutA1,238/240}} * \text{R}_{\text{cutA1,240/233}});$$

$$\text{Rcorr}_{\text{cutA2,238/233}} = \text{R}_{\text{cutA2,238/233}} - (\text{R}_{\text{cutA2,238/240}} * \text{R}_{\text{cutA2,240/233}});$$

$$\text{Rcorr}_{\text{cutB1,238/233}} = \text{R}_{\text{cutB1,238/233}} - (\text{R}_{\text{cutB1,238/240}} * \text{R}_{\text{cutB1,240/233}});$$

$$\text{Rcorr}_{\text{cutB2,238/233}} = \text{R}_{\text{cutB2,238/233}} - (\text{R}_{\text{cutB2,238/240}} * \text{R}_{\text{cutB2,240/233}});$$

Quantity	Unit	Definition
Wt _A		
Wt _B		

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Wt _A
Wt _B
wtBottle1 _{A,total}
wtBottle1 _{A,empty}
Wt _{vialA1,full}
Wt _{vialA1,empty}
Wt _{vialA2,full}
Wt _{vialA2,empty}
wtBottle1 _{B,total}
wtBottle1 _{B,empty}
Wt _{vialB1,full}
Wt _{vialB1,empty}
Wt _{vialB2,full}
Wt _{vialB2,empty}
R _{cutA1,238/240}
R _{cutA1,234/233}
R _{cutA1,235/233}
R _{cutA1,236/233}
R _{cutA1,238/233}
R _{cutA1,240/233}
R _{cutA2,238/240}
R _{cutA2,234/233}

taken from "XXXX- MS cuts.pdf"

GUM Workbench Pro - U-IDMS with Dilutions by Ion Counting Rev1.smu

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wtBottle1A,total

wtBottle1A,empty

Wt_vialA1,full

Wt_vialA1,empty

Wt_vialA2,full

Wt_vialA2,empty

wtBottle1B,total

wtBottle1B,empty

Wt_vialB1,full

Wt_vialB1,empty

Wt_vialB2,full

Observation:

No.	Observation
1	33.48282

Method:

Direct

Unit:

Arithmetic Mean:

33.4828200

Experimental Standard Deviation:

not valid!

Standard Uncertainty:

$26.0 \cdot 10^{-6}$

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GUM Workbench Pro - U-IDMS with Dilutions by Ion Counting Rev1.smu

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Model Observation **Correlation** Budget Last Result Diagram

?

Row:

WtA

 Col:

WtA

 Coefficient:

1

Correlation Matrix:

	WtA	WtB	wtBottle1A,total	wtBottle1A,empty	Wt_vialA1,full	Wt_vialA1,empty	Wt_vialA2,full	Wt_vialA2,empty	wtBottle1B,total	wtBottle1B,empty	Wt_vialB1,full
WtA	1										
WtB		1									
wtBottle1A,total			1								
wtBottle1A,empty				1							
Wt_vialA1,full					1						
Wt_vialA1,empty						1					
Wt_vialA2,full							1				
Wt_vialA2,empty								1			
wtBottle1B,total									1		
wtBottle1B,empty										1	
Wt_vialB1,full											1
Wt_vialB1,empty											
Wt_vialB2,full											
Wt_vialB2,empty											

Description:

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ASTM C1672 states that “In case that the ratios from the unknown sample material X, the known spike material Y, or the blend material B have been obtained by an isotope ratio measurement using the same reference material for the mass bias correction factor (that is K-factor, see Eq 1) or even within the same measurement sequence, the corrected ratios cannot be considered truly independent. In this case, it is recommended that the uncorrected ratios multiplied by the (common) K-factor be entered into Eq 6 to Eq 13 instead of the corrected ratios.”

Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
Wt _A	6.51370·10 ⁻³	1.85·10 ⁻⁶	normal	-300·10 ³	-0.55	22.9 %
wtBottle1 _{A,total}	33.4828200	26.0·10 ⁻⁶	normal	76	2.0·10 ⁻³	0.0 %
wtBottle1 _{A,empty}	8.1529300	26.0·10 ⁻⁶	normal	-76	-2.0·10 ⁻³	0.0 %
Wt _{vialA1,full}	15.7779200	26.0·10 ⁻⁶	normal	-800	-0.021	0.0 %
Wt _{vialA1,empty}	13.3733600	26.0·10 ⁻⁶	normal	800	0.021	0.0 %
R _{cutA1,238/240}	2.00000·10 ⁻³	8.80·10 ⁻⁶	normal	-0.096	-840·10 ⁻⁹	0.0 %
R _{cutA1,234/233}	5.2613·10 ⁻³	11.6·10 ⁻⁶	normal	2000	0.024	0.0 %
R _{cutA1,235/233}	0.878717	123·10 ⁻⁶	normal	2100	0.25	4.9 %
R _{cutA1,236/233}	0.052036	114·10 ⁻⁶	normal	2100	0.24	4.3 %
R _{cutA1,238/233}	1.7022·10 ⁻³	30.6·10 ⁻⁶	normal	2100	0.064	0.3 %
R _{cutA1,240/233}	45.900·10 ⁻⁶	826·10 ⁻⁹	normal	-4.2	-3.4·10 ⁻⁶	0.0 %
ugSpk ₂₃₃	1.259970	183·10 ⁻⁶	normal	1500	0.28	6.0 %
ugSpk ₂₃₄	0.013919	455·10 ⁻⁶	normal	-1.6	-740·10 ⁻⁶	0.0 %
ugSpk ₂₃₈	0.051483	288·10 ⁻⁶	normal	-1.6	-470·10 ⁻⁶	0.0 %
ppmU _{cutA1}	1927.52	1.14				

Result:
Value: 1927.5 Expanded Uncertainty Coverage Factor Coverage:
± 0.12 % (relative) 2.00 95% (normal)

GUM Workbench Pro - U-IDMS with Dilutions by Ion Counting Rev1.smu

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Quantity	Value	Expanded Uncertainty	Coverage- factor	Coverage
ppmU _{cutA1}	1927.5	0.12 % (relative)	2.00	95% (normal)
ppmU _{cutA2}	1927.4	0.12 % (relative)	2.00	95% (normal)
ppmU _{cutB1}	1926.8	0.12 % (relative)	2.00	95% (normal)
ppmU _{cutB2}	1937.1	0.12 % (relative)	2.00	95% (normal)
ppmU _{avg}	1929.7	0.11 % (relative)	2.00	95% (normal)

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10:13 AM
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Weighing uncertainties become important contributor to overall uncertainty in IDMS measurements.

Weighing process provides traceability of different kinds of measurements to the SI units

Anubis weighing the soul of the scribe Ani, from the Egyptian Book of the Dead, c. 1275 BCE.



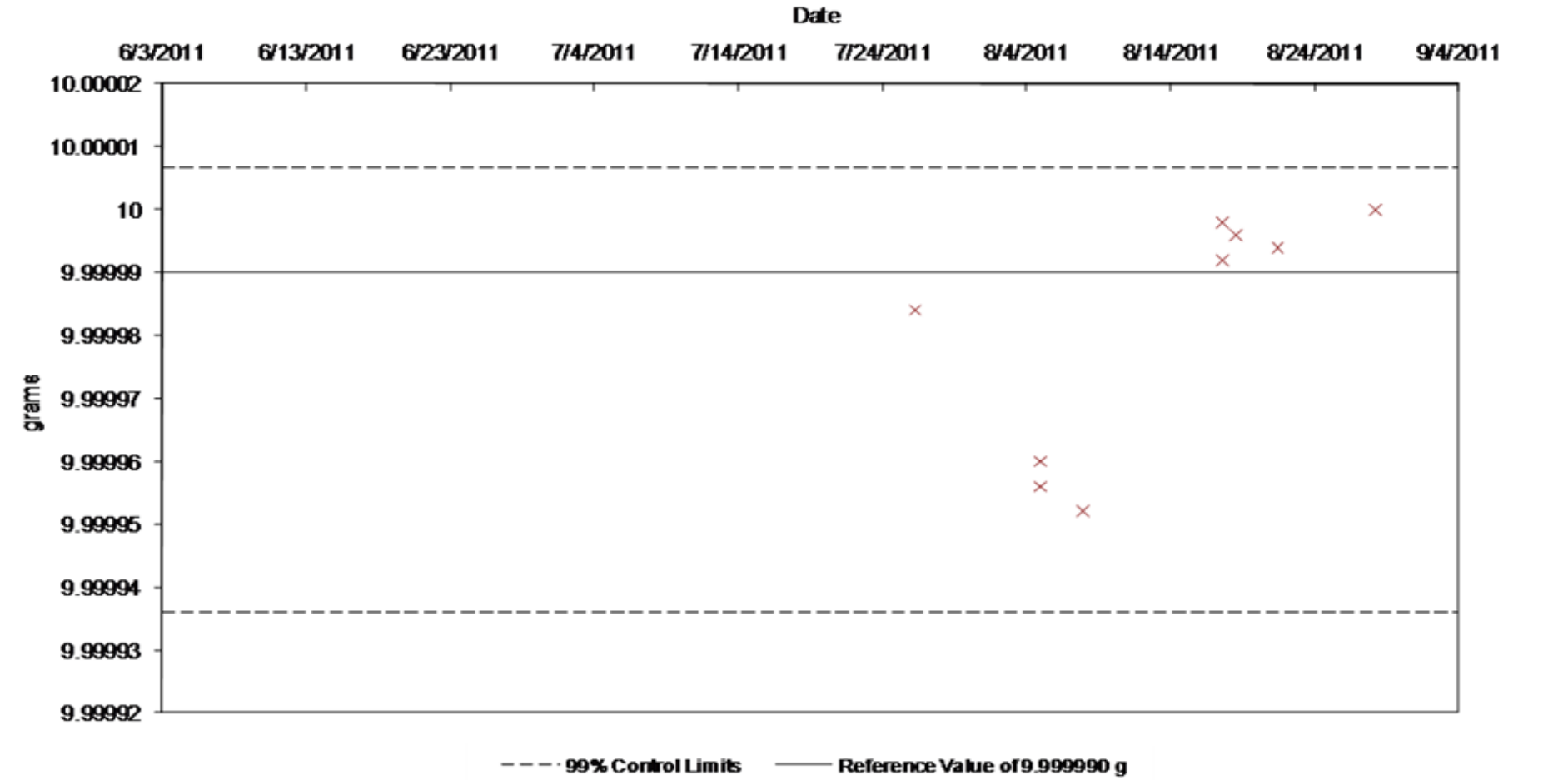
Difficult weighing measurement !

- **Adequacy of balance calibration or of the weight set is not the biggest uncertainty concern**
- **Assumes that balances & standards are handled properly**
- **Small masses might be a bigger concern**
- **Realize that “calibrations” as part of routine balance maintenance only do two point checks**
- **Linearity concerns for electronic balances – internal calibrations rely on reference voltage in precision resistor**

- **Methods of estimating weighing uncertainties**
 - Simulation**
 - Estimate from Balance QA**
- **Note that, generally, bias and reproducibility are estimated at half capacity**
- **Precision may be relative**
- **Bias may be absolute**
- **Important to ensure that weighed sample has a weight comparable to the calibrated weight used for testing**
- **If weighing by difference, bias is eliminated but precision is increased by $\sqrt{2} \approx 1.414$**

- **If the weighing uncertainties form at least 25 % of the total uncertainty, then simulation weighings will be beneficial**
- **In simulation weighing, it is important that the simulated weight is similar to sample weight and weighed in a similar manner**

NBL Balance QA Program
Balance E675 Bias and Reproducibility



- **Weighing standard uncertainty should never be smaller than the rounding error (e.g. for a five place balance should not be less than $0.00001/\sqrt{12}$)**
- **If using manufacturer specified tolerances (from the previous calibration of the balance) be aware that near the end of the calibration period the tolerances may be underestimates of the uncertainty**

Case Study

Different analysts using the same balance

Similar room conditions, and the same weight set.

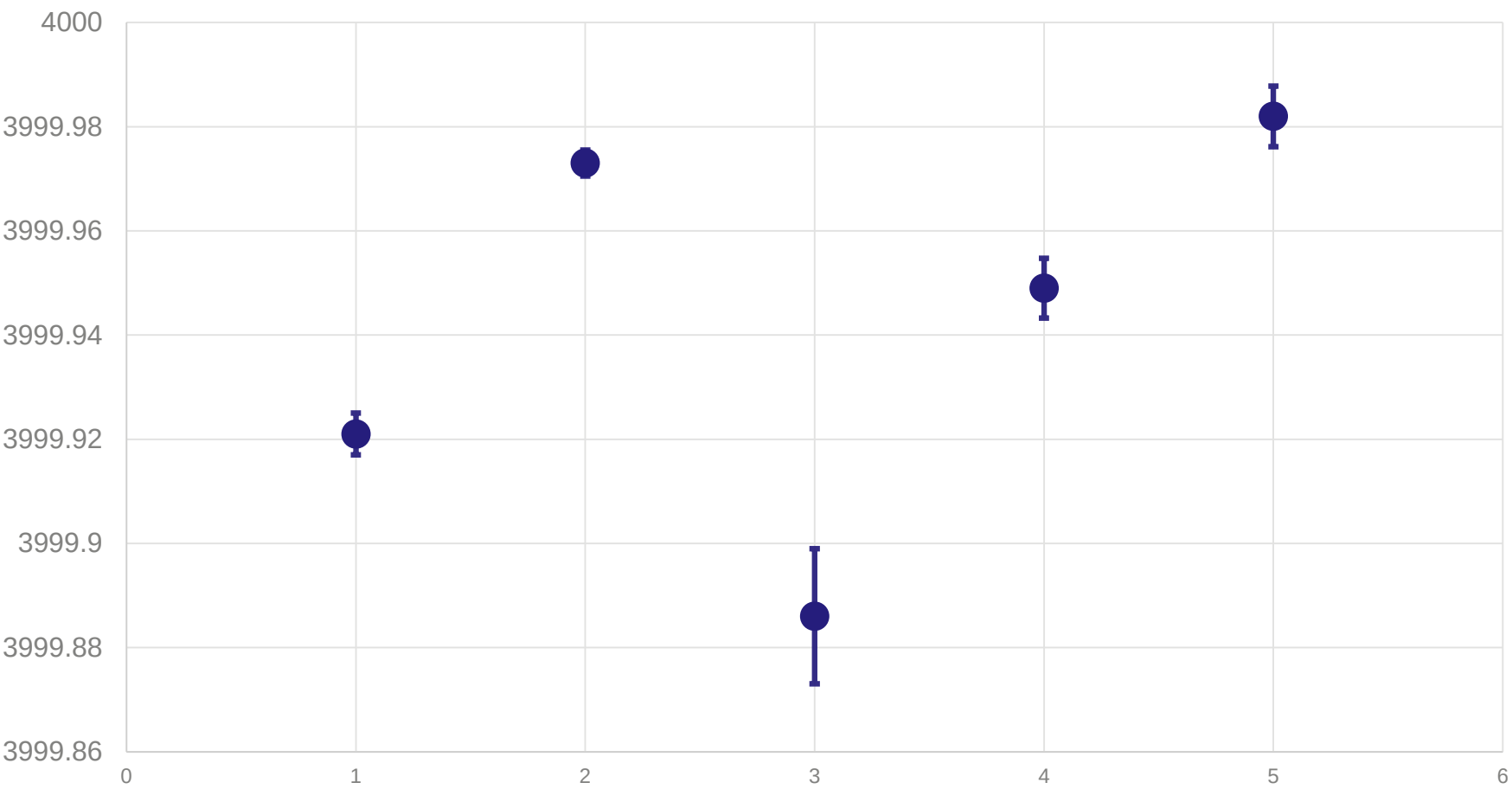
Nominally 4000 g weight is measured

Measurement results are summarized in the next slide

Weighing case study (NBL analysts)

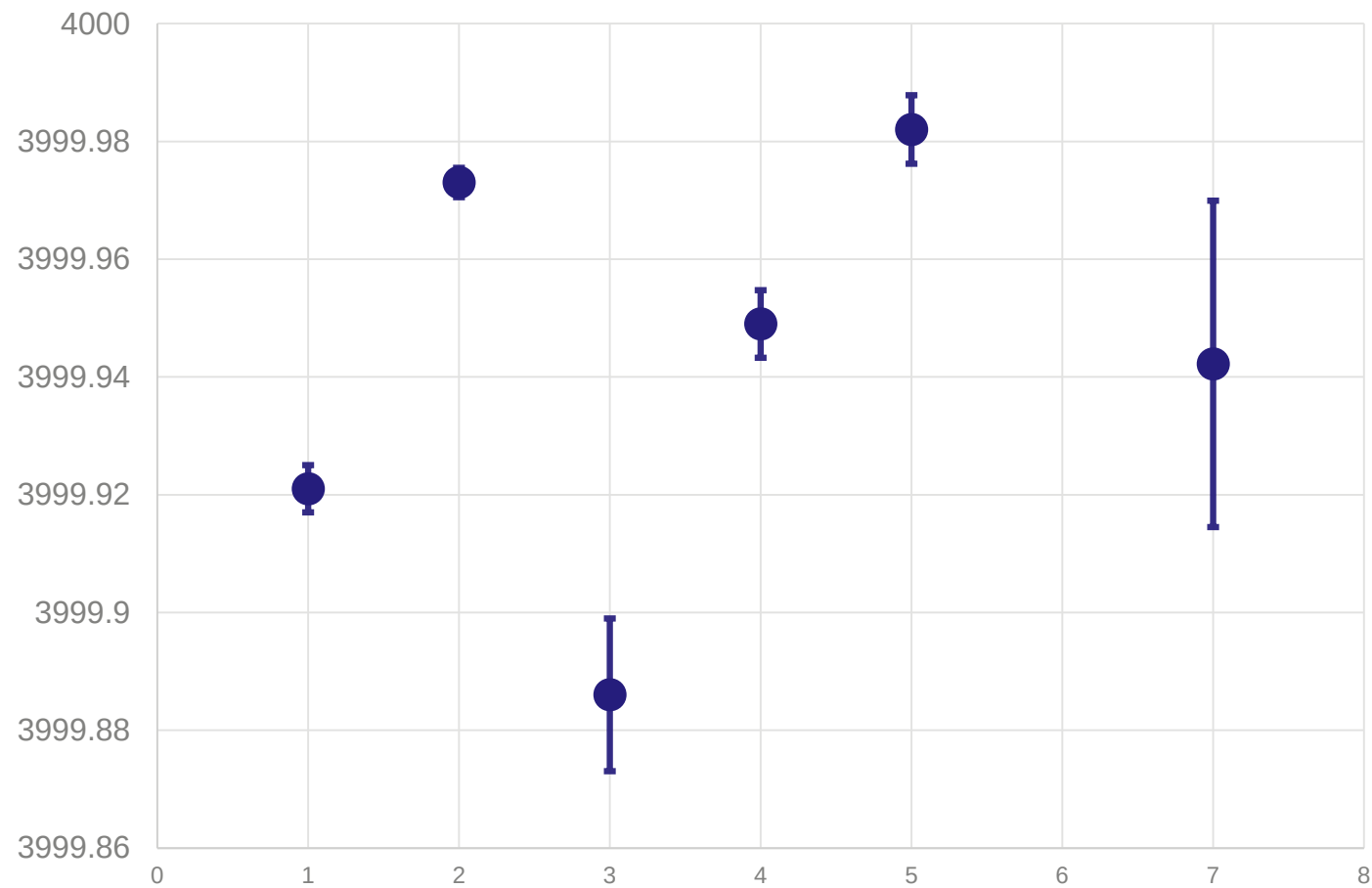
Mean value (g)	Std Dev (g)	Analyst	Number of observations
3999.921	0.035	A	76
3999.973	0.027	B	117
3999.886	0.029	C	5
3999.949	0.043	D	56
3999.982	0.024	E	17

Weighing case study (NBL analysts)



Within the standard uncertainties none of the weights are equal. Some trends are obvious (analysts A & C place the weight differently compared to analysts B, D, and E)

Weighing case study (NBL analysts)



A standard uncertainty of 0.0277 g will have to be added to the weight uncertainty to account for the analyst-to-analyst difference in the weights.

GUM – How to report Uncertainties

➤ Measured value should always be reported with its uncertainty and its unit

➤ Example

$$n = 2.01 \mu\text{mol} \pm 0.02 \mu\text{mol}$$

$$n = (2.01 \pm 0.02) \mu\text{mol}$$

$$n = 2.01(2) \mu\text{mol}$$

not $n = 2.01 \pm 0.02 \mu\text{mol}$

nor $n = 2.01 \pm 0.02$

GUM – How to report Uncertainties

- The word “uncertainty” should always be used; the term “error” should be avoided when referring to uncertainty

GUM – How to report Uncertainties

- Two significant digits should be reported for the uncertainty, and
- The number of reported digits of the value should match the number of digits of the uncertainty

➤ Example

$$n = (2.011 \pm 0.019) \mu\text{mol}$$

$$m = (0.057 \pm 0.010) \text{ g}$$

not $n = (2.011 \pm 0.0199) \mu\text{mol}$

nor $n = (2.0113 \pm 0.019) \mu\text{mol}$

Nor $m = (0.057 \pm 0.001) \text{ g}$

GUM – How to report Uncertainties

➤ It should be stated what uncertainty is reported

- ❖ The symbol for the **standard uncertainty** is **u** , the standard uncertainty of a quantity x can be written as $u(x)$
- ❖ The symbol for **combined standard uncertainty** is **u_c** , the combined standard uncertainty of x can be written as $u_c(x)$
- ❖ The symbol for **expanded uncertainty** is **U** , the expanded uncertainty of a quantity x can be written as $U(x)$
- ❖ The symbol for **coverage factor** is **k** , it should be reported what value of k was used to calculate U
- ❖ There is a difference between “**standard deviation**” and “**standard deviation of the mean**”

- A set of **prefixes** have been adopted **for use with the SI**, in order to express the values of quantities that are much larger than or much smaller than the SI unit used without any prefix

Factor	Name	Symbol	Factor	Name	Symbol
10^3	kilo	k	10^{-3}	milli	m
10^6	mega	M	10^{-6}	micro	μ
10^9	giga	G	10^{-9}	nano	n
10^{12}	tera	T	10^{-12}	pico	p
10^{15}	peta	P	10^{-15}	femto	f
10^{18}	exa	E	10^{-18}	atto	a

IUPAC/BIPM recommendations

- Commas should not be used as thousand separators. A space should be left between groups of 3 digits on either the right or left-hand side of the decimal place

- **Example**

$t = 212\ 458.37\ \text{s}$ or $t = 212458.37\ \text{s}$

not $t = 212,458.37\ \text{s}$

- Correct notation

$m = -0.8455\ \text{g}$

not $m = -.8455\ \text{g}$

IUPAC/BIPM recommendations

➤ Remarks

- The terms “parts per billion” and “parts per trillion”, and their respective abbreviations “ppb” and “ppt”, are frequently used, but their meanings are language dependent. **For this reason, the terms ppb and ppt are best avoided.**
- When any of the terms including %, ‰, and ppm are used it is important to state the dimensionless quantity whose value is being specified (e.g., referring to volume versus mass versus amount)

IUPAC/BIPM recommendations

- Do not confuse Type A evaluation with “random error” and Type B evaluation with “systematic error”.
- The terms “accuracy” and “precision” retain their meaning in GUM Guide. However, note that the term “precision” is frequently used to refer to many different things, standard deviation, standard deviation of the mean, reproducibility, repeatability, internal precision, external precision. Therefore, be precise in use of the term “precision”, state what is being referred to.
- If the analytical procedure is changed, the GUM uncertainty evaluation might also need to be changed.

Simplified GUM model for Total Evaporation isotope ratio analysis

- For the major ratio, the uncertainty budget is dominated by
 - Precision of the major isotope ratio of the sample
 - Precision of the comparator standard used for estimation of the mass bias correction factor
 - Certified ratio of the major isotope ratio of the comparator standard
- For the minor ratio, the uncertainty budget is dominated by
 - Precision of the minor isotope ratio of the sample
 - Peak-tailing correction at the minor isotope from the major isotope
 - Certified ratio of the major isotope ratio of the comparator standard
 - Contribution from filament blank (chemical prep) and background
 - For isotope abundance measurements involving the SEM, the SEM calibrations (darknoise, linearity of the SEM, SEM/Far inter-calibration)

Equation:

{GUM Uncertainty Calculations for Uranium Isotopic Ratio Calculations. Fractionation corrected data from TE/MTE are used as input. Fractionation corrections are performed on a turret by turret basis.}

$$R_{58\text{Sample}} = R_{58\text{corr}} * \delta_{\text{Cert}} * \delta_{\text{CFVar}};$$

{Fractionation and Peak-tail Corrected MTE/Conventional data are used as input.}

$$R_{38\text{Sample}} = R_{38\text{corr}} * \delta_{R58} * \delta_{\text{SEMCals}} - \delta_{233\text{bkgd}};$$

$$R_{48\text{Sample}} = R_{48\text{corr}} * \delta_{R58} - \delta_{234\text{bkgd}};$$

$$R_{68\text{Sample}} = R_{68\text{corr}} * \delta_{R58} - \delta_{236\text{bkgd}};$$

$$\text{Den} = (R_{38\text{Sample}} + R_{48\text{Sample}} + R_{58\text{Sample}} + R_{68\text{Sample}} + 1);$$

{Atom percent abundance calculations.}

$$\text{AtP}_{233\text{U}} = 100 * (R_{38\text{Sample}} / \text{Den});$$

$$\text{AtP}_{234\text{U}} = 100 * (R_{48\text{Sample}} / \text{Den});$$

$$\text{AtP}_{235\text{U}} = 100 * (R_{58\text{Sample}} / \text{Den});$$

$$\text{AtP}_{236\text{U}} = 100 * (R_{68\text{Sample}} / \text{Den});$$

$$\text{AtP}_{238\text{U}} = 100 * (1 / \text{Den});$$

{Atomic weight calculation.}

$$\text{At}_{\text{weight}} = ((\text{AtP}_{233\text{U}} * \text{AtMass}_{233\text{U}}) + (\text{AtP}_{234\text{U}} * \text{AtMass}_{234\text{U}}) + (\text{AtP}_{235\text{U}} * \text{AtMass}_{235\text{U}}) + (\text{AtP}_{236\text{U}} * \text{AtMass}_{236\text{U}}) + (\text{AtP}_{238\text{U}} * \text{AtMass}_{238\text{U}}))/100;$$

{Weight percent abundance calculations.}

$$\text{WtP}_{233\text{U}} = \text{AtP}_{233\text{U}} * \text{AtMass}_{233\text{U}} / \text{At}_{\text{weight}};$$

$$\text{WtP}_{234\text{U}} = \text{AtP}_{234\text{U}} * \text{AtMass}_{234\text{U}} / \text{At}_{\text{weight}};$$

$$\text{WtP}_{235\text{U}} = \text{AtP}_{235\text{U}} * \text{AtMass}_{235\text{U}} / \text{At}_{\text{weight}};$$

$$\text{WtP}_{236\text{U}} = \text{AtP}_{236\text{U}} * \text{AtMass}_{236\text{U}} / \text{At}_{\text{weight}};$$

$$\text{WtP}_{238\text{U}} = \text{AtP}_{238\text{U}} * \text{AtMass}_{238\text{U}} / \text{At}_{\text{weight}};$$

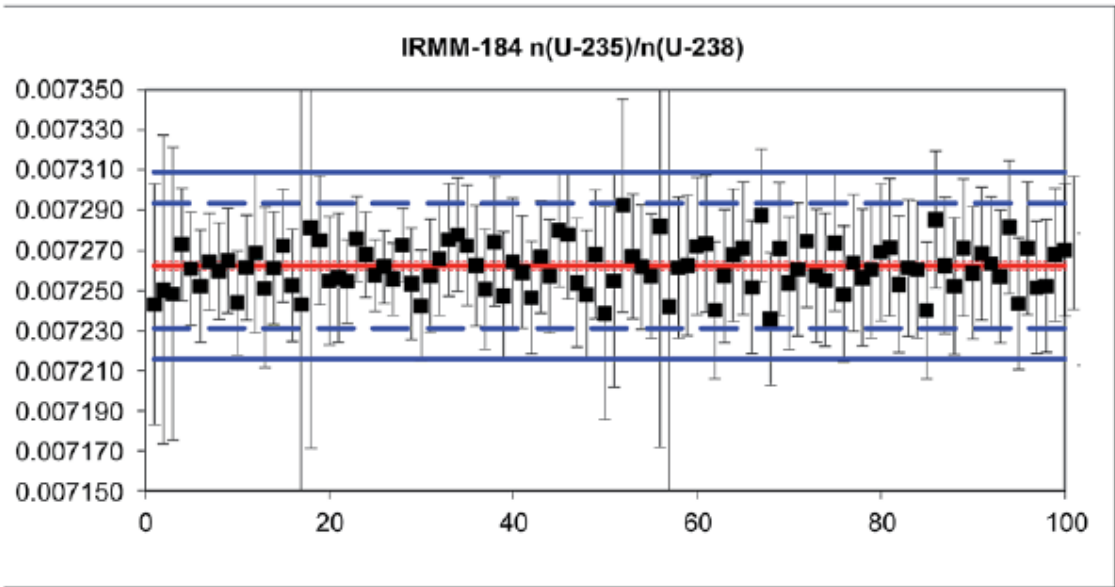
Table 6 Expanded uncertainties in the $n(^{235}\text{U})/n(^{238}\text{U})$ isotope ratios for different uncertainties in the comparator standard and for different precisions of the major ratio measurements using TE

$n(^{235}\text{U})/n(^{238}\text{U})_{\text{sample}}$ relative uncertainty (%)	Uncertainty of the $n(^{235}\text{U})/n(^{238}\text{U})_{\text{comparator}}$ isotope-amount ratio		
	0.015% ^a	0.053% ^a	0.10% ^a
0.01	0.038 (27.9, 15.7, 56.4)	0.063 (10, 70, 20.1)	0.11 (3.6, 89.2, 7.2)
0.02	0.051 (60.8, 8.6, 30.7)	0.072 (30.7, 53.9, 15.5)	0.11 (13.6, 79.9, 6.4)
0.05	0.11 (90.7, 2.0, 7.3)	0.12 (73.4, 20.6, 5.9)	0.14 (48.1, 48.1, 3.9)

^a Entries in parentheses indicate percent contributions to the final uncertainty from (i) assumed variability in the sample measurements (column 1), (ii) from uncertainty in the comparator $n(^{235}\text{U})/n(^{238}\text{U})$ ratio, and (iii) from variability in the mass bias correction (the average standard uncertainty in the TRITON mass bias correction factor is adopted).

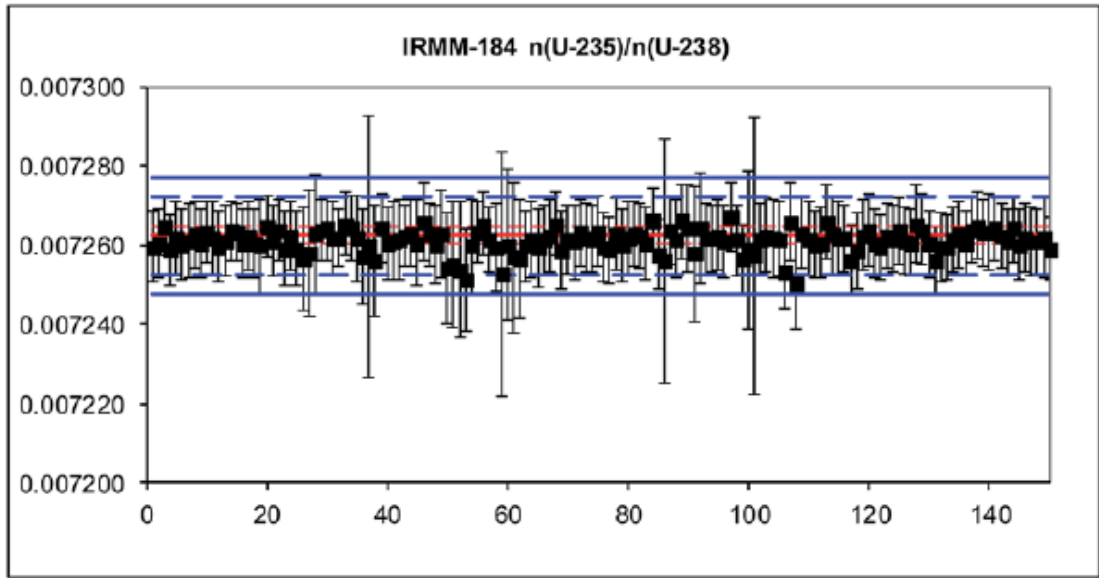
Mathew et al., JAAS 2013
Uncertainty budgets for isotope ratio measurements by TE

Control chart from Boulyga et al. JAAS 2016, (²³⁵U/²³⁸U ratio)



TIMS

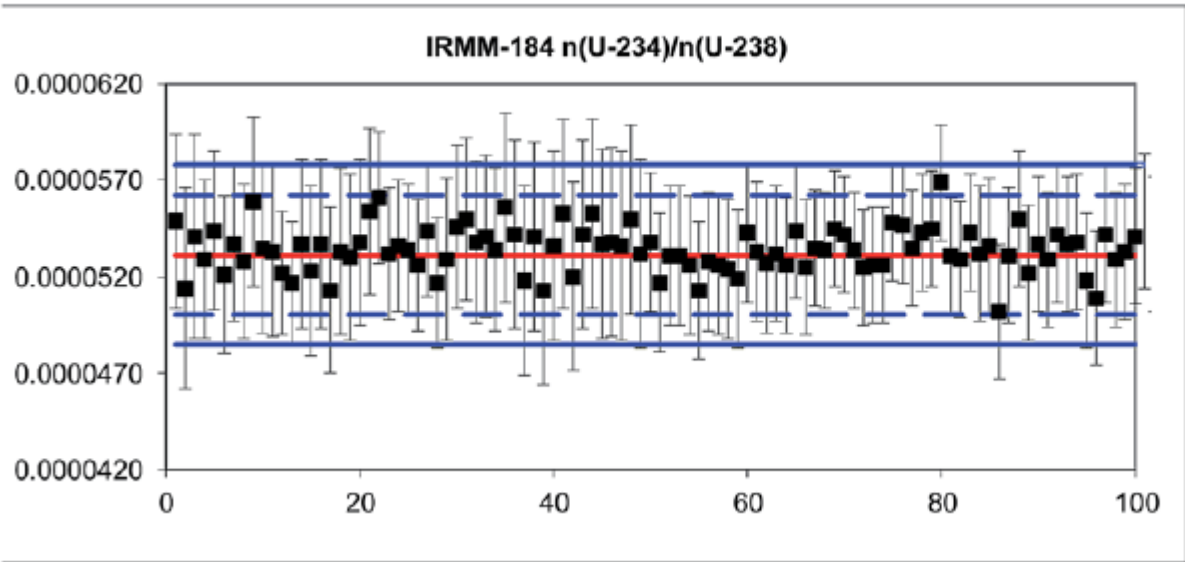
RSD = 0.17%



MC-ICP-MS

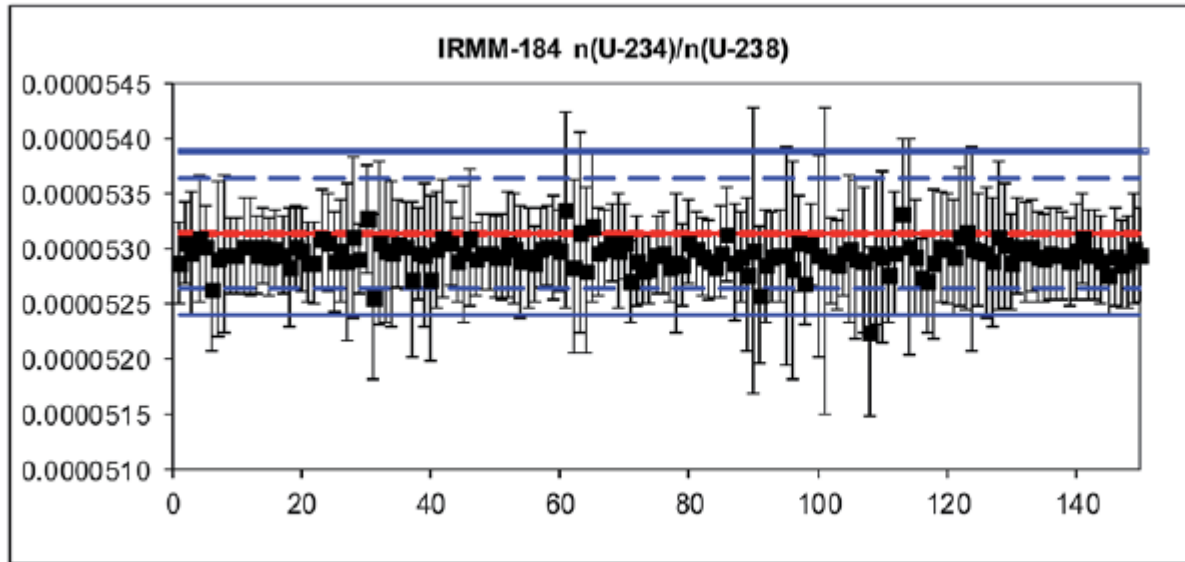
RSD = 0.04%

Control chart from Boulyga et al. $^{234}\text{U}/^{238}\text{U}$ ratio



TIMS

RSD = 2.12%

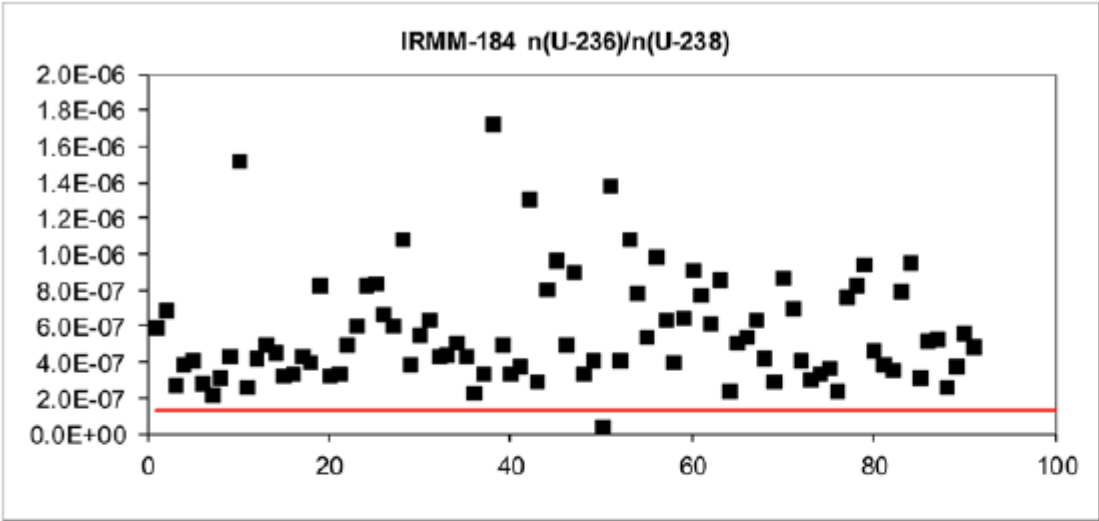


MC-ICP-MS

RSD = 0.25%

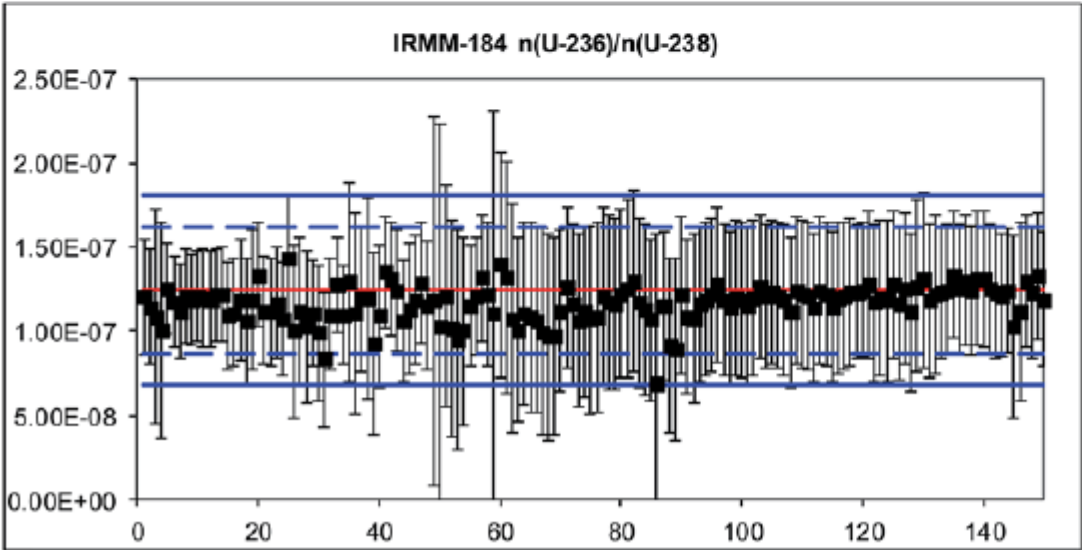
a

Control chart from Boulyga et al. (236/238)



TIMS:

 $n(236)/n(238)$ in
IRMM-184 is below
detection threshold



MC-ICP-MS

} RSD = 9.3%

Accuracy and precision of isotope ratio measurements from Boulyga et al.

Table 5 Precision and accuracy of uranium isotope ratio measurements at 1 ng mL⁻¹ concentration level in certified reference materials^a

CRM	Precision of uranium isotope ratio measurements (RSD)			Accuracy of uranium isotope ratio measurements			
	²³⁴ U/ ²³⁸ U	²³⁵ U/ ²³⁸ U	²³⁶ U/ ²³⁸ U	²³⁴ U/ ²³⁸ U	²³⁵ U/ ²³⁸ U	²³⁶ U/ ²³⁸ U	<i>n</i>
IRMM 183	0.26% 0.79	0.086% 0.20	0.23% 0.91	−0.30%, −0.06 ppm	+0.051%, +1.6 ppm	−0.39%, −0.58 ppm	104
IRMM 184	0.25% 0.89	0.04% 0.09	9.3% 22.5	−0.37%, −0.20 ppm	−0.018%, −1.3 ppm	−6.3%, −0.01 ppm	150
IRMM 185	0.23% 0.76	0.023% 0.06	0.74% 1.53	−0.30%, −0.53 ppm	+0.022%, +4.4 ppm	−0.19%, −0.01 ppm	112
IRMM 186	0.33% 0.88	0.037% 0.10	0.45% 0.91	−0.29%, −0.84 ppm	+0.031%, +9.4 ppm	−0.08%, −0.03 ppm	96
IRMM 187	0.19% 0.54	0.043% 0.09	0.23% 0.80	−0.19%, 0.72 ppm	+0.010%, +4.5 ppm	−0.33%, −0.23 ppm	66
NBL CRM U005a	0.33% 1.18	0.10% 0.21	0.48% 1.36	−0.49%, −0.17 ppm	+0.031%, +1.6 ppm	+0.48%, +0.06 ppm	80
NBL CRM U010	0.18% 1.45	0.017% 0.04	0.17% 0.96	−0.70%, −0.38 ppm	+0.009%, +0.89 ppm	+0.45%, +0.31 ppm	26

^a Precision is defined as the standard deviation normalized by the mean (*i.e.*, relative standard deviation) and accuracy is defined as the difference (relative: %, or absolute: ppm) between the measured value and the certified value, normalized by the certified value. “*n*” denotes the number of measurements (*i.e.*, aliquots analysed). The reported data are corrected for mass bias, background/memory effects, hydride formation, dead-time, and peak-tailing.

Uncertainties calculated by combining the accuracy and precision

Uncertainty budget for isotope ratio measurements from Boulyga et al.

Isotope ratio/parameter	CRM 112A (NU)	IRMM 184 (NU)	IRMM 183 (DU)	IRMM 185 (LEU)
²³⁴ U/ ²³⁸ U				
Certified ratio ²³⁴ U/ ²³⁸ U	9.91%	5.27%	8.55%	32.72%
Gain of Faraday cup L5	0.01%	0.01%	0.01%	0.04%
Non-linearity of SEM IC3 ^a	3.22%	1.72%	2.78%	10.65%
Ratio ²³⁴ U/ ²³⁸ U measured in standard 1	6.42%	3.43%	3.67%	3%
Ratio ²³⁴ U/ ²³⁸ U measured in the sample	73.83%	86.04%	81.15%	49.96%
Ratio ²³⁴ U/ ²³⁸ U measured in standard 2	6.42%	3.43%	3.67%	3%
Effect of dead time of IC3 ^a	0.19%	0.10%	0.17%	0.63%

Uncertainty budget for isotope ratio measurements from Boulyga et al.

Isotope ratio/parameter	CRM 112A (NU)	IRMM 184 (NU)	IRMM 183 (DU)	IRMM 185 (LEU)
²³⁵ U/ ²³⁸ U				
Certified ratio ²³⁵ U/ ²³⁸ U	9.22%	9.41%	2.14%	20.7%
Peak tailing from ²³⁸ U on <i>m/z</i> = 235 u	0.31%	0.32%	0.37%	0.09%
Gain of Faraday cup L5	0.37%	0.38%	0.09%	0.83%
Gain of Faraday cup L4	0.04%	0.04%	0.01%	0.09%
²³⁵ U blank measured before standard 1	0.29%	0.32%	0.05%	0.71%
²³⁵ U blank measured before the sample	7.92%	6.23%	6.23%	1.93%
²³⁵ U blank measured before standard 2	0.31%	0.23%	0.07%	0.61%
Ratio ²³⁵ U/ ²³⁸ U measured in standard 1	1.89%	1.93%	0.37%	2.50%
Ratio ²³⁵ U/ ²³⁸ U measured in the sample	77.8%	79.2%	90.3%	70.0%
Ratio ²³⁵ U/ ²³⁸ U measured in standard 2	1.89%	1.93%	0.37%	2.50%

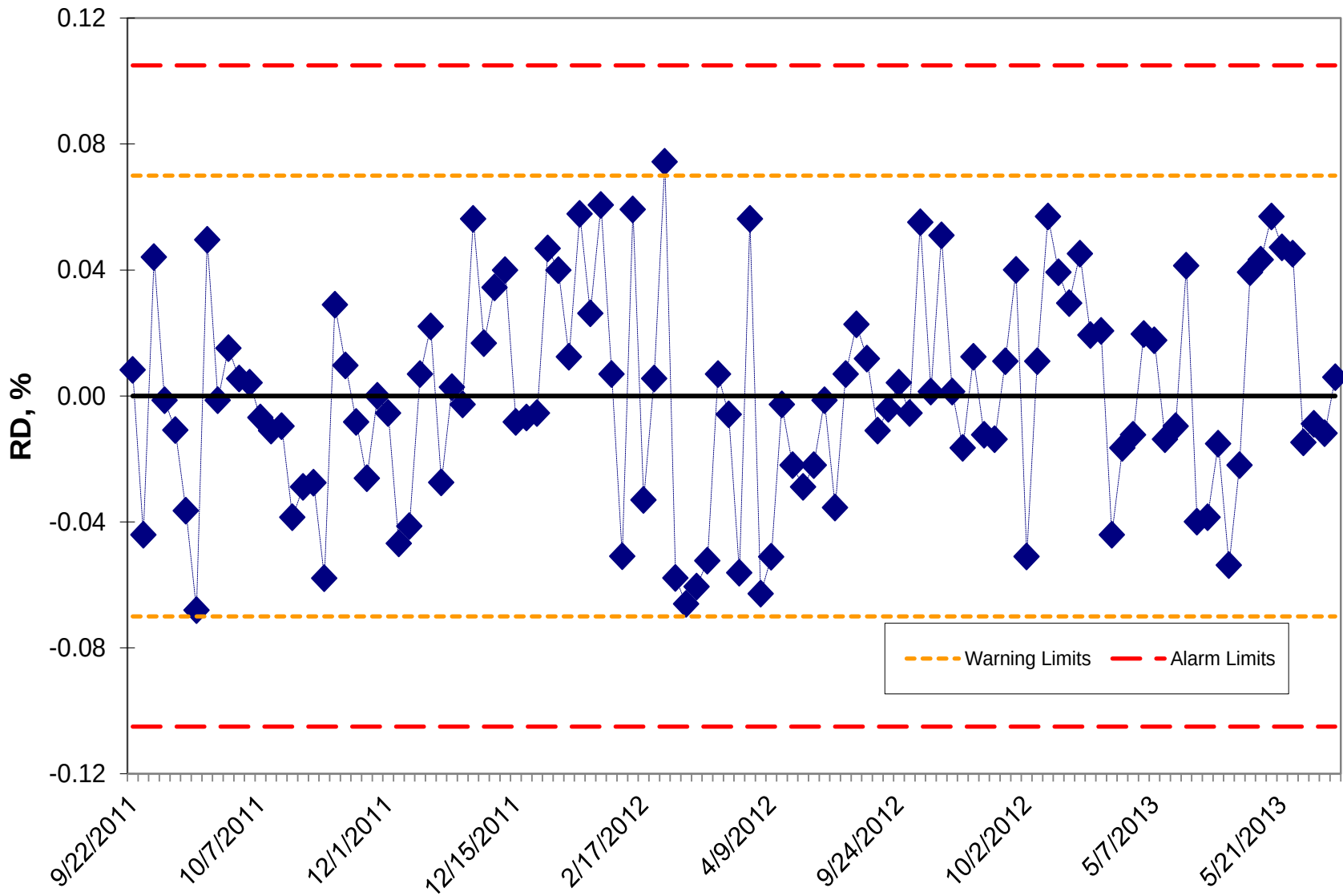
Uncertainty budget for isotope ratio measurements from Boulyga et al.

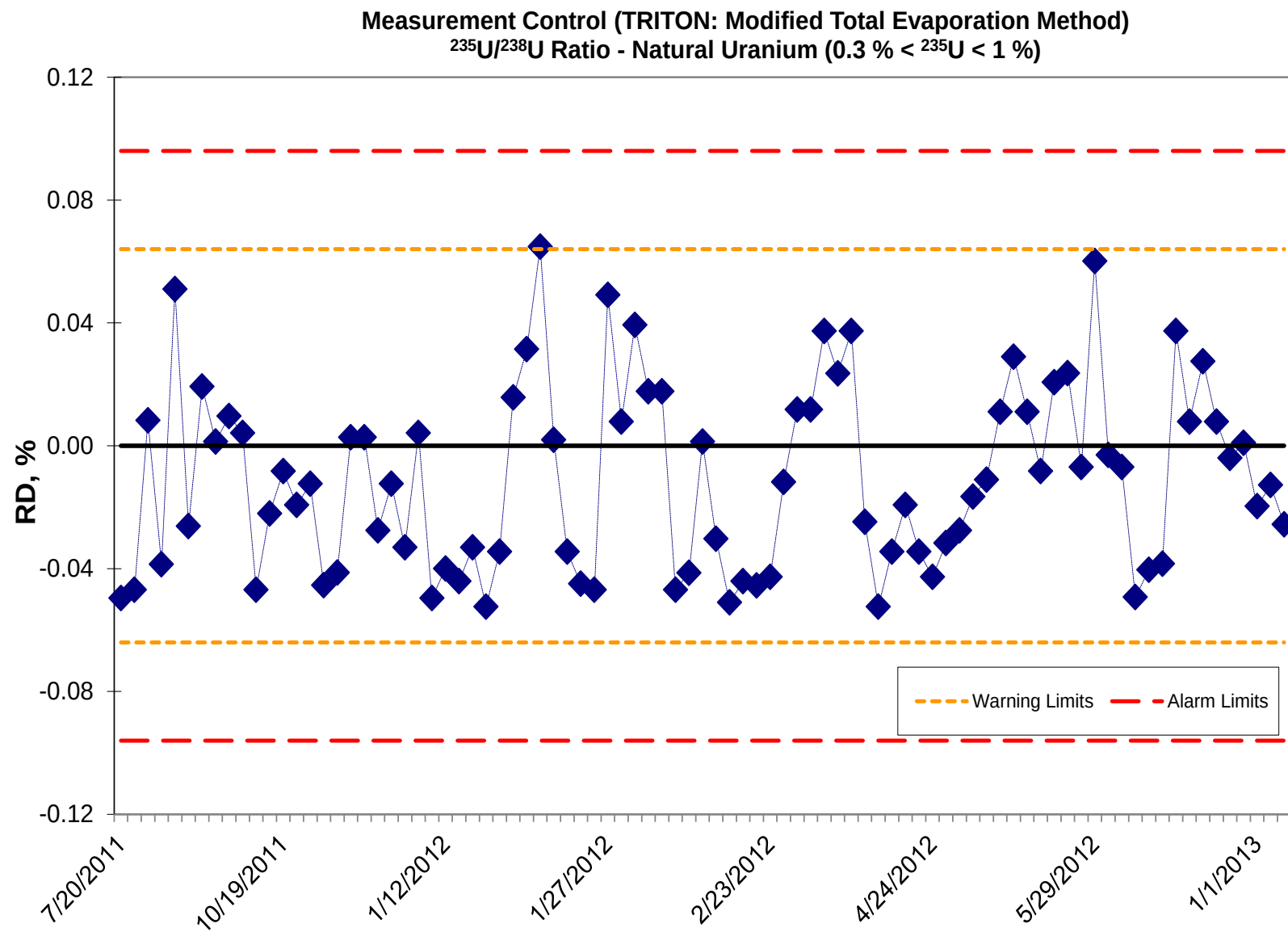
Isotope ratio/parameter	CRM 112A (NU)	IRMM 184 (NU)	IRMM 183 (DU)	IRMM 185 (LEU)
²³⁶ U/ ²³⁸ U				
Certified ratio ²³⁶ U/ ²³⁸ U	0%	0.03%	43.86%	8.14%
Combined effect of interference by ²³⁵ U (peak tailing at <i>m</i> + 1 u and ²³⁵ U ¹ H ions)	0.02%	0.02%	0%	0.07%
Interference by ²³⁸ U (peak tailing at <i>m</i> − 2 u)	1.19%	1.43%	0%	0.57%
Non-linearity of SEM IC1B ^a	0%	0%	1.26%	0.23%
²³⁶ U blank measured before the sample	0.08%	0.07%	0%	0.02%
Ratio ²³⁶ U/ ²³⁸ U measured in standard 1	0%	0.01%	23.88%	2.62%
Ratio ²³⁶ U/ ²³⁸ U measured in the sample	98.71%	98.43%	7.09%	85.73%
Ratio ²³⁶ U/ ²³⁸ U measured in standard 2	0%	0.01%	23.88%	2.62%
Effect of dead time of SEM IC1B ^a	0%	0%	0.03%	0%

^a Assessment of SEM linearity and dead time has been reported by Richter *et al.*¹⁵

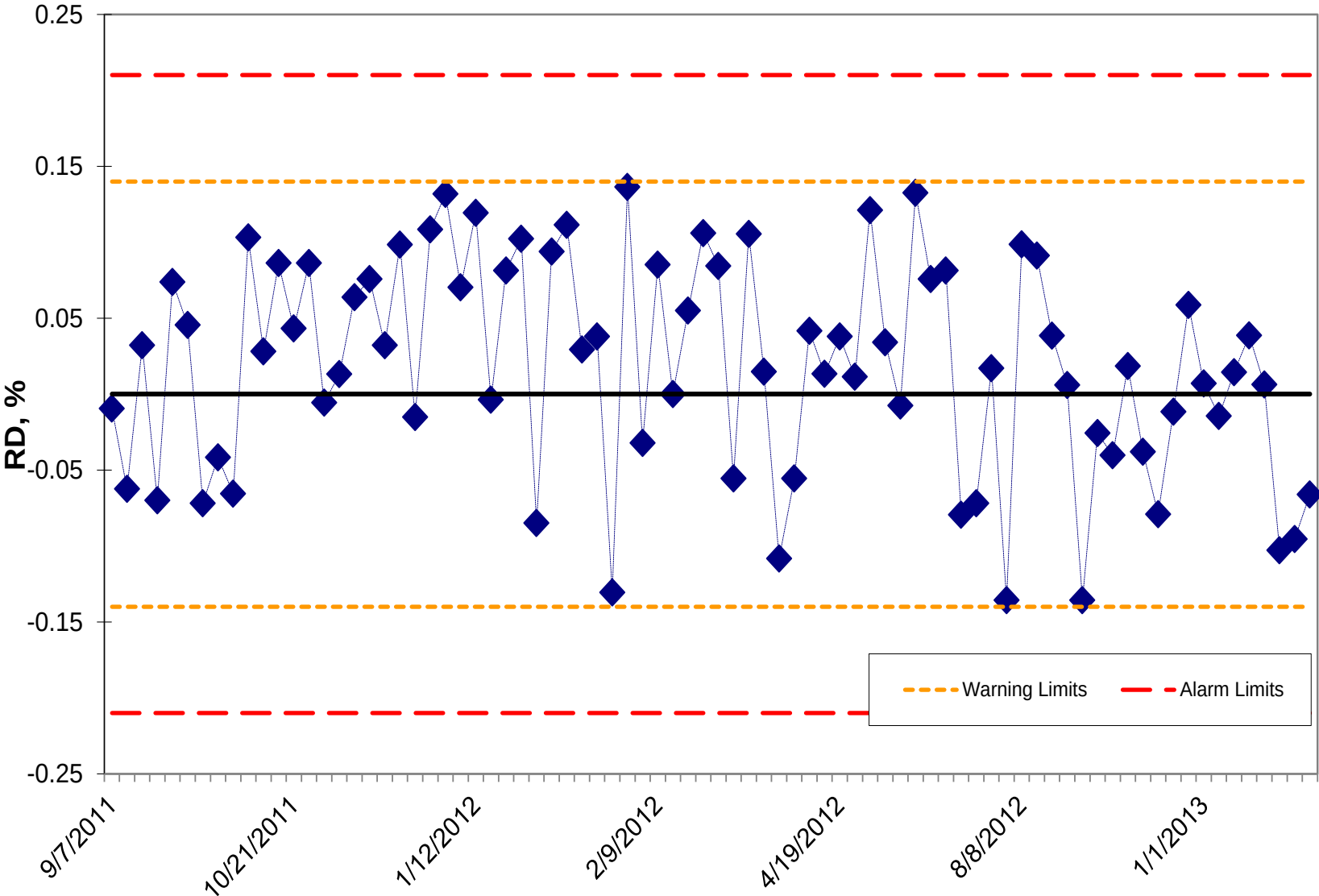
How does the uncertainties in the ICP-MS measurements shown above compare to Triton measurements quoted in literature. Let's look at a few control charts.

Measurement Control (TRITON: Total Evaporation Method)
 $^{235}\text{U}/^{238}\text{U}$ Ratio - Natural Uranium ($0.3\% < ^{235}\text{U} < 1\%$)





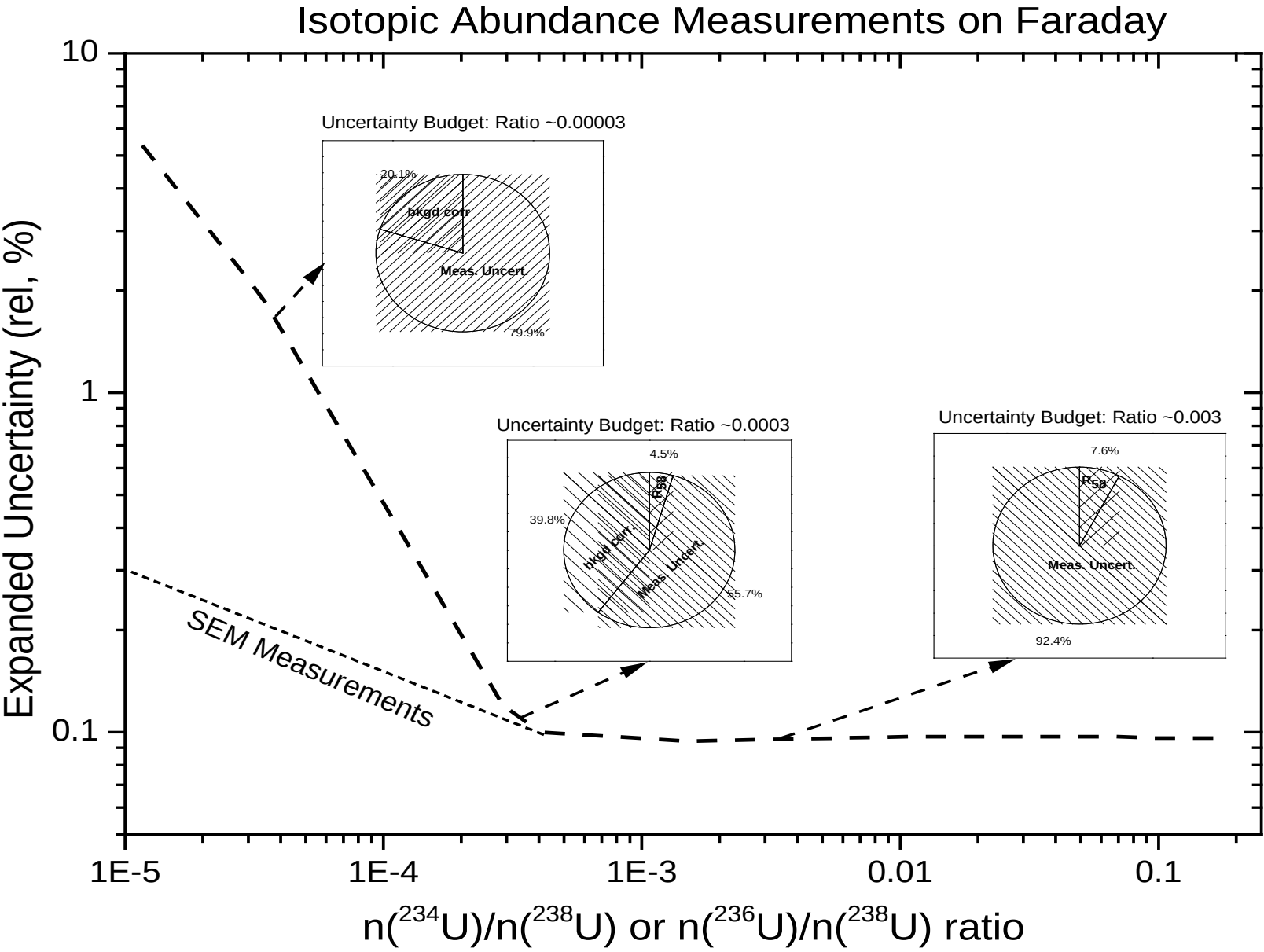
Measurement Control (TRITON: Modified Total Evaporation Method)
²³⁴U/²³⁸U Ratio - Minor U Techniques (²³⁵U < 50 %)



Mathew et al., Analytical Methods 2016

➤ Minor ratio uncertainty -- MTE

- From QC Measurements
 - Ave %RD in Chara Meas 0.07 %
 - Ave %RSD in Chara Meas 0.05 %
 - Comb Uncert 0.10 %
- Calc Uncert (GUM) 0.10 % (k =2, 95 % CL)
- These uncertainties are lower than certified uncertainties for the minor ratios by
 - factor of **~2** for CRMs **U030-A, U045, 112-A, U630**
 - factor of **~4 to 40** for CRMs **U900, U 930-D, U970, U500**



- Simplified model for IDMS uncertainties

GUM Workbench Pro - U IDMS uncertainties.smu

File Edit View Picture Diagram Option Tools Help

Model

Observation

Correlation

Budget

Last

Result

Diagram

Title

Model Equation

Quantity Data

Partial Derivatives

Title: U-IDMS Uncertainties using TIMS measurement of the isotopic ratios

Reference: Date: 10/14/2017 Version: Author:

General Description | Picture 1

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ModelObservationCorrelationBudgetLastResultDiagram?

TitleModel EquationQuantity DataPartial Derivatives

Equation:

Σδ...

f(x)...

Rename

Order

Experts

{The concentration of Uranium sample is calculated using the De Bièvre and Peiser equation}

$$C_{\text{Usample}} = ((R_{58\text{mix}} - R_{58\text{spike}})/(R_{58\text{sample}} - R_{58\text{mix}})) * (M_{\text{spike}}/M_{\text{sample}}) * (C_{238\text{spike}} / AF_{238\text{Usample}}) ;$$
$$C_{238\text{spike}} = C_{\text{spike}} * AF_{238\text{spike}} ;$$
$$C_{\text{spike}} = C_{\text{spike}g} / At_{\text{wtspike}} ;$$
$$C_{\text{spike}g} = Wt_{\text{piece}}/Wt_{\text{solution}} * Purity ;$$
$$AF_{238\text{Usample}} = 1 / ((R_{48\text{sample}} + R_{58\text{sample}} + R_{68\text{sample}}) * \delta_{R58\text{comparator}} + 1) ;$$

Quantity	Unit	Definition
C_{Usample}	mol U / g	Uranium concentration in sample
$R_{58\text{mix}}$	mol / mol	235U/238U ratio in sample/spike mixture
$R_{58\text{spike}}$	mol / mol	certified 235U/238U of the spike
$R_{58\text{sample}}$	mol / mol	measured 235U/238U ratio of sample
M_{spike}	g	mass of spike used for preparation of the sample/spike mixture

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File Edit View Picture Diagram Option Tools Help

Model

Observation

Correlation

Budget

Last

Result

Diagram

?

Title

Model Equation

Quantity Data

Partial Derivatives

C_{sample}

R_{58mix}

R_{58spike}

R_{58sample}

M_{spike}

M_{sample}

C_{238spike}

AF_{238Usample}

C_{spike}

AF_{238spike}

C_{spikeg}

At_{wtspike}

Wt_{piece}

Wt_{solution}

Purity

R_{48sample}

R_{68sample}

δ_{R58comparator}

certified 235U/238U of the spike

Type: Type B

Distribution: Normal

Value: 0.0072543 mol / mol

Expanded Uncertainty: 0.0000022 mol / mol

Coverage Factor: 2

Description

Picture 1

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ModelObservationCorrelationBudgetResultDiagram

?

C_Usample

Uranium concentration in sample

Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
R _{58mix}	1.000000 mol / mol	150·10 ⁻⁶ mol / mol	normal	0.050	7.5·10 ⁻⁶ mol U / g	8.6 %
R _{58spike}	7.25430·10 ⁻³ mol / mol	1.10·10 ⁻⁶ mol / mol	normal	-0.047	-52·10 ⁻⁹ mol U / g	0.0 %
R _{58sample}	17.34870 mol / mol	2.60·10 ⁻³ mol / mol	normal	-350·10 ⁻⁶	-900·10 ⁻⁹ mol U / g	0.1 %
M _{spike}	1.000000 g	250·10 ⁻⁶ g	normal	0.047	12·10 ⁻⁶ mol U / g	21.0 %
M _{sample}	1.000000 g	250·10 ⁻⁶ g	normal	-0.047	-12·10 ⁻⁶ mol U / g	21.0 %
C _{238spike}	0.0416965 mol / g	14.8·10 ⁻⁶ mol / g				
AF _{238U} sample	0.0538000 mol / g	10.7·10 ⁻⁶ mol / g				
C _{spike}	420.012·10 ⁻⁶ mol / g	149·10 ⁻⁹ mol / g				
AF _{238spike}	99.274580 mol / g	250·10 ⁻⁶ mol / g	normal	470·10 ⁻⁶	120·10 ⁻⁹ mol U / g	0.0 %
C _{spike} g	0.0999750 mol / g	35.5·10 ⁻⁶ mol / g				
At _{wtspike}	238.02891800 u	6.00·10 ⁻⁶ u	normal	-200·10 ⁻⁶	-1.2·10 ⁻⁹ mol U / g	0.0 %
Wt _{piece}	1.000000 g	250·10 ⁻⁶ g	normal	0.047	12·10 ⁻⁶ mol U / g	21.0 %
Wt _{solution}	10.00000 g	2.50·10 ⁻³ g	normal	-4.7·10 ⁻³	-12·10 ⁻⁶ mol U / g	21.0 %
Purity	0.9997500 g U / g	30.0·10 ⁻⁶ g U / g	normal	0.047	1.4·10 ⁻⁶ mol U / g	0.3 %
C _U sample	0.0470622 mol U / g	25.7·10 ⁻⁶ mol U / g				

Result:

Value:Expanded UncertaintyCoverage FactorCoverage:

0.047062 mol U / g ± 0.11 % (relative) 2.00 95% (normal)

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Model Observation Correlation Budget Last Result Diagram

?

Result

Quantity	Value	Expanded Uncertainty	Coverage- factor	Coverage
C _{Usample}	0.047062 mol U /g	0.11 % (relative)	2.00	95% (normal)

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Chronometric Ages calculated from U/Pu isotope ratios

- Simplified model for chronometry

GUM Workbench Pro - Chronometric ages using assay values.smu

File Edit View Picture Diagram Option Tools Help

Model Observation Correlation Budget Last Result Diagram

?

Title

Model Equation

Quantity Data

Partial Derivatives

Title:chronometric age from isotope ratios

Reference: Date:05/17/2016 Version: Author:KMathew

General Description Picture 1

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Model Observation Correlation Budget Last Result Diagram

Title Model Equation Quantity Data Partial Derivatives

Equation: $\Sigma\delta...$ $f(x)...$ Rename Order Experts

$\lambda_{238\text{Pu}} = \ln(2) / \text{HL}_{238\text{Pu}} ;$
 $\lambda_{234\text{U}} = \ln(2) / \text{HL}_{234\text{U}} ;$
 $\lambda_{239\text{Pu}} = \ln(2) / \text{HL}_{239\text{Pu}} ;$
 $\lambda_{235\text{U}} = \ln(2) / \text{HL}_{235\text{U}} ;$
 $\lambda_{240\text{Pu}} = \ln(2) / \text{HL}_{240\text{Pu}} ;$
 $\lambda_{236\text{U}} = \ln(2) / \text{HL}_{236\text{U}} ;$
 $\lambda_{242\text{Pu}} = \ln(2) / \text{HL}_{242\text{Pu}} ;$
 $\lambda_{238\text{U}} = \ln(2) / \text{HL}_{238\text{U}} ;$

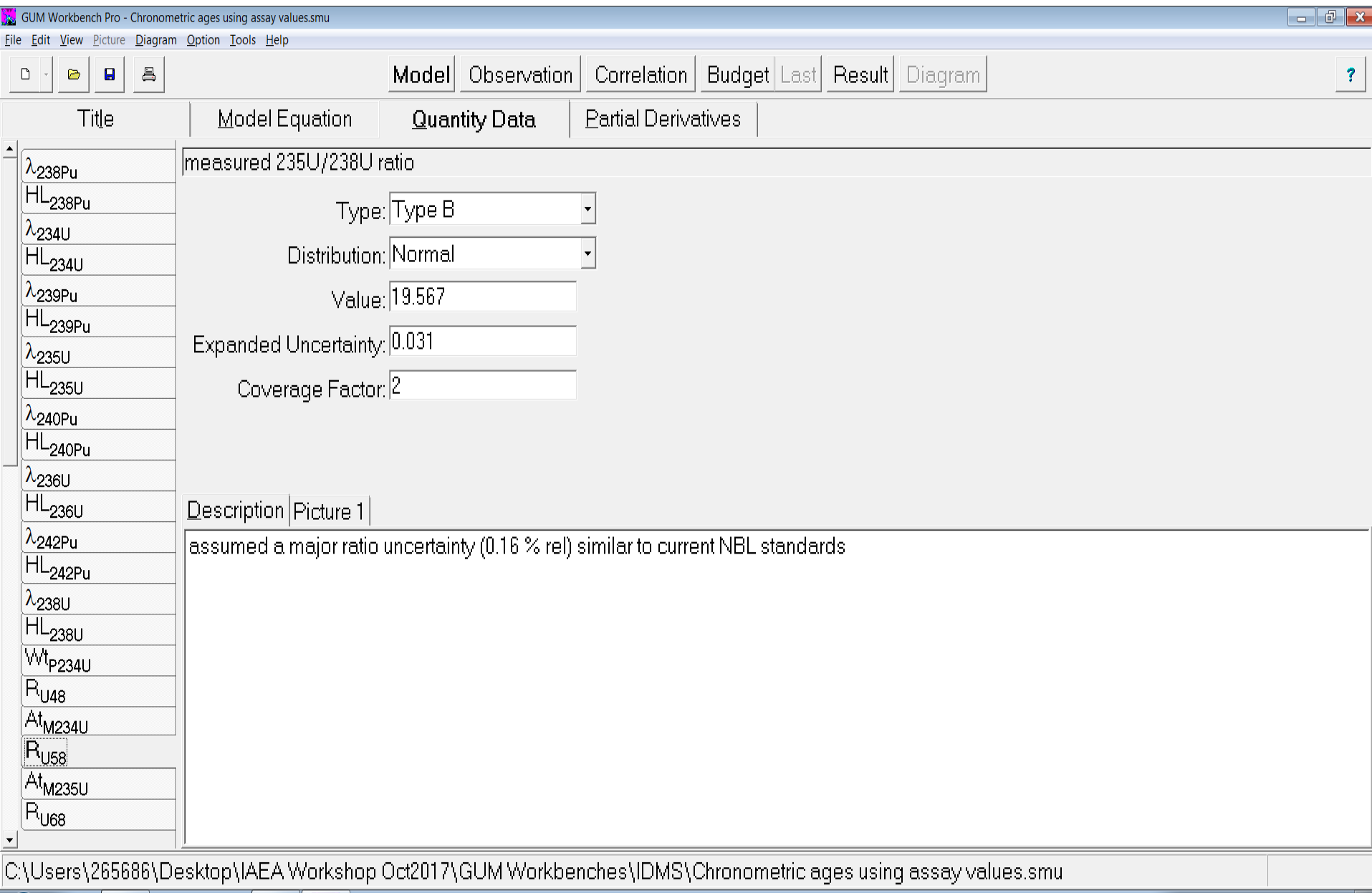
$\text{Wt}_{\text{P}234\text{U}} = (\text{R}_{\text{U}48} * \text{At}_{\text{M}234\text{U}}) / (\text{R}_{\text{U}48} * \text{At}_{\text{M}234\text{U}} + \text{R}_{\text{U}58} * \text{At}_{\text{M}235\text{U}} + \text{R}_{\text{U}68} * \text{At}_{\text{M}236\text{U}} + 1 * \text{At}_{\text{M}238\text{U}}) ;$
 $\text{Wt}_{\text{P}235\text{U}} = (\text{R}_{\text{U}58} * \text{At}_{\text{M}235\text{U}}) / (\text{R}_{\text{U}48} * \text{At}_{\text{M}234\text{U}} + \text{R}_{\text{U}58} * \text{At}_{\text{M}235\text{U}} + \text{R}_{\text{U}68} * \text{At}_{\text{M}236\text{U}} + 1 * \text{At}_{\text{M}238\text{U}}) ;$
 $\text{Wt}_{\text{P}236\text{U}} = (\text{R}_{\text{U}68} * \text{At}_{\text{M}236\text{U}}) / (\text{R}_{\text{U}48} * \text{At}_{\text{M}234\text{U}} + \text{R}_{\text{U}58} * \text{At}_{\text{M}235\text{U}} + \text{R}_{\text{U}68} * \text{At}_{\text{M}236\text{U}} + 1 * \text{At}_{\text{M}238\text{U}}) ;$
 $\text{Wt}_{\text{P}238\text{U}} = (1 * \text{At}_{\text{M}238\text{U}}) / (\text{R}_{\text{U}48} * \text{At}_{\text{M}234\text{U}} + \text{R}_{\text{U}58} * \text{At}_{\text{M}235\text{U}} + \text{R}_{\text{U}68} * \text{At}_{\text{M}236\text{U}} + 1 * \text{At}_{\text{M}238\text{U}}) ;$

$\text{Wt}_{\text{P}238\text{Pu}} = (\text{R}_{\text{Pu}89} * \text{At}_{\text{M}238\text{Pu}}) / (\text{R}_{\text{Pu}89} * \text{At}_{\text{M}238\text{Pu}} + \text{R}_{\text{Pu}09} * \text{At}_{\text{M}240\text{Pu}} + \text{R}_{\text{Pu}19} * \text{At}_{\text{M}241\text{Pu}} + \text{R}_{\text{Pu}29} * \text{At}_{\text{M}242\text{Pu}} + 1 * \text{At}_{\text{M}239\text{Pu}}) ;$

Quantity	Unit	Definition
$\lambda_{238\text{Pu}}$		decay constant (238Pu)
$\text{HL}_{238\text{Pu}}$		half-life (238Pu)
$\lambda_{234\text{U}}$		decay constant (234U)
$\text{HL}_{234\text{U}}$		half-life (234U)
$\lambda_{238\text{U}}$		decay constant (238U)

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chronometric age from 238Pu-234U

Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
$\lambda_{238\text{Pu}}$	$7.90362 \cdot 10^{-3}$	$9.01 \cdot 10^{-6}$				
$HL_{238\text{Pu}}$	87.700	0.100	normal	0.59	0.059	0.3 %
$\lambda_{234\text{U}}$	$2.81767 \cdot 10^{-6}$	$6.87 \cdot 10^{-9}$				
$HL_{234\text{U}}$	$246.000 \cdot 10^3$	600	normal	$-13 \cdot 10^{-9}$	$-8.0 \cdot 10^{-6}$	0.0 %
$Wt_{P234\text{U}}$	0.0150832	$39.2 \cdot 10^{-6}$				
R_{U48}	0.375700	$950 \cdot 10^{-6}$	normal	110	0.11	1.0 %
$At_{M234\text{U}}$	234.04095230	$1.90 \cdot 10^{-6}$	normal	$-2.7 \cdot 10^{-3}$	$-5.2 \cdot 10^{-9}$	0.0 %
R_{U58}	19.5670	0.0155	normal	-1.7	-0.026	0.0 %
$At_{M235\text{U}}$	235.04393010	$1.90 \cdot 10^{-6}$	normal	-0.14	$-270 \cdot 10^{-9}$	0.0 %
R_{U68}	3.83200	$9.50 \cdot 10^{-3}$	normal	-1.7	-0.016	0.0 %
$At_{M236\text{U}}$	236.04556820	$1.90 \cdot 10^{-6}$	normal	-0.028	$-53 \cdot 10^{-9}$	0.0 %
$At_{M238\text{U}}$	238.05078840	$2.00 \cdot 10^{-6}$	normal	$-7.3 \cdot 10^{-3}$	$-15 \cdot 10^{-9}$	0.0 %
$Wt_{P238\text{Pu}}$	$59.34 \cdot 10^{-6}$	$1.46 \cdot 10^{-6}$				
R_{Pu89}	$62.80 \cdot 10^{-6}$	$1.55 \cdot 10^{-6}$	normal	$-680 \cdot 10^3$	-1.0	95.8 %
t_1	51.60	1.07				

Result:
Value: 51.6 Expanded Uncertainty Coverage Factor Coverage:
± 4.1 % (relative) 2.00 95% (normal)

Quantity	Value	Expanded Uncertainty	Coverage- factor	Coverage
t_1	51.6	4.1 % (relative)	2.00	95% (normal)
t_2	57.24	0.89 % (relative)	2.00	95% (normal)
t_3	57.28	0.99 % (relative)	2.00	95% (normal)

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Model Observation Correlation Budget Last **Result** Diagram



Result

Quantity	Value	Expanded Uncertainty	Coverage- factor	Coverage
t_1	52.48	1.7 % (relative)	2.00	95% (normal)
t_2	58.43	0.38 % (relative)	2.00	95% (normal)
t_3	58.46	0.37 % (relative)	2.00	95% (normal)

Guide to the Expression of Uncertainty in Measurement (GUM)

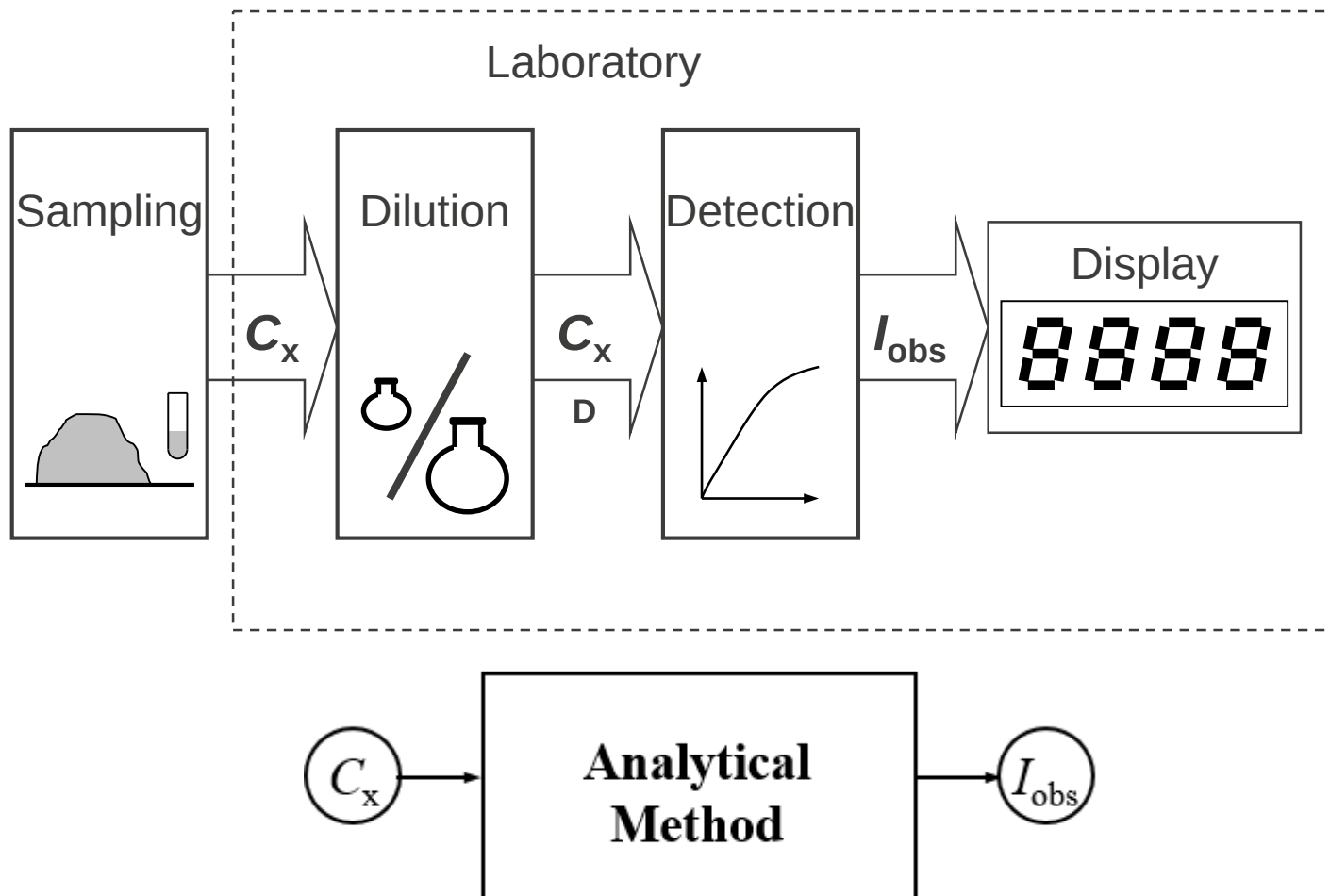
Regression

Module 5

Authors: K. J. Mathew (LANL)

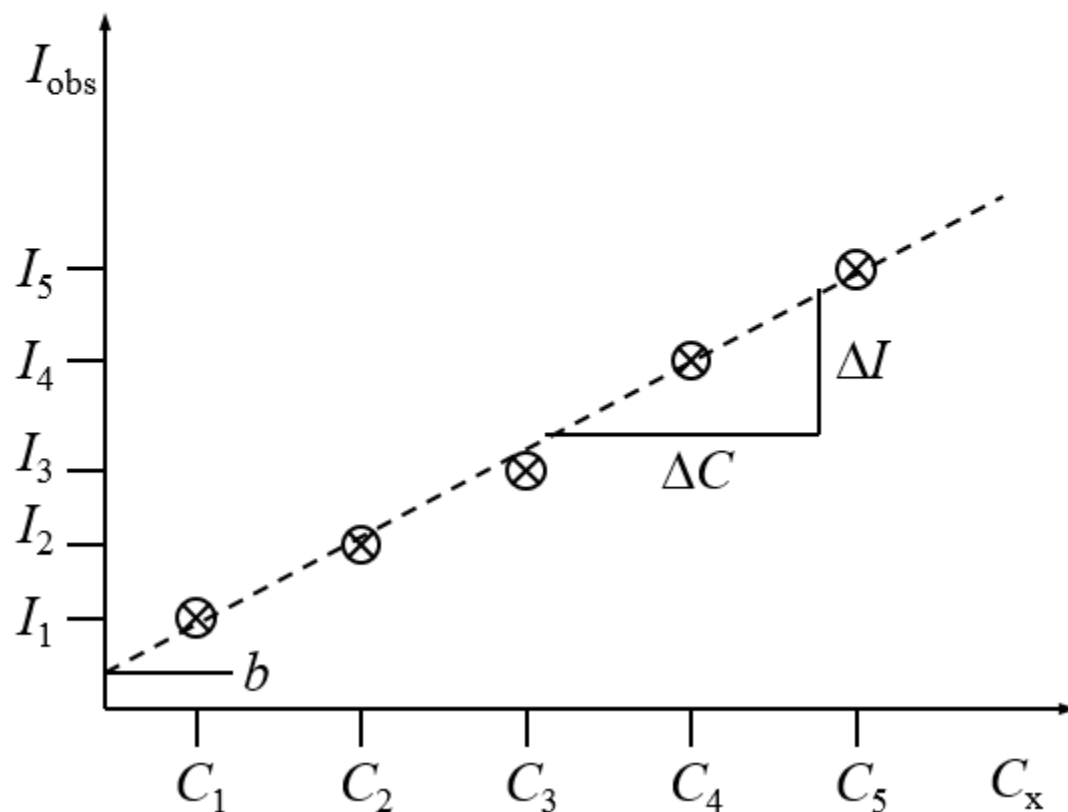
- Regression is a widely used evaluation technique for chemical analysis.
- Regression is statistically based.
- Only for linear regression a explicit solution is known.
- The calculation rules are complex.
- The regression is an additional source of uncertainty.

Typical chemical measurement



Slide courtesy of R. Kessel

Relation between indication and concentration



Assumption:
linear relation !

$$m = \frac{\Delta I}{\Delta C} = ?$$

$$b = ?$$

$$m = \frac{\sum_{i=1}^n (x_i - \bar{x}) \cdot (y_i - \bar{y})}{\sum_{i=1}^n (x_i - \bar{x})^2}$$

$$b = \bar{y} - m \cdot \bar{x}$$

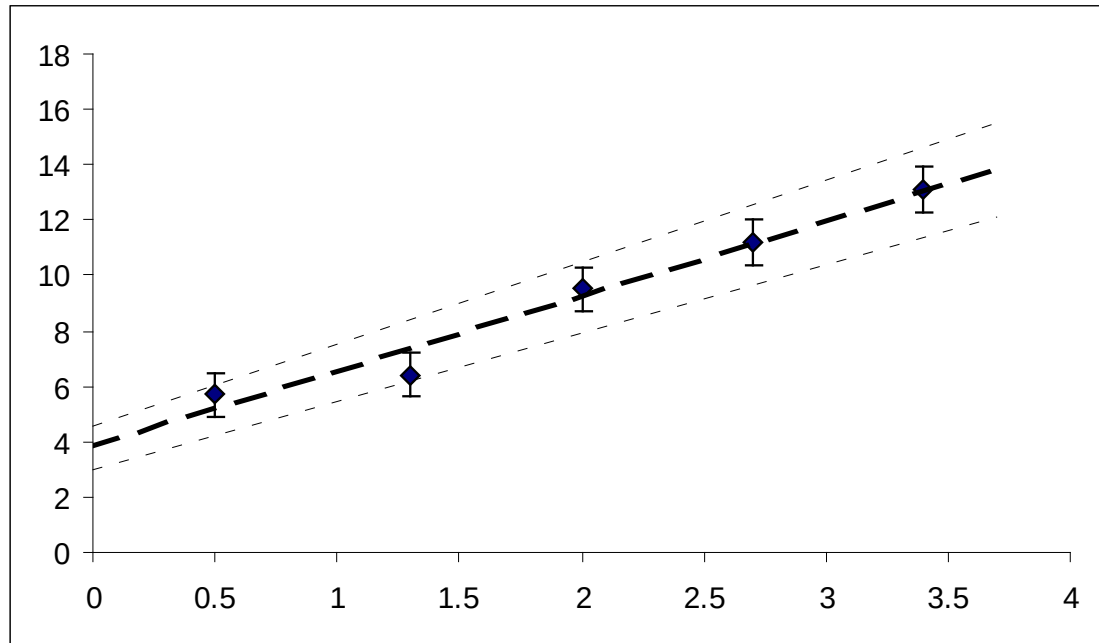
$$\bar{x} = \frac{1}{n} \cdot \sum_{i=1}^n x_i$$

$$\bar{y} = \frac{1}{n} \cdot \sum_{i=1}^n y_i$$

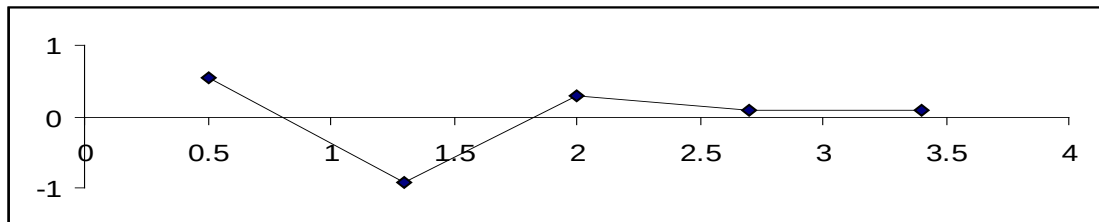
x_i	y_i	$s(y_i)$
0.5	5.7	0.8
1.3	6.4	0.8
2	9.5	0.8
2.7	11.2	0.8
3.4	13.1	0.8

Example data:

Linear regression



Function:



Residuals:

Uncertainty Budgets

Quantity	Value	Standard Uncertainty	Uncertainty Contribution	Index
y ₁	5.700	0.800	-0.23	42.2 %
y ₂	6.400	0.800	-0.10	8.9 %
y ₃	9.500	0.800	$3.1 \cdot 10^{-3}$	0.0 %
y ₄	11.200	0.800	0.11	10.0 %
y ₅	13.100	0.800	0.22	38.9 %
m	2.712	0.351		

Quantity	Value	Standard Uncertainty	Uncertainty Contribution	Index
y ₁	5.700	0.800	0.61	61.2 %
y ₂	6.400	0.800	0.37	22.1 %
y ₃	9.500	0.800	0.15	3.9 %
y ₄	11.200	0.800	-0.060	0.6 %
y ₅	13.100	0.800	-0.27	12.2 %
b	3.811	0.782		

80% of the uncertainty from 2 points!

Highlights from regression analyses

- More than half of the data contribute not significantly to the uncertainty of the parameter.
- The situation is similar, if we add an uncertainty to the x-values.
- The uncertainty of the parameter is independent from the residuals of the fit, which does not agree with the idea of quality statement of the fit.
- The main purpose of the regression is to get a linear relation between measurand and observation.

Guide to the Expression of Uncertainty in Measurement (GUM)

Uncertainty estimation for C & S

Module 6

Authors: K. J. Mathew (LANL)

This Test Method is for the determination of the carbon and sulfur contents in plutonium oxide (PuO_2) powder. The method utilizes an induction furnace purged with oxygen for combustion of the sample. Carbon dioxide and sulfur dioxide produced by the combustion are swept into absorption cells and quantified by infrared absorption spectrophotometers.

The overall uncertainty achieved by this analytical technique is related to the concentration of carbon and sulfur in the sample. Often, samples in the weight range of 0.1 to 1 grams are analyzed. Typical MOX PuO_2 powder contains low concentrations of both carbon and sulfur. Annex A1 provides precision and bias data for both carbon and sulfur. These data were generated at two different analytical facilities as part of routine sample analysis. Carbon abundances can be determined with relative uncertainties of ~ 6 to 8% (expanded uncertainties at the 95% level of confidence with a coverage factor $k = 2$) and sulfur abundances can be determined with relative uncertainties of ~ 15 to 20% (expanded uncertainties at the 95% level of confidence with a coverage factor $k = 2$). At 200 mg sample size, the limit of detection, LOD for carbon and sulfur are, $\sim 12\ \mu\text{g/g}$ and $10\ \mu\text{g/g}$, respectively.

Date	Measured C (ppm)	Certified C (ppm)	% Recovery	Rel. Diff., %	Average % Recovery	(Average % Recovery) Rel. Std Dev., %	Average Rel. Diff., %
10/15/2012	48	49	98.0	-2.04	98.9	6.13	-1.1
10/15/2012	46.6	49	95.1	-4.90			
10/15/2012	52.3	49	106.7	6.73			
10/15/2012	44.9	49	91.6	-8.37			
10/15/2012	50.5	49	103.1	3.06			
10/22/2012	134	137	97.8	-2.19	101.5	5.09	1.5
10/22/2012	144	137	105.1	5.11			
10/25/2012	129	137	94.2	-5.84	94.2	1.90	-5.8
10/25/2012	132	137	96.4	-3.65			
10/25/2012	129	137	94.2	-5.84			
10/25/2012	126	137	92.0	-8.03			
10/30/2012	308	280	110.0	10.00	104.3	7.91	4.3
10/30/2012	263	280	93.9	-6.07			
10/30/2012	284	280	101.4	1.43			
10/30/2012	313	280	111.8	11.79			
10/30/2012	52.2	49	106.5	6.53	105.2	1.78	5.2
10/30/2012	50.9	49	103.9	3.88			
11/1/2012	207	195	106.2	6.15	99.7	5.74	-0.3
11/1/2012	190	195	97.4	-2.56			
11/1/2012	186	195	95.4	-4.62			
11/1/2012	131	137	95.6	-4.38	97.3	4.39	-2.7
11/1/2012	131	137	95.6	-4.38			
11/1/2012	136	137	99.3	-0.73			
11/1/2012	128	137	93.4	-6.57			
11/1/2012	130	137	94.9	-5.11			
11/1/2012	144	137	105.1	5.11			
11/28/2012	166	160	103.8	3.75	104.1	0.42	4.1
11/28/2012	167	160	104.4	4.38			
11/28/2012	153	137	111.7	11.68	102.0	7.18	2.0
11/28/2012	128	137	93.4	-6.57			
11/28/2012	147	137	107.3	7.30			
11/28/2012	135	137	98.5	-1.46			
11/28/2012	136	137	99.3	-0.73			
1/7/2013	273	280	97.5	-2.50	98.1	1.05	-1.9
1/7/2013	278	280	99.3	-0.71			
1/7/2013	273	280	97.5	-2.50			
1/18/2013	291	280	103.9	3.93	107.0	3.70	7.0
1/18/2013	292	280	104.3	4.29			
1/18/2013	300	280	107.1	7.14			
1/18/2013	315	280	112.5	12.50			
1/24/2013	287	280	102.5	2.50	105.3	1.93	5.3
1/24/2013	297	280	106.1	6.07			
1/24/2013	296	280	105.7	5.71			
1/24/2013	292	280	104.3	4.29			
1/24/2013	289	280	103.2	3.21			
1/24/2013	303	280	108.2	8.21			
1/24/2013	299	280	106.8	6.79			

Combining accuracy and precision: Example C & S Standard

Precision & Accuracy Statistics from LANL (C Standards)

Date	Measured C (ppm)	Certified C (ppm)	% Recovery	Rel. Diff., %	Average % Recovery	(Average % Recovery) Rel. Std Dev., %	Average Rel. Diff., %
9/26/2014	1.50%	1.47%	102.0	2.04	99.8	2.97	-0.2
9/26/2014	19.22	19.05	100.9	0.89			
9/26/2014	18.37	19.05	96.4	-3.57			
10/1/2014	1.47%	1.47%	100.3	0.32	100.8	0.70	0.8
10/1/2014	1.49%	1.47%	101.0	1.02			
10/1/2014	1.50%	1.47%	101.9	1.95			
10/1/2014	1.47%	1.47%	100.2	0.24			
10/1/2014	1.48%	1.47%	100.5	0.51			
10/1/2014	17.21%	17.92%	96.0	-3.96	96		-3.96
10/1/2014	18.88%	19.05%	99.1	-0.89	99.1		-0.89
3/10/2015	1.44%	1.47%	98.2	-1.76	98.1	0.66	-1.9
3/10/2015	1.43%	1.47%	97.3	-2.69			
3/10/2015	1.44%	1.47%	98.1	-1.88			
3/10/2015	1.45%	1.47%	98.9	-1.11			
8/18/2015	273	280	97.5	-2.50	100.4	3.67	0.4
8/18/2015	282	280	100.7	0.71			
8/18/2015	288	280	102.9	2.86			
8/18/2015	294	280	105.0	5.00			
8/18/2015	269	280	96.1	-3.93			
8/18/2015	158	160	98.8	-1.25	98.8		-1.25
5/5/2016	305	280	108.9	8.93	106.9	1.90	6.9
5/5/2016	296	280	105.7	5.71			
5/5/2016	293	280	104.6	4.64			
5/5/2016	303	280	108.2	8.21			
8/4/2016	295	280	105.4	5.36	101.2	3.34	1.2
8/4/2016	279	280	99.6	-0.36			
8/4/2016	273	280	97.5	-2.50			
8/4/2016	286	280	102.1	2.14			
					Min	0.10	-5.84
					Max	7.91	8.65
					Average	2.88	1.00

Precision & Accuracy
Statistics from LANL (C
Standards)

Date	Measured S (ppm)	Certified S (ppm)	% Recovery	Rel. Diff., %	Average % Recovery	(Average % Recovery) Rel. Std Dev., %	Average Rel. Diff., %
10/30/2012	85.5	80	106.9	6.88	108.79	2.60	8.79
10/30/2012	89.4	80	111.8	11.75			
10/30/2012	86.2	80	107.8	7.75			
1/7/2013	14	13	107.7	7.69	104.62	6.71	4.62
1/7/2013	14.2	13	109.2	9.23			
1/7/2013	12.6	13	96.9	-3.08			
1/18/2013	86.5	80	108.1	8.13	110.31	1.72	10.31
1/18/2013	87.9	80	109.9	9.88			
1/18/2013	89.7	80	112.1	12.13			
1/18/2013	88.9	80	111.1	11.13			
1/31/2013	78.1	80	97.6	-2.38	97.38	4.81	-2.63
1/31/2013	80.7	80	100.9	0.88			
1/31/2013	80.4	80	100.5	0.50			
1/31/2013	72.4	80	90.5	-9.50			
2/7/2013	89.5	80	111.9	11.88	104.75	10.08	4.75
2/7/2013	78.1	80	97.6	-2.38			
3/15/2013	75.4	80	94.3	-5.75	101.56	7.11	1.56
3/15/2013	79.2	80	99.0	-1.00			
3/15/2013	88.9	80	111.1	11.13			
3/15/2013	81.5	80	101.9	1.88			
4/24/2013	91.1	80	113.9	13.88	104.31	8.24	4.31
4/24/2013	75.1	80	93.9	-6.13			
4/24/2013	84.8	80	106.0	6.00			
4/24/2013	82.8	80	103.5	3.50			
4/24/2013	25.6	23	111.3	11.30	111.3		11.30
					Min	1.72	-2.63
					Max	10.08	11.30
					Average	5.90	5.38

Precision & Accuracy
Statistics from LANL (S
Standards)

Date	Measured C (wt %)	Certified C (wt %)	% Recovery	Rel. Diff., %	Average % Recovery	(Average % Recovery) Rel. Std Dev., %	Average Rel. Diff., %
6/9/2016	1.36	1.38	98.6	-1.45	97.2	13.20	-2.75
6/9/2016	1.55	1.38	112.3	12.32			
6/9/2016	1.32	1.38	95.7	-4.35			
6/9/2016	1.51	1.38	109.4	9.42			
6/9/2016	1.64	1.38	118.8	18.84			
6/9/2016	1.27	1.38	92.0	-7.97			
6/9/2016	1.35	1.38	97.8	-2.17			
6/9/2016	1.11	1.38	80.4	-19.57			
6/9/2016	1.09	1.38	79.0	-21.01			
6/9/2016	1.22	1.38	88.4	-11.59			
6/29/2016	1.47	1.38	106.5	6.52	100.5	5.24	0.48
6/29/2016	1.35	1.38	97.8	-2.17			
6/29/2016	1.34	1.38	97.1	-2.90			
8/9/2016	1.38	1.38	100.0	0.00	97.5	3.59	-2.54
8/9/2016	1.31	1.38	94.9	-5.07			
8/9/2016	1.38	1.38	100.0	0.00			
8/16/2016	1.46	1.38	105.8	5.80	97.4	10.68	-2.61
8/16/2016	1.21	1.38	87.7	-12.32			
8/16/2016	1.54	1.38	111.6	11.59			
8/16/2016	1.28	1.38	92.8	-7.25			
8/16/2016	1.23	1.38	89.1	-10.87			
9/9/2016	1.47	1.38	106.5	6.52	104.6	3.34	4.64
9/9/2016	1.48	1.38	107.2	7.25			
9/9/2016	1.41	1.38	102.2	2.17			
9/9/2016	1.48	1.38	107.2	7.25			
9/9/2016	1.38	1.38	100.0	0.00			
					Min	1.02	-8.70
					Max	13.20	7.25
					Average	3.87	-0.78

Precision & Accuracy
Statistics from SRNL (C
Standards)

Date	Measured S (wt %)	Certified S (wt %)	% Recovery	Rel. Diff., %	Average % Recovery	(Average % Recovery) Rel. Std Dev., %	Average Rel. Diff., %
6/9/2016	1.03	1.36	75.7	-24.26	108.6	18.28	8.62
6/9/2016	1.79	1.36	131.6	31.62			
6/9/2016	1.69	1.36	124.3	24.26			
6/9/2016	1.85	1.36	136.0	36.03			
6/9/2016	1.15	1.36	84.6	-15.44			
6/9/2016	1.36	1.36	100.0	0.00			
6/9/2016	1.49	1.36	109.6	9.56			
6/9/2016	1.55	1.36	114.0	13.97			
6/9/2016	1.38	1.36	101.5	1.47			
6/9/2016	1.47	1.36	108.1	8.09			
6/9/2016	1.49	1.36	109.6	9.56			
6/29/2016	1.34	1.36	98.5	-1.47	99.0	4.43	-0.98
6/29/2016	1.29	1.36	94.9	-5.15			
6/29/2016	1.41	1.36	103.7	3.68			
8/9/2016	1.59	1.36	116.9	16.91	112.7	3.63	12.75
8/9/2016	1.51	1.36	111.0	11.03			
8/9/2016	1.50	1.36	110.3	10.29			
8/16/2016	1.39	1.36	102.2	2.21	104.0	6.51	3.97
8/16/2016	1.32	1.36	97.1	-2.94			
8/16/2016	1.53	1.36	112.5	12.50			
8/16/2016	1.48	1.36	108.8	8.82			
8/16/2016	1.35	1.36	99.3	-0.74			
9/9/2016	1.46	1.36	107.4	7.35	113.1	5.56	13.09
9/9/2016	1.54	1.36	113.2	13.24			
9/9/2016	1.64	1.36	120.6	20.59			
9/9/2016	1.47	1.36	108.1	8.09			
9/9/2016	1.58	1.36	116.2	16.18			
					Min	0.00	-8.46
					Max	18.28	18.01
					Average	5.46	2.56

Precision & Accuracy
Statistics from SRNL (C
Standards)

Date	Measured S (wt %)	Certified S (wt %)	% Recovery	Rel. Diff., %	Average % Recovery	(Average % Recovery) Rel. Std Dev., %	Average Rel. Diff., %
6/9/2016	1.03	1.36	75.7	-24.26	108.6	18.28	8.62
6/9/2016	1.79	1.36	131.6	31.62			
6/9/2016	1.69	1.36	124.3	24.26			
6/9/2016	1.85	1.36	136.0	36.03			
6/9/2016	1.15	1.36	84.6	-15.44			
6/9/2016	1.36	1.36	100.0	0.00			
6/9/2016	1.49	1.36	109.6	9.56			
6/9/2016	1.55	1.36	114.0	13.97			
6/9/2016	1.38	1.36	101.5	1.47			
6/9/2016	1.47	1.36	108.1	8.09			
6/9/2016	1.49	1.36	109.6	9.56			
6/29/2016	1.34	1.36	98.5	-1.47	99.0	4.43	-0.98
6/29/2016	1.29	1.36	94.9	-5.15			
6/29/2016	1.41	1.36	103.7	3.68			
8/9/2016	1.59	1.36	116.9	16.91	112.7	3.63	12.75
8/9/2016	1.51	1.36	111.0	11.03			
8/9/2016	1.50	1.36	110.3	10.29			
8/16/2016	1.39	1.36	102.2	2.21	104.0	6.51	3.97
8/16/2016	1.32	1.36	97.1	-2.94			
8/16/2016	1.53	1.36	112.5	12.50			
8/16/2016	1.48	1.36	108.8	8.82			
8/16/2016	1.35	1.36	99.3	-0.74			
9/9/2016	1.46	1.36	107.4	7.35	113.1	5.56	13.09
9/9/2016	1.54	1.36	113.2	13.24			
9/9/2016	1.64	1.36	120.6	20.59			
9/9/2016	1.47	1.36	108.1	8.09			
9/9/2016	1.58	1.36	116.2	16.18			
					Min	0.00	-8.46
					Max	18.28	18.01
					Average	5.46	2.56

Precision & Accuracy
Statistics from SRNL (S
Standards)

Uncertainty in trace element contents

Two Pu materials –

- chloride line and nitrate line
- Trace element contents
 - High priority elements (Al, Ca, Co, Cr, Fe, Mo, Ni, Ti, V, W, Zr)
 - Moderate priority elements (B, Cu, Ga, La, Li, Mg, Mn, Si, Ta)
 - Low priority elements (Be, P)
- Previous analytical effort was unable to characterize all high priority elements
- Three units each (from each material) were re-analyzed
- Two different QC standards analyzed (16V and a Blind QC)
- Analysis performed in different runs (sequences) consisting of
 - Blanks, Calibration Standards, Matrix Spike, QCs

Uncertainty in trace element contents

JY ICP-AES																		
JY040717A																		
CUSTOMER REPORT																		
Analyte																		
	Run-1						Run-2						Run-3					
Name	unit-44	GUM	unit-73	GUM	unit-111	GUM	unit-44	GUM	unit-73	GUM	unit-111	GUM	unit-44	GUM	unit-73	GUM	unit-111	GUM
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
ALUMINUM	75.0	6.9	74.0	7.7	69.9	7.6	74.2	5.9	70.8	5.5	68.5	6.7	69.8	5.6	72.8	6.7	59.5	5.9
BORON	< 1	N/A	< 1	N/A	< 1	N/A	< 1	N/A	< 1	N/A	< 1	N/A	< 1	N/A	< 1	N/A	< 1	N/A
CALCIUM	180	16	181	15	192	16	181	14	183	14	193	15	191	15	187	15	191	19
CHROMIUM	31.3	4.2	30.2	4.1	29.8	3.7	30.1	4.1	28.3	3.7	28.7	3.8	25.5	3.4	22.7	3.3	23.4	3.4
IRON	214	22	208	19	206	21	200	21	200	22	198	20	220	24	208	20	216	23
MAGNESIUM	15.4	1.3	16.1	1.4	18.3	1.6	14.7	1.6	15.4	1.8	17.4	1.5	12.5	1.4	12.1	1.3	15.1	1.7
MOLYBDENUM	< 2	N/A	< 2	N/A	< 2	N/A	< 2	N/A	< 2	N/A	< 2	N/A	< 2	N/A	< 2	N/A	< 2	N/A
NICKEL	29.9	4.7	29.7	4.6	31.4	4.8	26.6	4.4	25.7	4.4	25.3	4.5	30.9	4.8	28.6	4.6	28.8	4.6
PHOSPHORUS	< 8	N/A	< 8	N/A	8.7	5.5	< 8	N/A	< 8	N/A	< 8	N/A	< 8	N/A	< 8	N/A	< 8	N/A
SILICON	175	17	171	17	177	22	176	18	179	18	174	17	194	20	185	18	190	20
TANTALUM	< 19	N/A	< 19	N/A	< 19	N/A	< 19	N/A	< 19	N/A	< 19	N/A	< 19	N/A	< 19	N/A	< 19	N/A
TUNGSTEN	214	29	186	24	129	16	208	25	191	23	125	16	242	29	219	27	129	18
Mo	5.1	0.5	previous (ICPMS)															

Uncertainty in trace element contents

ICP-MS																								
AG042017A																								
CUSTOMER REPORT																								
MEAN DATA																								
	DAY1												DAY2											
Element	unit-44	GUM	unit-73	GUM	Unit-111	GUM	unit-44	GUM	unit-73	GUM	Unit-111	GUM	unit-44	GUM	unit-73	GUM	Unit-111	GUM	unit-44	GUM	unit-73	GUM	Unit-111	GUM
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
BERYLLIUM	0.66	0.33	0.76	0.55	0.27	0.19	0.10	0.21	0.23	0.33	0.48	0.29	0.97	0.72	0.98	0.26	0.97	0.50	0.99	0.60	0.41	0.49	0.17	0.43
COBALT	0.230	0.05	0.193	0.070	0.226	0.03	0.205	0.04	0.210	0.09	0.210	0.05	0.137	0.03	0.209	0.066	0.156	0.05	0.174	0.039	0.230	0.027	0.156	0.046
COPPER	10.37	0.55	10.78	0.29	10.77	0.69	10.80	0.55	10.55	0.27	10.79	0.53	8.51	0.43	8.38	0.16	8.95	0.20	8.88	0.35	9.26	0.46	9.34	0.57
GALLIUM	14.28	0.98	14.16	0.29	13.63	0.94	13.73	0.26	13.67	0.94	13.81	0.29	11.86	0.56	11.67	0.38	12.0	1.1	11.92	0.40	11.7	1.1	11.42	0.65
LANTHANUM	0.080	0.030	0.071	0.02	0.060	0.06	0.052	0.05	0.087	0.03	0.058	0.04	0.069	0.02	0.090	0.06	0.055	0.02	0.062	0.028	0.069	0.014	0.074	0.014
LITHIUM	< 0.5	N/A	< 0.5	N/A	< 0.4	N/A	< 0.4	N/A	< 0.4	N/A	< 0.4	N/A	< 0.4	N/A	< 0.4	N/A	< 0.4	N/A	< 0.4	N/A	< 0.4	N/A	< 0.4	N/A
MANGANESE	2.52	0.12	3.45	0.28	2.474	0.07	3.11	0.11	2.58	0.18	3.43	0.35	2.54	0.23	3.18	0.16	2.90	0.11	3.32	0.54	2.93	0.44	3.27	0.63
VANADIUM	< 0.6	N/A	< 0.6	N/A	< 0.6	N/A	< 0.6	N/A	< 0.6	N/A	< 0.6	N/A	0.58	0.51	< 0.5	N/A	0.58	0.38	0.64	0.12	< 0.5	N/A	< 0.5	N/A
ZIRCONIUM	1.99	0.15	1.96	0.23	1.719	0.1	1.92	0.11	1.83	0.29	1.91	0.10	1.63	0.23	1.69	0.49	1.497	0.09	1.57	0.25	1.59	0.19	1.59	0.23
Vanadium	4	1.2	previous																					

Uncertainty in trace element contents

Analyte		Measured Content	Std Dev	%RD (Measured Value)	Rel Uncertainty (% , 95 % CL)
Al	Known QC	172.9	2.9	-1.75	4.85
	Blind QC	23.8	2.2	-11.8	30.1
Ca	Known QC	< 0.8			
	Blind QC	< 0.8			
Cr	Known QC	234.6	12.4	2.45	11.69
	Blind QC	29.6	3.3	13.8	35.4
Fe	Known QC	277.5	11.1	2.01	8.98
	Blind QC	405.2	13.9	14.79	30.4
Mo	Known QC	< 2			
	Blind QC	< 2			
Ni	Known QC	201.6	10.7	3.93	13.22
	Blind QC	47.4	3.5	7.8	21.6
P	Known QC	23.7	3.4		29.07
	Blind QC	8.2	1.1		25.5
Si	Known QC	17.4	1.7	-8.18	25.47
	Blind QC	102.1	6.3	-8.8	21.6
Ti	Known QC	2.3	0.1	-1.74	3.51
	Blind QC				
W	Known QC	10.6	0.7	-11.88	27.35
	Blind QC	53.7	3.4	-0.5	12.5

Accuracy and precision of QC standards by ICP-AES

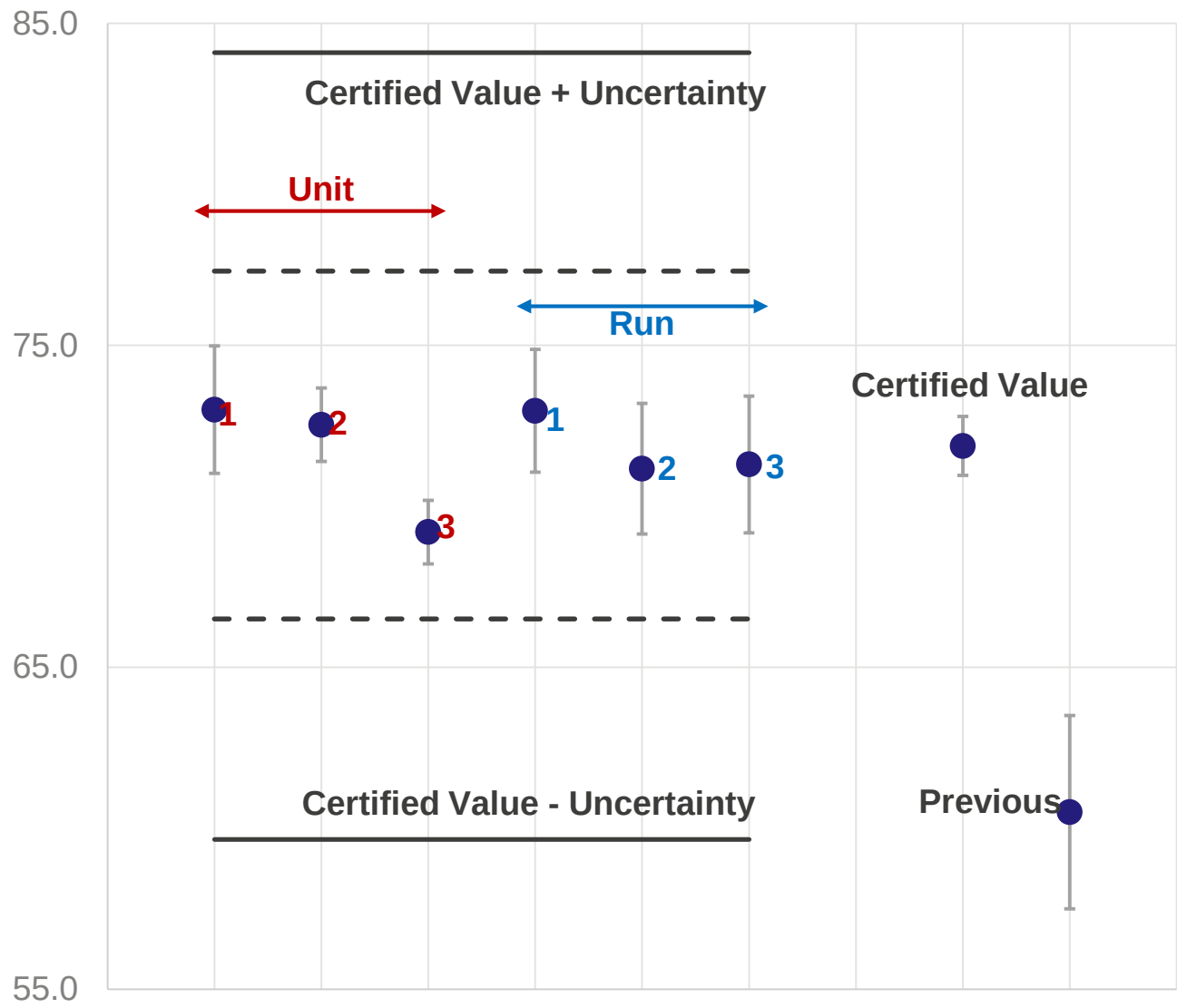
Uncertainty in trace element contents

Analyte		Measured Content	Std Dev	%RD (Measured Value)	Rel Uncertainty (% , 95 % CL)
Be	Known QC	0.27	0.10	2.00	71.31
	Blind QC	2.32	0.24	-10.7	29.5
Co	Known QC	0.81	0.11		27.46
	Blind QC	0.59	0.06		18.7
Cu	Known QC	25.6	2.6	3.97	22.18
	Blind QC	9.7	1.4	-20.2	49.4
Ga	Known QC	468.1	46.5		19.86
	Blind QC	6325.0	482.0		15.2
Mn	Known QC	17.5	1.5	12.67	30.53
	Blind QC	7.72	0.41	4.3	13.6
Zr	Known QC	2.46	0.23	-9.01	25.96
	Blind QC	0.22	0.04	-6.0	34.3

Accuracy and precision of QC standards by ICP-MS

Uncertainty in trace element contents

RM1-- ICP-AES, Analyte: Al

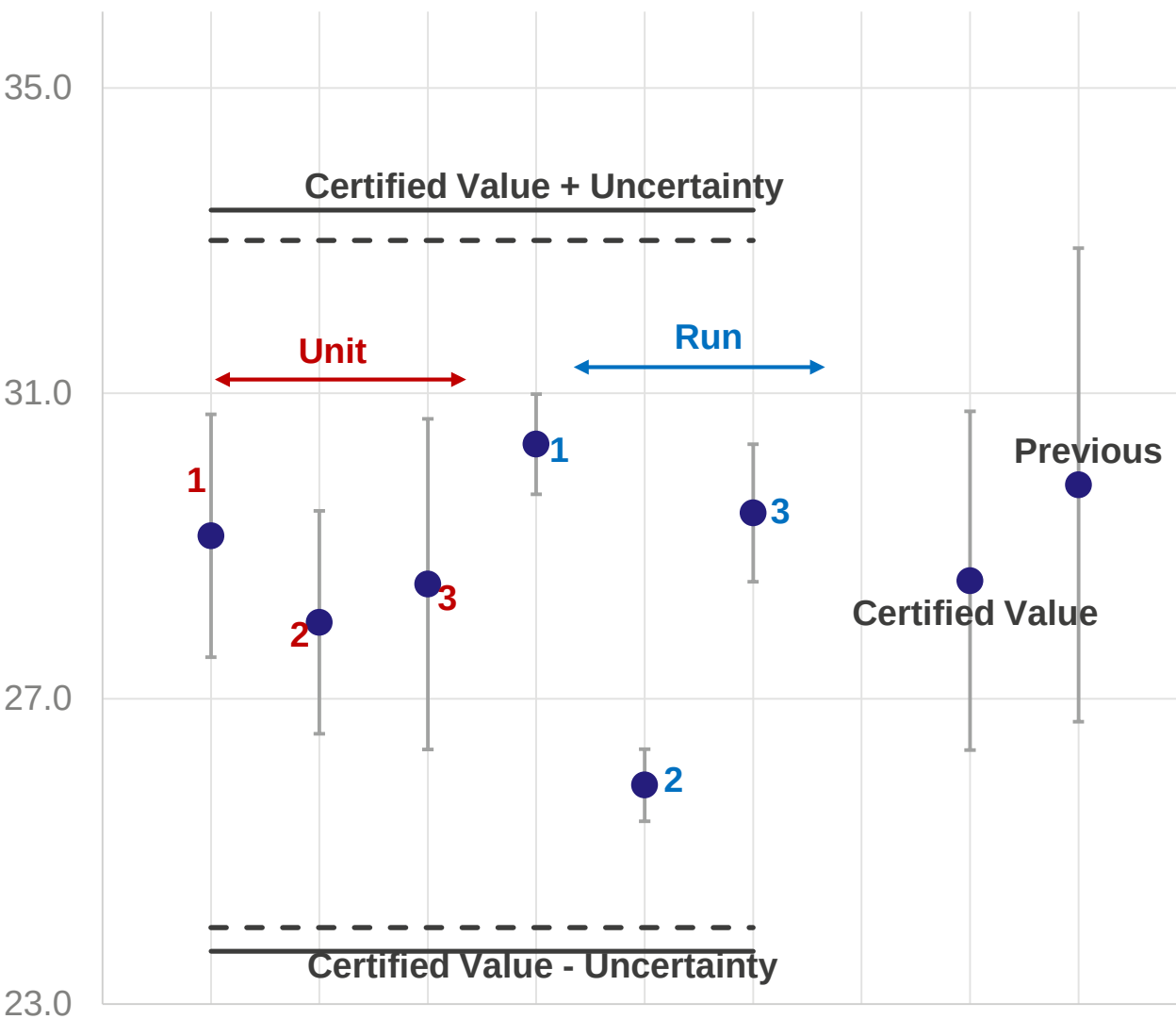


Agreement with previously reported value and between ICP-AES & ICP-MS requires higher uncertainty than calculated by GUM. (period-to-period and instrument-to-instrument) differences

There are unit-to-unit differences that would have to be included into models for uncertainty estimation

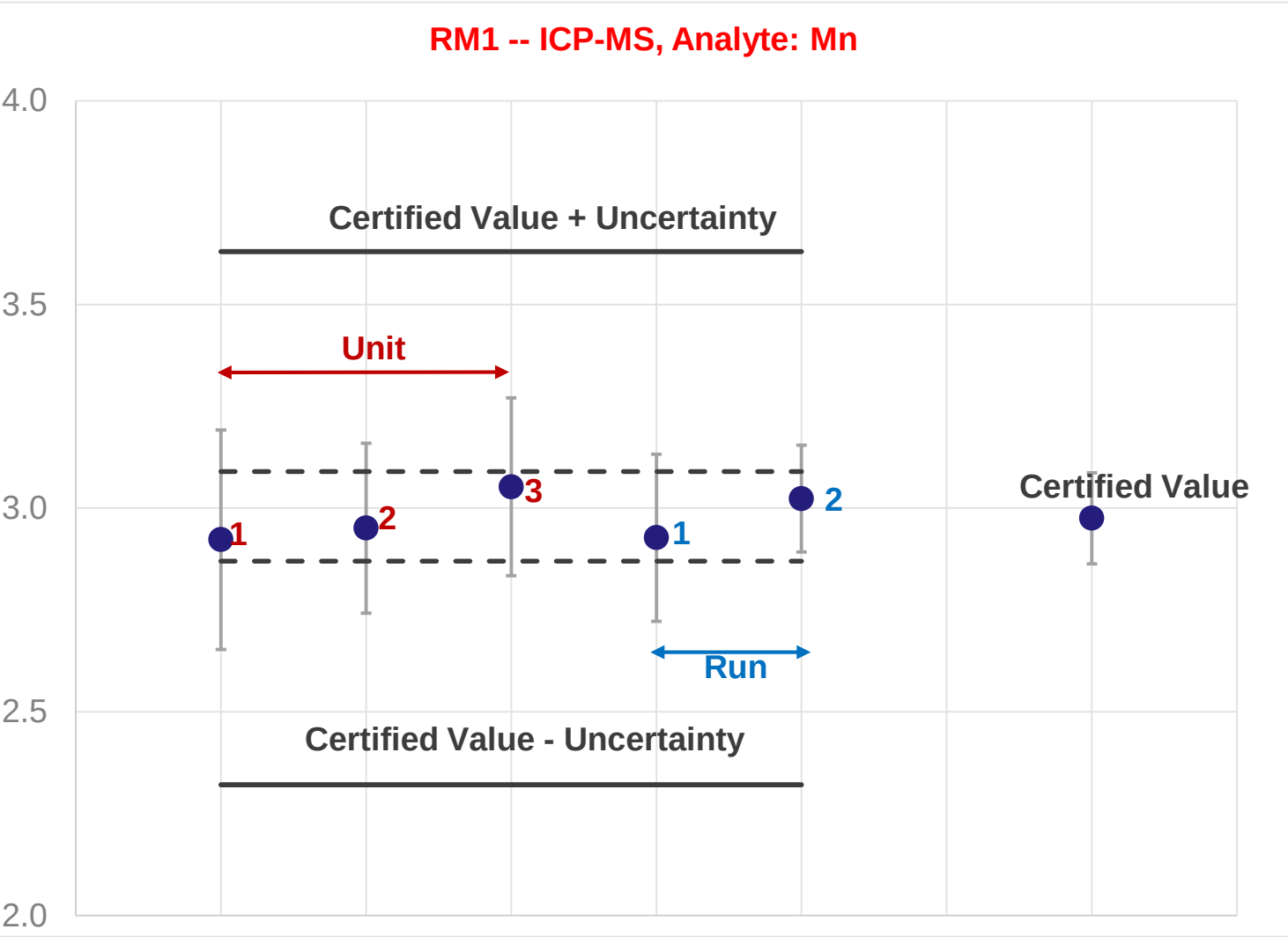
Uncertainty in trace element contents

RM1 -- ICP-AES, Analyte: Ni



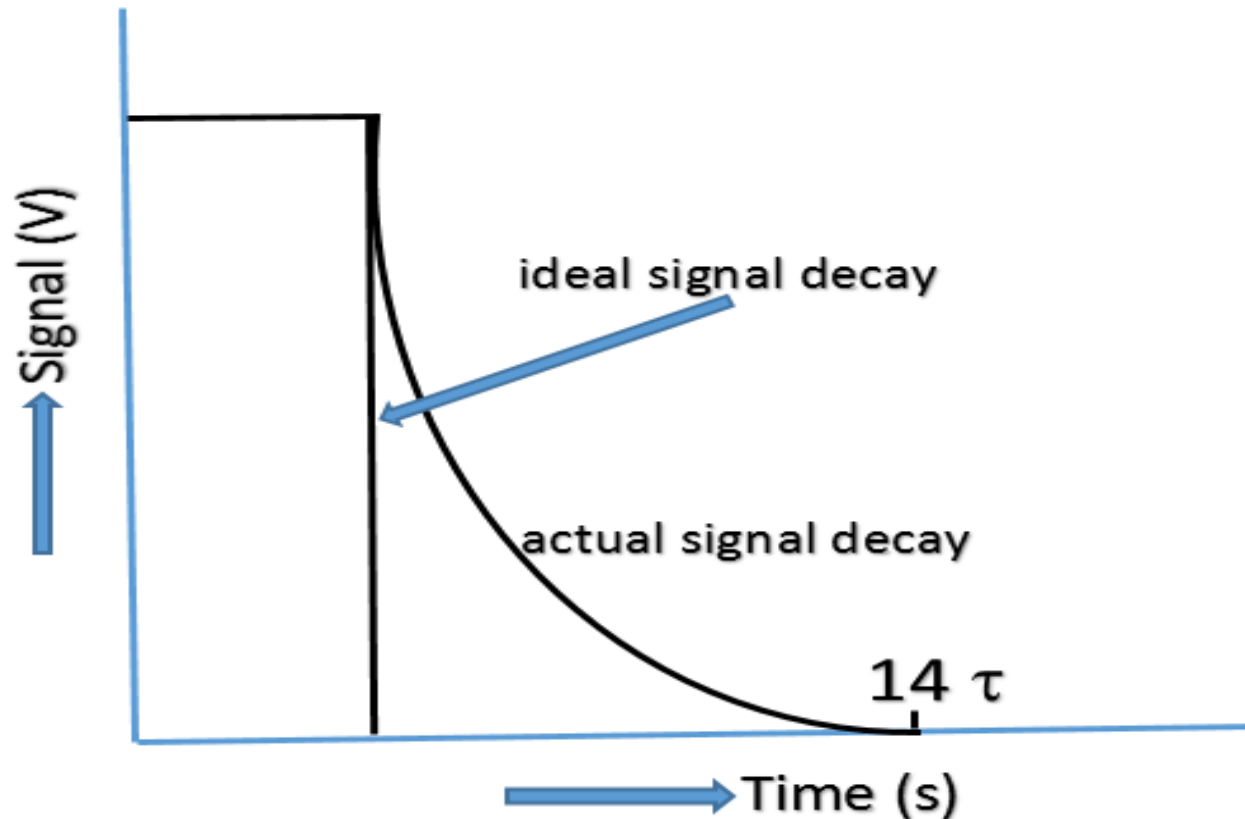
There are run-to-run differences that would have to be included into models for uncertainty estimation

Uncertainty in trace element contents



GUM uncertainty is seriously underestimated (whereas the uncertainty estimate obtained by combining accuracy and precision of the QC standard is a more conservative estimate of the actual uncertainty)

Amplifier Decay Characteristics & Isotope Ratio Measurements



Ideal & Real Amplifiers

Amplifier Decay Characteristics & Isotope Ratio Measurements

- The characteristic time of the amp circuit

$$\tau = R \bullet C$$

R = resistance,

C = Capacitance

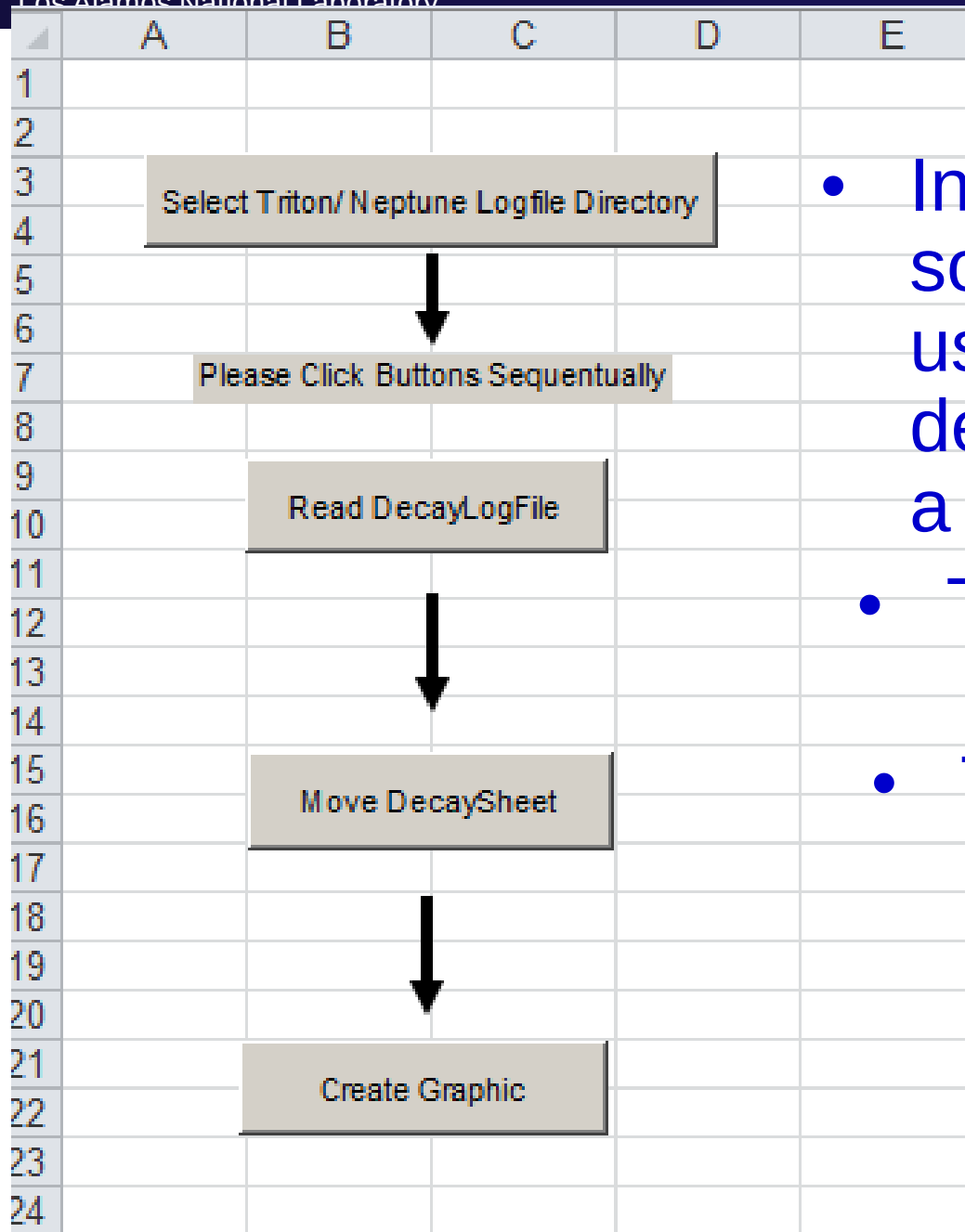
- For $10^{11} \Omega$ amplifiers, $\tau = 0.1$ s.
- In 1.4 s (or so) the signal should be zero

!! assumes a perfect world !!

Line	Ampl No.	Date	Resistor [Ohm]	Type	Usable	Offset [Hz]	Baseline [V]	Baseline Date	Gain	Gain Date	lamp [A]	Corr Dac	Decay Dac	C Cup [F]	C In [F]	C Total [F]	R Cup [Ohm]	R In [Ohm]	R Total [Ohm]	UFC Rate [Hz/V]	Temperature [Deg. C]
1	1	12/7/2016 11:52:24 AM	1.000e+011	CAMP	1	9.993e+002	-0.0004035977975988	12/7/2016 11:41:55 AM	1.0195595793733956	12/7/2016 11:52:24 AM	4.22989e-015	98	255	1.019e-010	1.274e-011	1.147e-010	1.027e+014	1.471e+014	6.049e+013	500.000	36.58
2	2	12/7/2016 11:52:24 AM	1.000e+012	CAMP	1	9.996e+002	-0.0003902993384846	12/7/2016 11:41:55 AM	0.0990254749216267	12/7/2016 11:52:24 AM	6.32235e-016	79	255	1.210e-010	1.325e-011	1.343e-010	9.315e+013	3.435e+014	7.328e+013	500.000	36.58
3	3	12/7/2016 11:52:25 AM	1.000e+012	CAMP	1	1.000e+003	-0.0003627865779602	12/7/2016 11:41:55 AM	0.0996706096582748	12/7/2016 11:52:25 AM	4.89610e-016	86	255	1.122e-010	1.301e-011	1.252e-010	9.123e+013	3.665e+014	7.305e+013	500.000	36.58
4	4	12/7/2016 11:52:25 AM	1.000e+012	CAMP	1	9.989e+002	-0.0003958657608317	12/7/2016 11:41:55 AM	0.1015185016129858	12/7/2016 11:52:25 AM	5.85053e-016	77	255	1.035e-010	1.282e-011	1.164e-010	9.746e+013	3.687e+014	7.708e+013	500.000	36.58
5	5	12/7/2016 11:52:25 AM	1.000e+012	CAMP	1	9.992e+002	-0.0000755798524433	12/7/2016 11:41:55 AM	0.1010753446272135	12/7/2016 11:52:25 AM	3.02116e-016	107	255	1.145e-010	1.310e-011	1.276e-010	1.083e+014	3.285e+014	8.144e+013	500.000	36.58
6	6	12/7/2016 11:52:25 AM	1.000e+011	CAMP	1	9.999e+002	-0.0004068333078451	12/7/2016 11:41:55 AM	1.0145608990397192	12/7/2016 11:52:25 AM	4.50729e-015	105	255	9.927e-011	1.270e-011	1.120e-010	1.044e+014	1.252e+014	5.693e+013	500.000	36.58
7	7	12/7/2016 11:52:25 AM	1.000e+011	CAMP	1	9.991e+002	-0.0002079725932495	12/7/2016 11:41:55 AM	1.0212173281374588	12/7/2016 11:52:25 AM	2.26431e-015	92	255	1.115e-010	1.255e-011	1.240e-010	9.038e+013	2.544e+014	6.668e+013	500.000	36.58
8	8	12/7/2016 11:52:25 AM	1.000e+011	CAMP	1	9.995e+002	-0.0004163765115729	12/7/2016 11:41:55 AM	1.0180996403044060	12/7/2016 11:52:25 AM	4.62488e-015	111	255	1.166e-010	1.251e-011	1.291e-010	1.092e+014	1.157e+014	5.619e+013	500.000	36.58
9	9	12/7/2016 11:52:26 AM	1.000e+011	CAMP	1	9.997e+002	-0.0006299405500376	12/7/2016 11:41:55 AM	1.0207491065925522	12/7/2016 11:52:26 AM	6.46316e-015	89	255	1.060e-010	1.257e-011	1.186e-010	8.442e+013	1.622e+014	5.552e+013	500.000	36.58
10	10	12/7/2016 11:52:26 AM	1.000e+010	CAMP	1	9.997e+002	-0.0002500236739575	7/5/2000 4:49:16 PM	10.0943440413081390	12/7/2016 11:52:26 AM	0.00000e+000	110	255	1.398e-011	1.179e-011	2.577e-011	7.950e+013	1.282e+013	1.104e+013	500.000	36.58

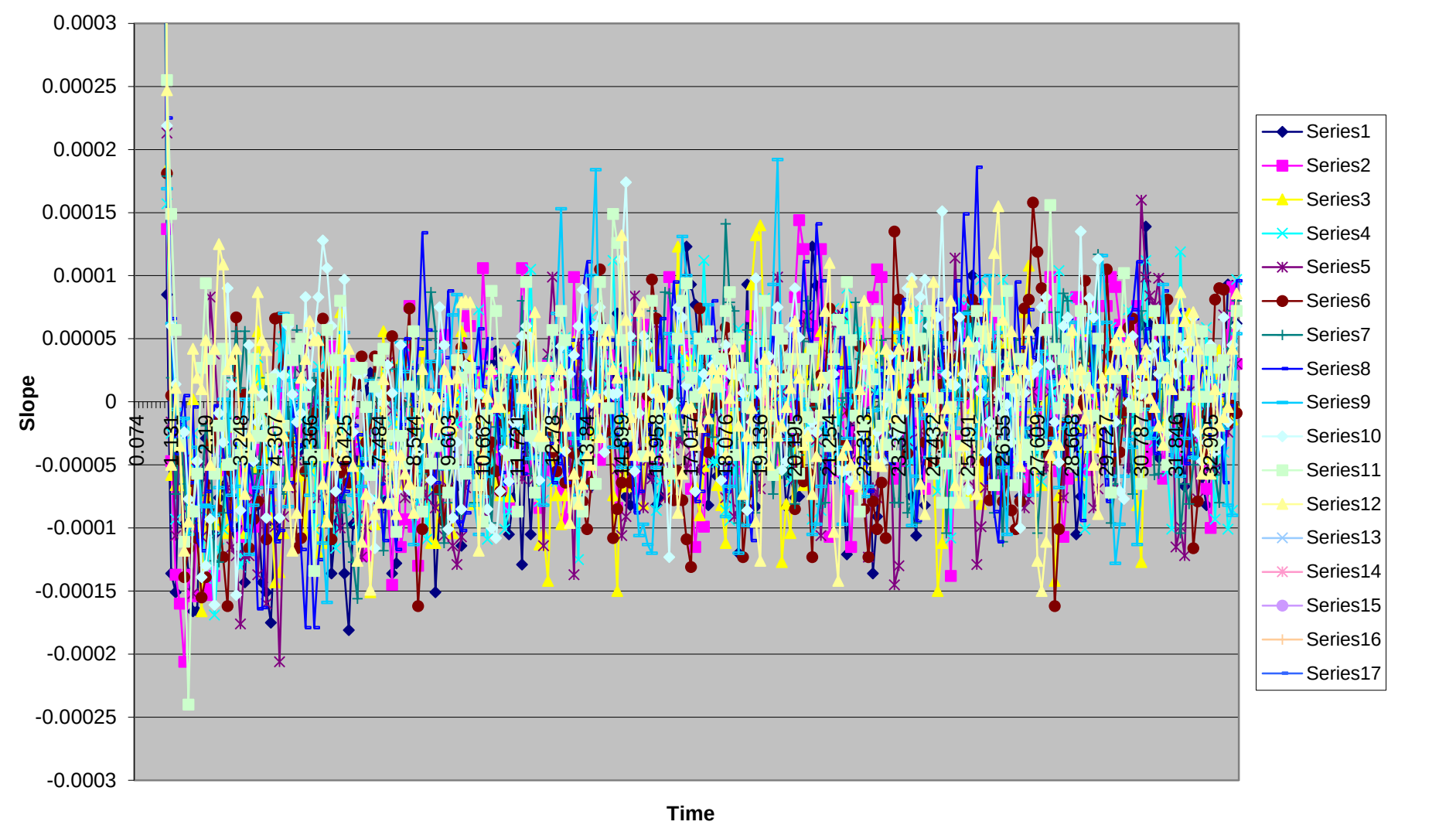
Corr Dac	Decay Dac
98	255
79	255
86	255
77	255
107	255
105	255
92	255
111	255
89	255
110	255

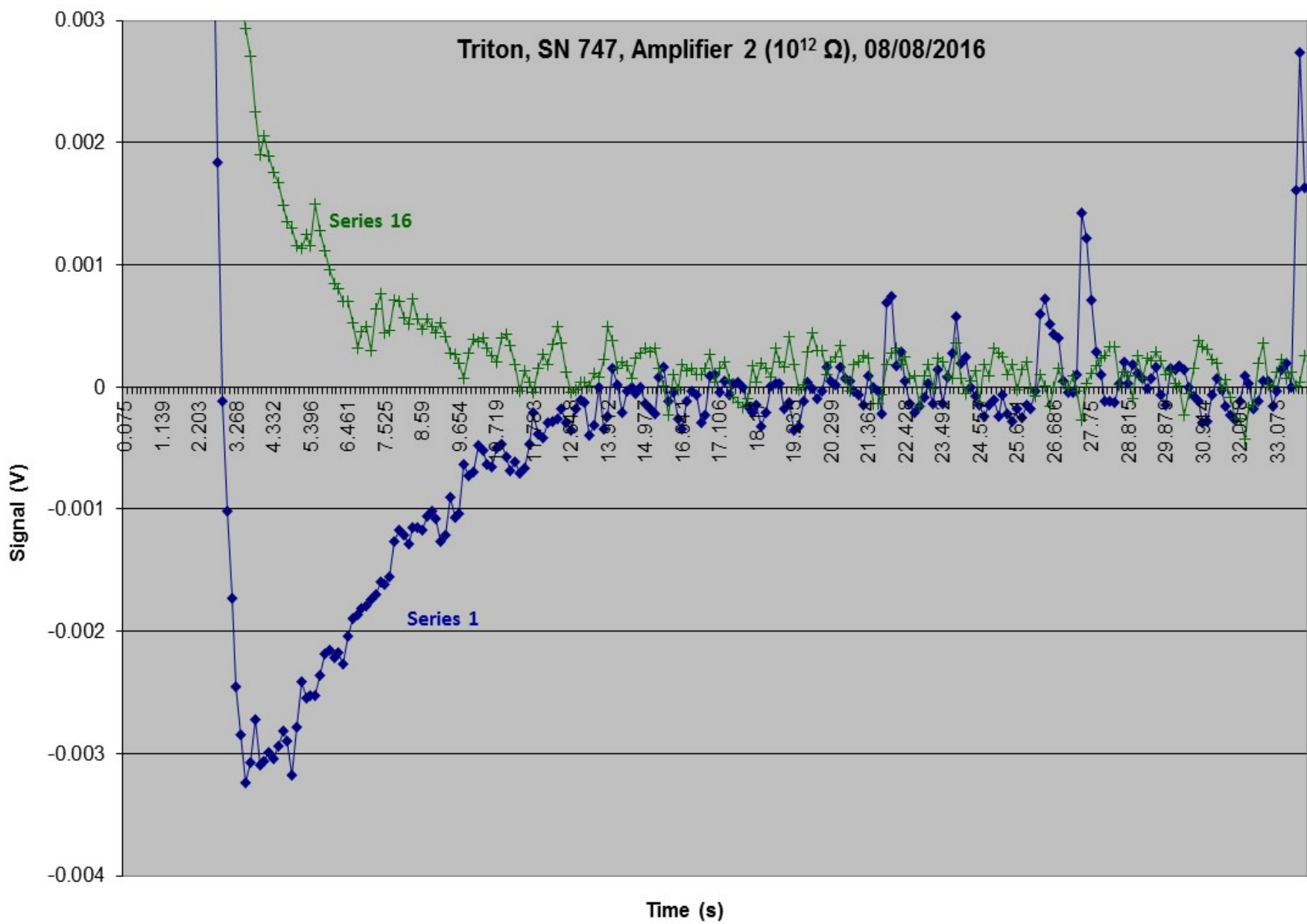
- “Corr Dac” is factory set value based on actual C and R
- “Decay Dac” is observed decay characteristic
- Triton software makes corrections for the difference between the two !!



- In good old days Thermo software allowed the user to create all the decay plots by “clicking” a few buttons
- The new software does not allow that
- There is a workaround (always !!)

Amplifier 4





- Once the right decay series is selected calculate the “Decay Dac” value as follows
- $16 * (\text{series} - 1) - 1$. The values will be 15, 30, 45, 60, ... 255.
- Input the correct “Decay Dac” into the “Executive/Amplifier”

Practical Implications

- Need to add sufficient amount of idle time before measuring the peak-tail intensities or intensities of minor isotopes (as shown below)

TABLE 1 Mass Cycle for MTE

Cup	L2	L1	SEM (or FAR)	H1	H2	Idle Time/ Measurement Time
Step 1	²³⁴ U	²³⁵ U	²³⁶ U	²³⁷ u	²³⁸ U	12 s/16 s
Step 2			²³⁴ U	²³⁵ U		6 s/4 s
Step 3	²³⁴ U - 0.35 u	²³⁵ U - 0.35 u	²³⁶ U - 0.35 u		²³⁸ U - 0.35 u	5 s/ 8 s
Step 4	²³⁴ U + 0.35 u	²³⁵ U + 0.35 u	²³⁶ U + 0.35 u		²³⁸ U + 0.35 u	5 s/8 s
Step 5	²³⁴ U	²³⁵ U	²³⁶ U	²³⁷ u	²³⁸ U	3 s/1 s

Take Away Message !

- Isotope Measurements is not as trivial as it sounds.
- To generate “good” numbers some understanding of the instrument and of the underlying electronics is needed.

Guide to the Expression of Uncertainty in Measurement (GUM)

Turn in the Evaluations !