



HAL
open science

Improvements in the determination of uncertainties of isotopic ratios for uranium samples thanks to IAEA Round Robin

O. Vigneau, N. Arnal, C. Winkelmann

► **To cite this version:**

O. Vigneau, N. Arnal, C. Winkelmann. Improvements in the determination of uncertainties of isotopic ratios for uranium samples thanks to IAEA Round Robin. EWPCS 2019 - European winter conference on plasma spectrochemistry, Feb 2019, Pau, France. cea-02394081

HAL Id: cea-02394081

<https://cea.hal.science/cea-02394081>

Submitted on 24 Feb 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

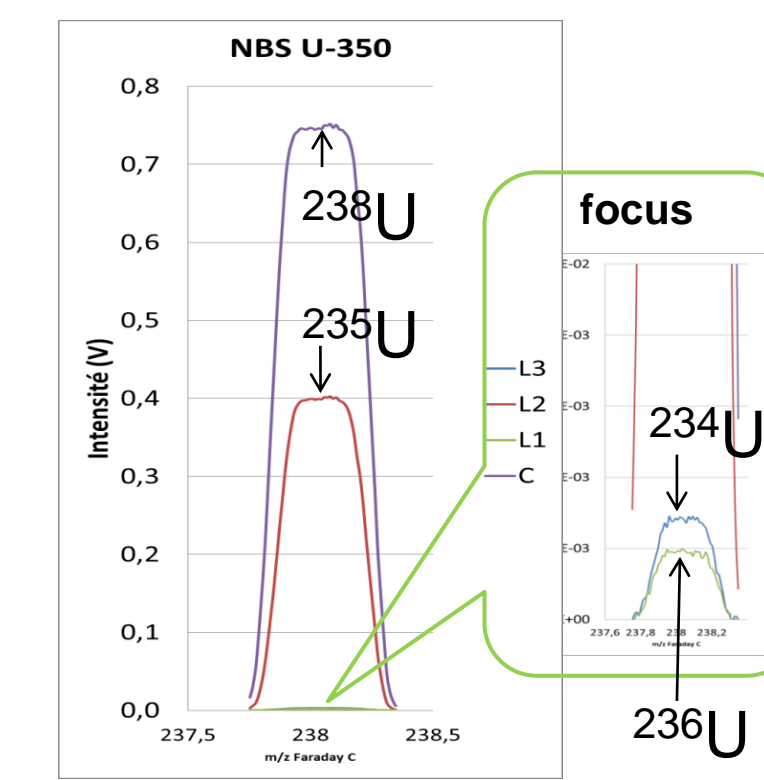
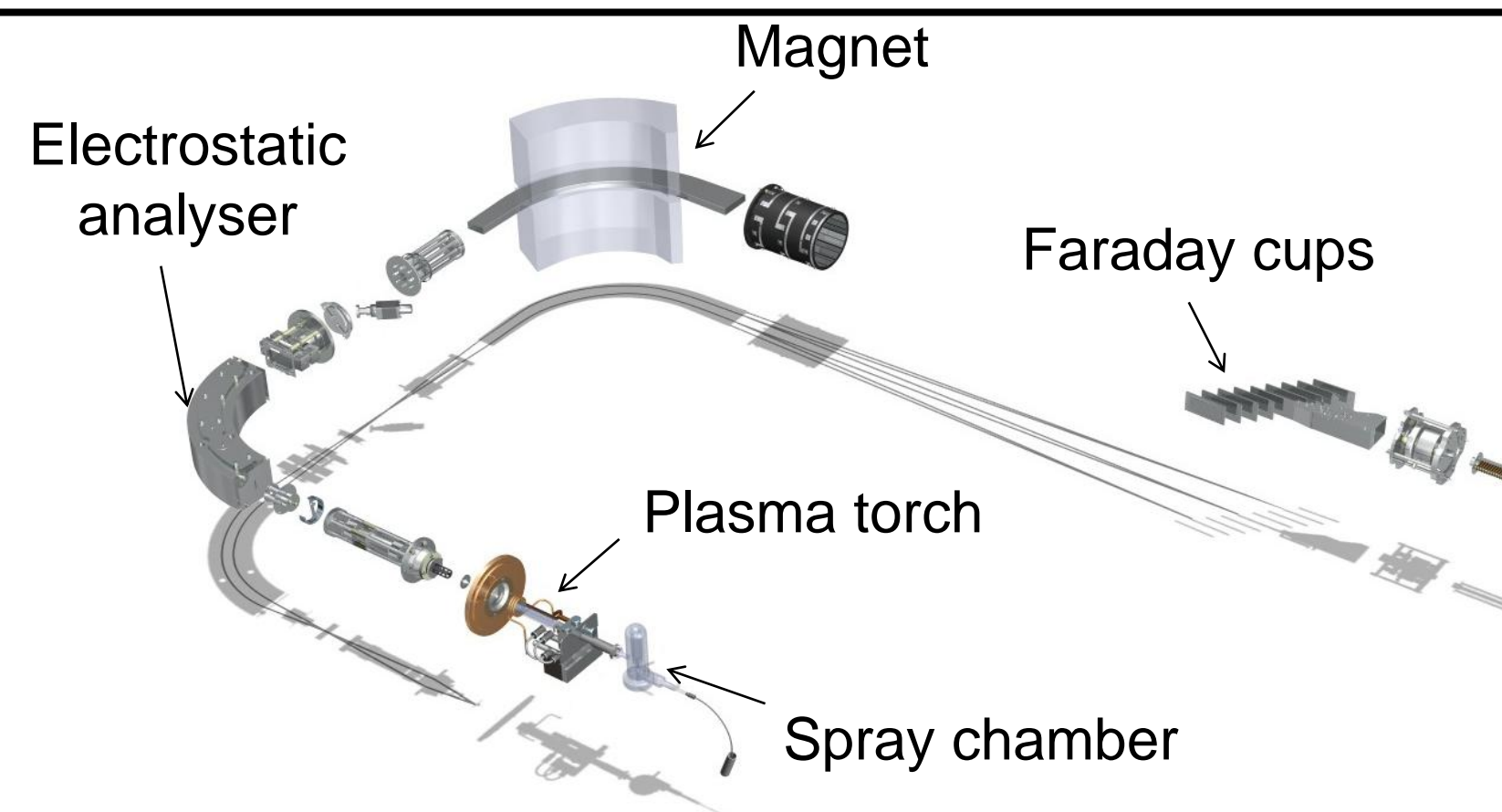
L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Introduction

During MC ICP/MS measurements, all ion currents are biased by mass discrimination, and other effects (detector gain, abundance sensitivity background, dead time...). So, various corrections must be applied to all measurements to determine accurate and precise isotope ratios. The use of certified isotopic reference materials (IRM) associated to a sample standard bracketing (SSB) method allows us to determine accurate isotope ratios. The ratios are determined taking into account in particular the mass discrimination, the uranium hydride ions, blanks and isotopic reference materials measurements. The uncertainties associated to those ratios are then calculated. The performance of the laboratory to determine uranium isotope ratios and the uncertainties associated is evaluated by participating to inter-laboratory tests. The nuclear material Round Robin proficiency testing scheme (NM RORO), organized by the International Atomic Energy Agency (IAEA) is a reliable and objective tool for assessing and monitoring analytical performance of laboratories in the area of nuclear material analysis.

MC ICP/MS

- Simultaneous measurement of 9 different isotopes thanks to 9 Faraday cups connected to current amplifiers 10^{10} à $10^{12} \Omega$
- Dynamic range : 100 000 (from $0.5 \cdot 10^{-3}$ V to 50 V)



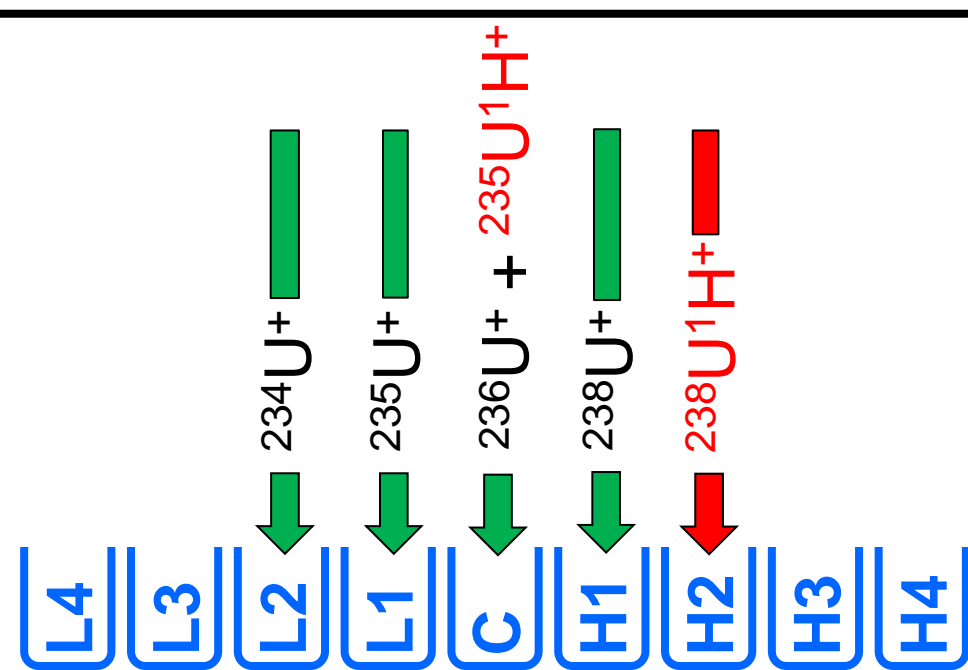
Isotopic measurements

Sample Standard Bracketing

In isotopic measurements, mass bias occurs when ions of different mass are transmitted through the mass spectrometer with different efficiencies within the MC ICP/MS instrument, resulting in non-uniform response across the mass range and inaccurate isotope ratio measurements. "Sample Standard Bracketing" (SSB) method used to correct instrumental bias (based on external correction) SSB perfectly adapted to determine isotopic composition of uranium (wide range of uranium certified reference materials, from highly enriched to depleted available) An isotopic reference material is measured and the relative bias between the true and the experimental value of the ratio is assumed to be valid for the sample as well.

$$\left(\frac{R_{sample}}{R_{Sample}^{meas}}\right) = \left(\frac{R_{Std}^{True}}{R_{Std}^{meas}}\right) \implies R_{sample} = R_{sample}^{meas} \times \left(\frac{R_{Std}^{True}}{R_{Std}^{meas}}\right) \text{ with } R_z = \left(\frac{^{23x}U}{^{238}U}\right)_z \text{ with } x=4, 5 \text{ or } 6 \text{ and } z = \text{sample, } \begin{matrix} \text{meas} \\ \text{sample,} \end{matrix} \begin{matrix} \text{True} \\ \text{Std,} \end{matrix} \begin{matrix} \text{meas} \\ \text{Std} \end{matrix}$$

Faraday cups



Measure of 239 m/z for hydride correction

$$m/z \ 236 = ^{236}U^{++} + ^{235}U^1H^+$$

$$f_H = \frac{^{238}U^1H^+ / ^{238}U^+}{^{235}U^1H^+ / ^{235}U^+}$$

$$^{236}U^+ = m/z \ 236 - f_H \times ^{235}U^+$$

Analytical run

A certified isotopic reference material is analysed before and after the sample
Blanks are also introduced in the analytical run

- 1 - Blank
- 2 - CRM
- 3 - Blank
- 4 - Sample
- 5 - Blank
- 6 - CRM
- 7 - Blank

IAEA NM RORO 2015 and 2017

Proficiency assessment

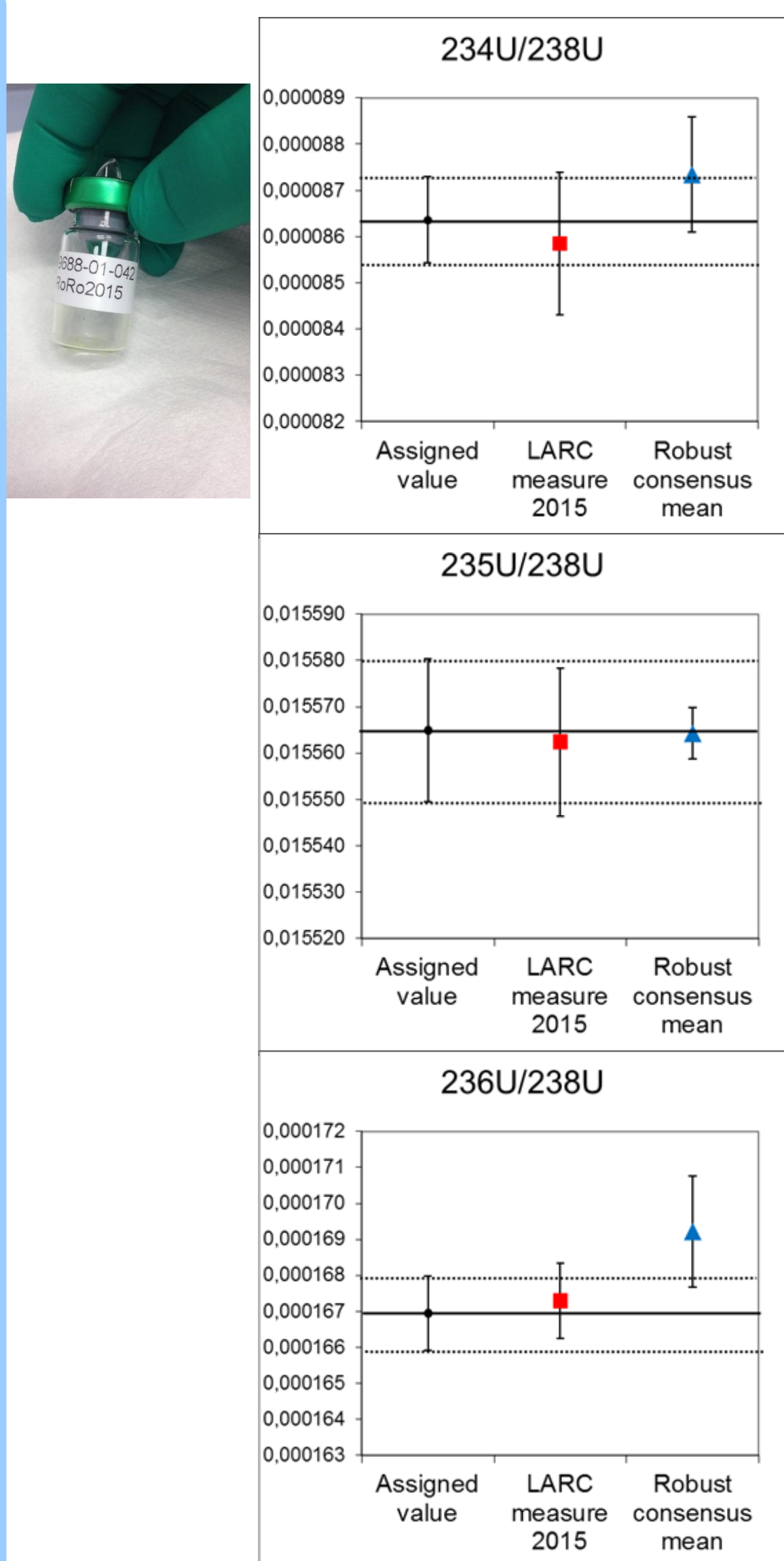
Analytical performance of laboratories is assessed through trueness and precision thanks to z and zeta scores (as described in ISO 13528)

$$z = \frac{(\text{Laboratory measure} - \text{Robust consensus mean})}{\text{standard deviation of proficiency assessment}}$$

$$\text{zeta} = \frac{(\text{Laboratory measure} - \text{Robust consensus mean})}{\sqrt{((\text{uncertainty of laboratory})^2 + (\text{uncertainty of robust consensus mean})^2)}}$$

- |score| ≤ 2.0 – acceptable result
- 2.0 < |score| ≤ 3.0 – uncertain result
- |score| > 3.0 – unacceptable result

NM RORO 2015 / dried uranium nitrate



	234U/238U	235U/238U	236U/238U
z score	-0.78	-0.22	-0.8
zeta score	-1.96	-0.35	-2.31

For NM RORO 2015 f_H ($^{238}U^1H^+ / ^{238}U^+$) and the associated uncertainty are determined daily, before measurement of uranium samples with CRM

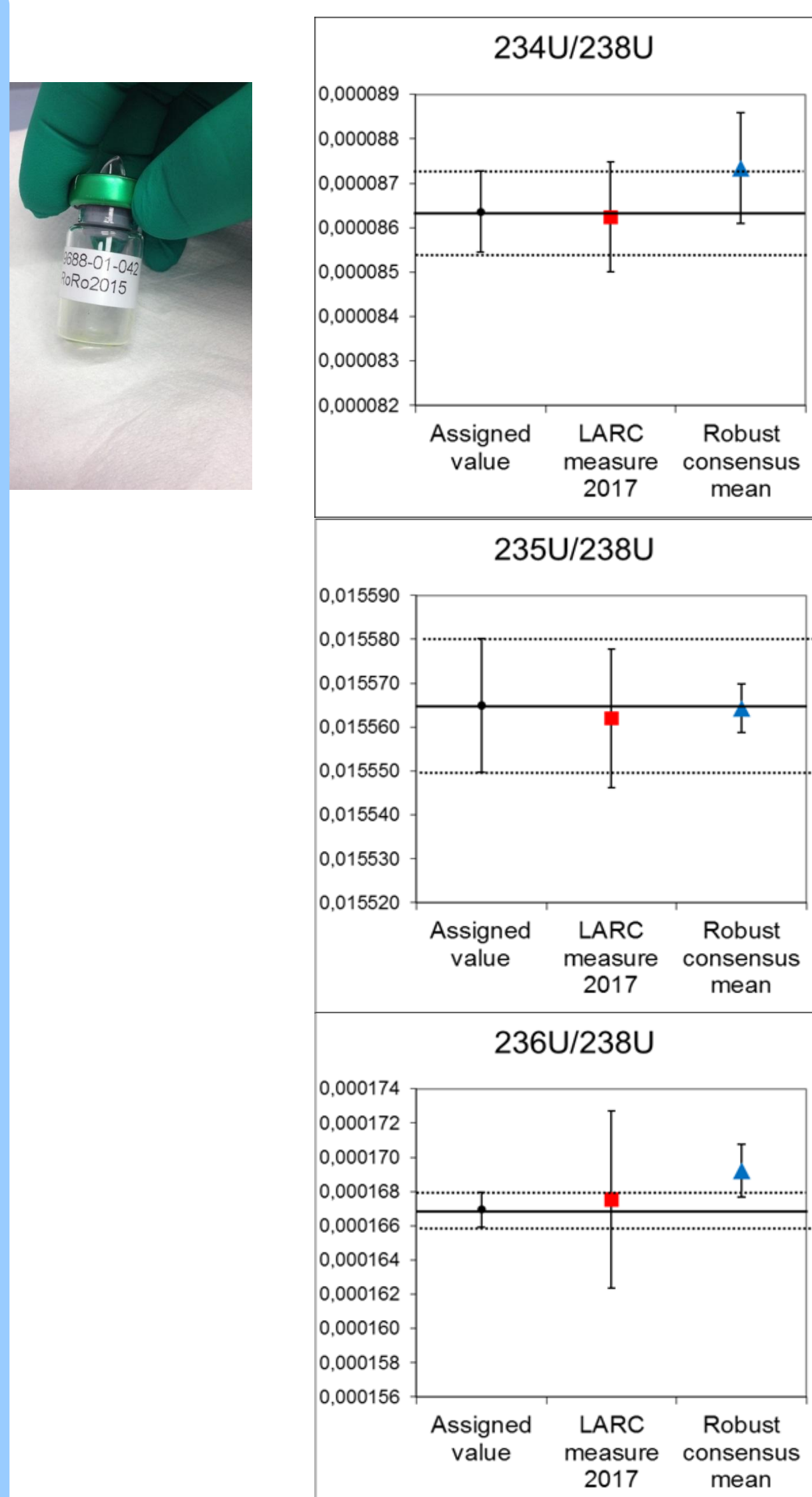
But, the hydride formation varies during the analytical run and the uncertainty of f_H is then underestimated (zeta = -2.31)

The determination of f_H and its uncertainty are then realised for each measurement (CRM and sample), line to line (30 replicates for each measurement)

A better evaluation of the uncertainty of f_H and then of the ^{236}U signal and the $^{236}U / ^{238}U$ ratio is expected

New measurement of the NM RORO 2015 in solution

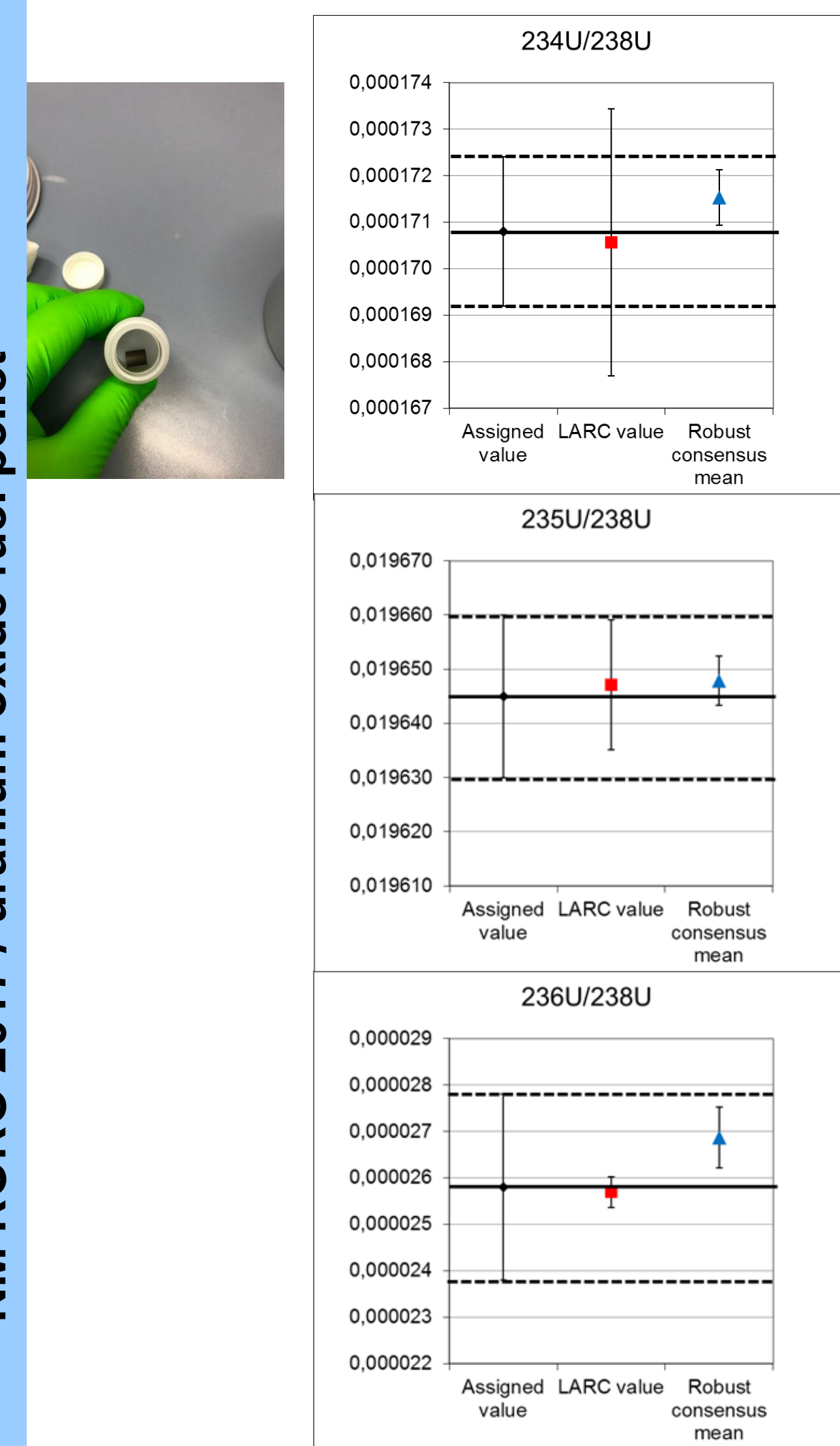
NM RORO 2015 / new measurement 2017



	234U/238U	235U/238U	236U/238U
z score	-0.58	-0.26	-0.70
zeta score	-1.22	-0.08	-0.63

✓ All ratios and uncertainties associated are correctly assessed

NM RORO 2017 / uranium oxide fuel pellet



	234U/238U	235U/238U	236U/238U
z score	-0.18	0.22	-0.07
zeta score	-0.14	0.22	-0.10

✓ All ratios and uncertainties associated are correctly assessed

Conclusion

The nuclear material Round Robin proficiency testing scheme (NM RORO), organized by IAEA allow us to testify the accuracy of the SSB method to determine uranium isotope ratios and help us to improve the determination of the uncertainty associated to the $^{236}U / ^{238}U$ ratio.