

Optimization of the sample preparation and measurement protocol for the analysis of uranium isotopes by MC-ICP-MS without spike addition

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Electronic Supplementary Information (ESI)

Results and discussion

Optimization of measurements of uranium isotope ratios using MC-ICP-MS

To achieve suitable performance for low-level uranium samples, it is important to optimize the uranium concentration introduced into the MC-ICP-MS. In general, higher concentrations yield better signal intensities and consequently better isotope ratio results. However, this poses higher risks for contamination of the system, which results in memory effect owing to the high concentration of uranium, matrix effects, and results in longer wash time between samples^{1,2}. To establish the most appropriate concentration of the aliquot of a purified natural uranium fraction to be introduced into MC-ICP-MS, seven different concentrations of uranium isotopic standard (IRMM-184) were measured and

compared with respect to the influence on the precision and accuracy of measured $^{235}\text{U}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ ratios on MC-ICP-MS. The concentrations were 0.1–10 ng/mL. The results in Figure S1 indicate that the most optimal uranium concentration for measurements is 5 ng/mL. This concentration was selected as the lowest concentration with the smallest difference of $^{235}\text{U}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ isotope ratios from the certified value. In addition, at uranium concentration of 5 ng/mL and above, the difference in dispersion from the estimated mean value for both uranium isotope ratios becomes less pronounced compared to lower concentrations.

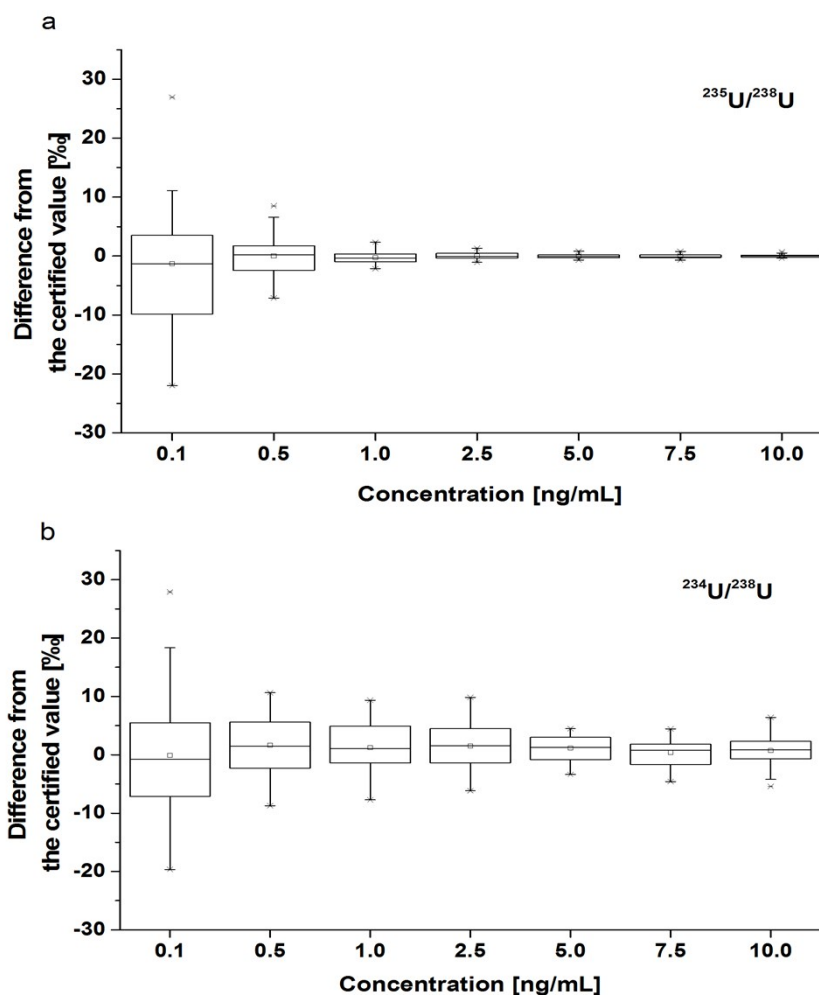


Figure S1 Difference from the certified value (in %) for (a) $^{235}\text{U}/^{238}\text{U}$ and (b) $^{234}\text{U}/^{238}\text{U}$ at different uranium concentrations. For each plot, the line within the box represents the median. The lower and upper lines of the box represent the 25th and 75th percentiles, respectively, and the lower and upper adjacent lines represent the 10th and 90th percentiles, respectively. Crosses indicate outliers.

Samples for uranium isotope analyses normally have low-level uranium concentrations and high dynamic range is required for simultaneous measurements of high and low abundant isotopes. This can be achieved by using an ion counting system in conjunction with Faraday cups. For samples, where an only a small amount of material is available or the uranium concentration is very low, both ^{234}U and ^{235}U isotopes should be measured on ion counter detectors. However, this requires careful characterization and correction of the instrument detectors to achieve the most precise and accurate results ³. The typical protocol used for measuring uranium isotopes using MC-ICP-MS was a combination of ^{238}U and ^{235}U ions on the Faraday detectors (L2 and L5 cups, respectively) and ^{234}U ions on the ion counter detector (IC0 cup). To determine the protocol with which the uranium isotope signal is the most stable if sample concentrations require measurements at concentrations lower than 5 ng/mL, a comparison with another cup configuration was performed. With the second configuration, only ^{238}U ions were measured on the Faraday detector (L3 cup) and ^{235}U and ^{234}U ions were measured on the ion counter detectors (IC0 and IC1 cups, respectively). Figure S2 shows the difference from certified value

for $^{235}\text{U}/^{238}\text{U}$ ratios if ^{235}U is measured on a Faraday detector (F) or on an ion counter detector (IC) for three different uranium concentrations of 0.1–1.0 ng/mL. These results show that the smallest scattering of measured uranium isotope ratios is when ^{235}U ions were measured on a Faraday detector at a concentration greater than 0.5 ng/mL. However, at 0.1 ng/mL, the results showed a smaller deviation when ^{235}U ions were measured on the ion counter detector. Here, we can conclude that for samples with uranium concentrations lower than 0.5 ng/mL, it is better to use the cup configuration in which ^{238}U ions are measured on a Faraday detector (L3 cup) and ^{235}U and ^{234}U ions are measured on ion counter detectors (IC0 and IC1 cups, respectively). However, measurements of ^{235}U ions on ion counter detectors have to be done with extreme care, because of possible errors that can occur during measurement. Potential uncertainties can result from ion counter dead time corrections, non-linear behaviour or dark noise. In addition, ion counter detectors are very sensitive and their dynamic range goes only up to 10^6 cps. If the sample concentration is too high, the count rate will exceed this threshold and the instrument will deflect the signal to prevent damage to the multiplier ^{3,4}.

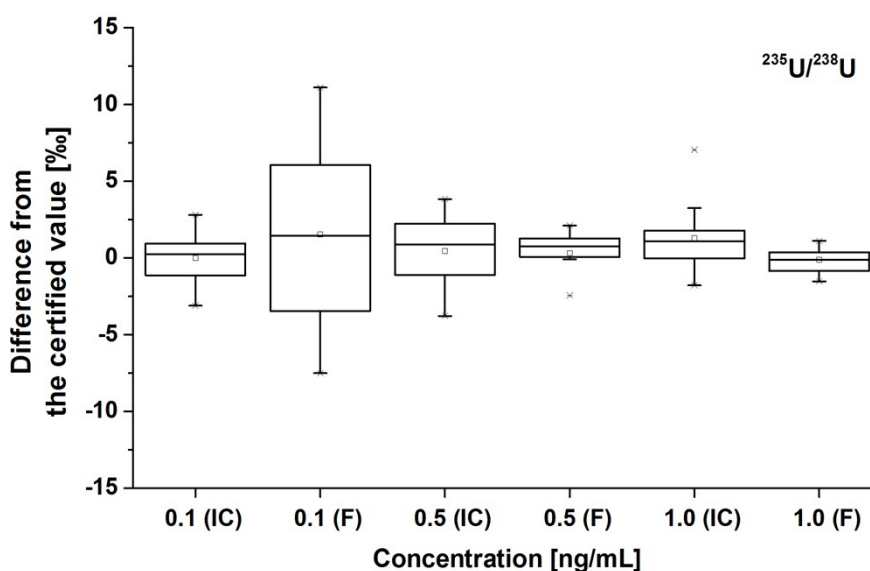


Figure S2 Difference from the certified value (in %) for $^{235}\text{U}/^{238}\text{U}$ ratios if ^{235}U is measured on a Faraday detector (F) or on an ion counter detector (IC) at different uranium concentrations.

To assess the long-term analytical performance of MC-ICP-MS and to test the instrument accuracy and precision for uranium isotope ratio measurements, a uranium isotopic standard (IRMM-184) at 5 ng/mL concentration was measured over 15 months (Figure S3). The results of the mean values of 10 measurements of uranium isotopic standard of each month were corrected for mass bias and compared to the results obtained from the certified values. The quality of results was expressed with the expanded uncertainty, where the main source of uncertainty is the uncertainty of the certified standard. The analytical performance of MC-ICP-MS demonstrates relatively good repeatability between uranium isotopic standard measurements for each month (about 0.04% to 0.11% RSD for $^{235}\text{U}/^{238}\text{U}$ and about 0.12% to 0.46% RSD for $^{234}\text{U}/^{238}\text{U}$). Figure S3 shows that the analytical performance of MC-ICP-MS for the measured isotopic ratios of the uranium standard is in good agreement with the certified value. The analytical performance for $^{234}\text{U}/^{238}\text{U}$ ratios shows

some small deviations from the certified value. This can be explained by the smaller ion-beam intensity produced by the low ^{234}U abundance in the natural uranium standard. A correlation is also seen between the measurement uncertainty and the signal intensity for ^{238}U during measurement sessions. The expanded uncertainty of the measured uranium standard is seen to be lower when the ^{238}U signal intensity is high (2.0–3.9 V) for a 5 ng/mL solution. In contrast, when the signal intensity of ^{238}U is very low (<1 V), then the expanded uncertainty of the measured uranium isotope ratio is much larger. Consequently, the best results can be achieved with ^{238}U signal intensity higher than 2 V per 5 ng/mL of uranium. The analytical performance of MC-ICP-MS mostly depends on the actual daily experimental conditions. It is important to spend sufficient time and energy on properly optimizing the instrument by adjusting the torch position, instrumental gas flows, ion lens positions, and high-tension (HT) voltages.

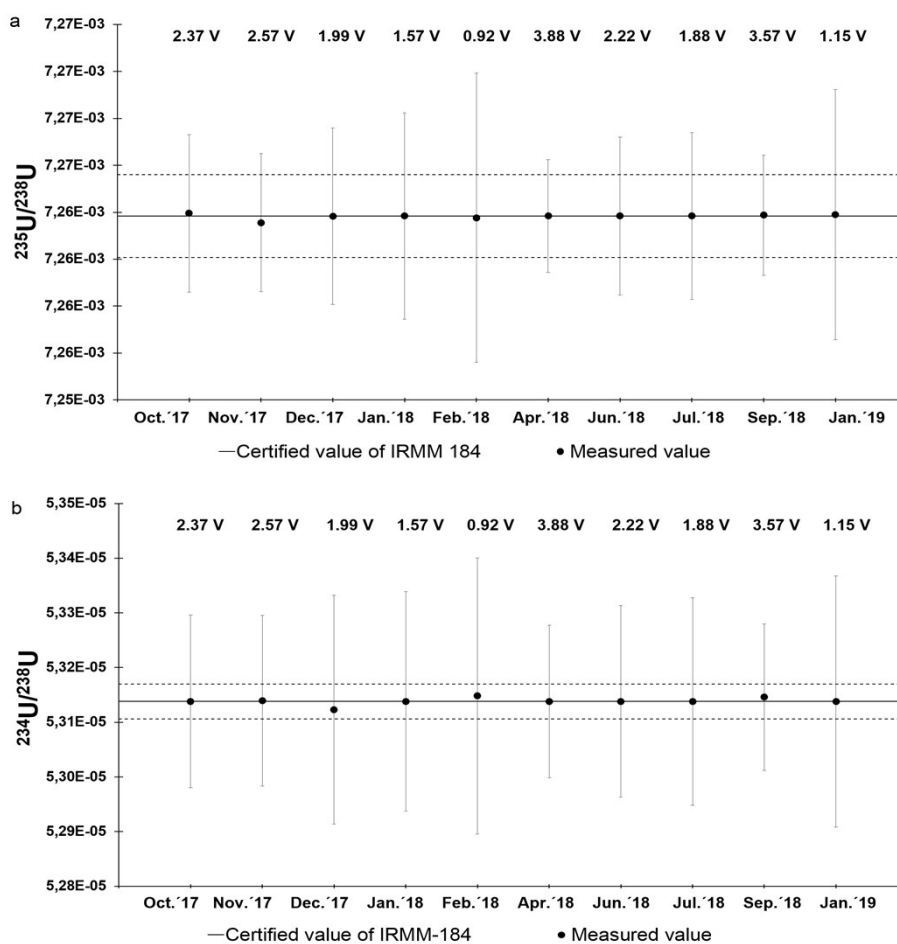


Figure S3 Long-term results of mean values of (a) $^{235}\text{U}/^{238}\text{U}$ and (b) $^{234}\text{U}/^{238}\text{U}$ ratios in uranium isotopic standard IRMM-184 together with the certified value (solid line) and signal intensity of ^{238}U during measurement sessions. Uncertainties are expanded measurement uncertainties with a coverage factor of 2. Data were collected over a period of 15 months.

The analytical precision of the instrument was further assessed by analysing two uranium isotopic standards: depleted uranium standard (IRMM-183) and enriched uranium standard (IRMM-185) (Table

S1). The experimental values are in good agreement with the corresponding certified values, which demonstrates the high precision of MC-ICP-MS measurements.

Table S1 Measured isotope ratios of investigated uranium standards (mean values, n = 5 for each sample) together with certified values. Uncertainties are expanded measurement uncertainties with a coverage factor of 2. Bias and zeta-score of uranium isotopic measurements are also given. Reported data are corrected for mass bias.

Sample	$^{235}\text{U}/^{238}\text{U}$	$^{234}\text{U}/^{238}\text{U}$
IRMM-183		
Measured value	$(3.2154 \pm 0.0048) \times 10^{-3}$	$(1.9755 \pm 0.0083) \times 10^{-5}$
Certified value	$(3.2157 \pm 0.0016) \times 10^{-3}$	$(1.9755 \pm 0.0022) \times 10^{-5}$
Bias (%) ^a	-0.008	-0.0003
ζ-score ^b	-0.05	-0.0008
IRMM-185		
Measured value	$(2.00550 \pm 0.00047) \times 10^{-2}$	$(1.795 \pm 0.010) \times 10^{-4}$
Certified value	$(2.00552 \pm 0.00060) \times 10^{-2}$	$(1.79474 \pm 0.00080) \times 10^{-4}$
Bias (%) ^a	-0.0008	0.0002
ζ-score ^b	-0.02	0.0003

^a Bias is defined as the relative difference between the measured value ($R_{\text{Sample},m}$) and the certified value ($R_{\text{Std},m}$) which is then normalized by the certified value. Results are in good agreement with the certified value if absolute bias is $\leq 0.1\%$.

$$\left(\frac{R_{\text{Sample},m} - R_{\text{Std},m}}{R_{\text{Std},m}} \right) \times 100\%$$

^b Zeta-score (ζ) is calculated to quantitatively compare the measured value with a standard uncertainty with the certified value and its associated standard uncertainty. Results are in good agreement with the certified value if absolute zeta-score is ≤ 2.0 (95% confidence).

$$\zeta = \frac{R_{\text{Sample},m} - R_{\text{Std},m}}{\sqrt{\frac{u_{\text{Sample},m}^2}{2} + \frac{u_{\text{Std},m}^2}{2}}}$$

Bias of uranium isotopes during different sample preparation and separation techniques

Table S2 Measured uranium isotope ratios with expanded measurement uncertainties ($k = 2$) and their deviations from the certified value (IRMM-184) (in ‰) for various analytical methods.

Analytical method		Isotope ratio with expanded measurement uncertainty ($k = 2$)		Deviations from uranium isotopic standard (IRMM-184) [‰]	
Pre-concentration	Separation	$^{235}\text{U}/^{238}\text{U}$	$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$	$^{234}\text{U}/^{238}\text{U}$
Fe-precipitation	UTEVA _{MQ}	7.257E-03 ± 4.434E-06	5.346E-05 ± 2.209E-07	-0.689	6.035
	UTEVA _{HNO3}	7.263E-03 ± 2.352E-06	5.339E-05 ± 2.833E-07	0.052	4.648
	DOWEX-UTEVA	7.268E-03 ± 3.519E-06	5.285E-05 ± 5.915E-07	0.735	-5.604
	DOWEX	7.281E-03 ± 6.342E-06	5.084E-05 ± 3.271E-07	2.604	-56.296
Ca-precipitation	UTEVA _{MQ}	7.257E-03 ± 4.122E-06	5.324E-05 ± 2.060E-07	-0.725	1.898
	UTEVA _{HNO3}	7.259E-03 ± 1.299E-06	5.353E-05 ± 2.473E-07	-0.424	7.243
	DOWEX-UTEVA	7.265E-03 ± 3.355E-06	5.326E-05 ± 1.980E-07	0.335	2.232
	DOWEX	7.264E-03 ± 1.314E-06	5.305E-05 ± 3.037E-07	0.268	-1.725
Mn-precipitation	UTEVA _{MQ}	7.258E-03 ± 3.059E-06	5.332E-05 ± 1.735E-07	-0.567	3.376
	UTEVA _{HNO3}	7.260E-03 ± 3.473E-06	5.362E-05 ± 6.935E-08	-0.343	8.902
	DOWEX-UTEVA	7.257E-03 ± 6.512E-06	5.318E-05 ± 1.884E-07	-0.686	0.724
	DOWEX	7.263E-03 ± 1.865E-06	5.324E-05 ± 5.818E-08	0.154	1.959
Evaporation	UTEVA _{MQ}	7.258E-03 ± 4.343E-06	5.344E-05 ± 2.398E-07	-0.575	5.619
	UTEVA _{HNO3}	7.262E-03 ± 4.817E-07	5.332E-05 ± 9.650E-08	-0.059	3.357
	DOWEX-UTEVA	7.264E-03 ± 6.713E-06	5.328E-05 ± 1.008E-07	0.259	2.589
	DOWEX	7.259E-03 ± 1.757E-06	5.347E-05 ± 1.526E-09	-0.400	6.173
	TBP	5.791E-03 ± 3.056E-06	4.089E-05 ± 1.320E-07	-254	-299

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