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ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Performance and optimisation of triple quadrupole ICP-MS for accurate measurements of uranium isotopic ratios

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Electronic supporting information includes 2 tables and 12 figures.

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Table S1. Certified U isotopic ratios[a] for the IRMM074 standard solutions used in the study. Uncertainties expressed as combined standard uncertainty with coverage factor k = 2.

Code number	**$^{233}U/^{235}U$**	**$^{233}U/^{238}U$**	**$^{235}U/^{238}U$**
IRMM-074/1	1.02685 ± 0.00026	1.02711 ± 0.00026	1.00025 ± 0.00015
IRMM-074/2	0.30799 ± 0.00008	0.30807 ± 0.00008	1.00026 ± 0.00015
IRMM-074/3	0.0102288 ± 0.0000026	0.0102314 ± 0.0000026	1.00026 ± 0.00015

[a]Taken from Richter et al., 2009, International Journal of Mass Spectrometry, 115-125.

Table S2. Comparing calculated detector dead time and instrumental dead time for U isotopes measured by Agilent 8900 ICP-MS/MS. Uncertainties expressed as combined standard uncertainty with coverage factor k = 2.

Source for calculation	**Dead time ($\times 10^{-8}$ s)**
IRMM-074/2	4.05 ± 0.21
IRMM-074/3	4.05 ± 0.08
Instrumental	4.13 ± 0.01

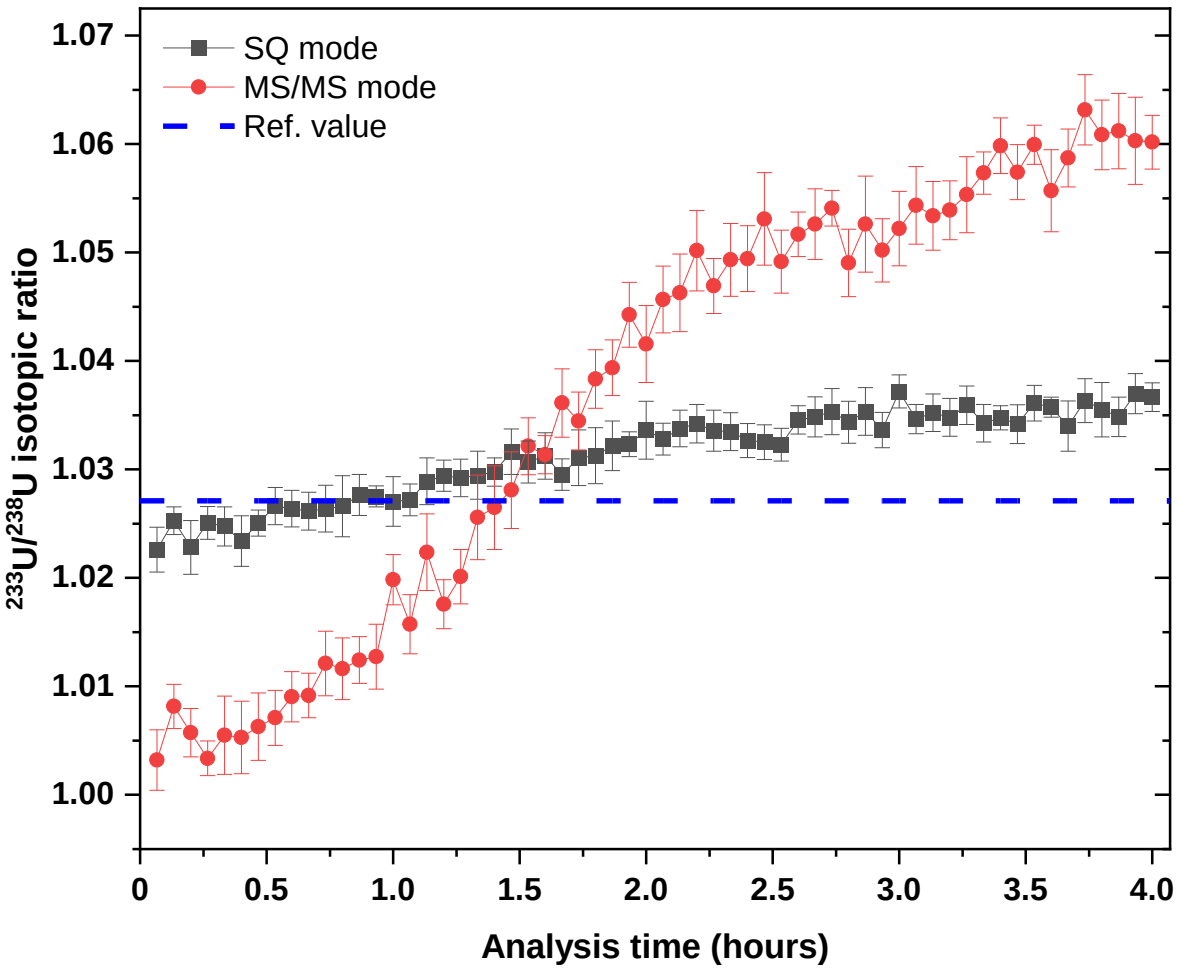

Figure S1. Repeated measurements (n = 60) of $^{233}U/^{238}U$ isotopic ratio (not mass bias corrected) in a uranium standard reference solutions (IRMM-074/1; ~0.75 µg L^{-1} total U) using the first installed Agilent 8900 ICP-MS/MS instrument. Measurements were carried out in SQ mode and MS/MS mode. Default start-up tuning parameter values and automatically lens tuning, with standard resolution settings for Q1 and Q2. Each value represents the average of 10 replicates with error bars representing combined standard uncertainty with coverage factor k = 2. Dashed line represents the certified reference value of 1.02711 ± 0.00026 (k = 2).

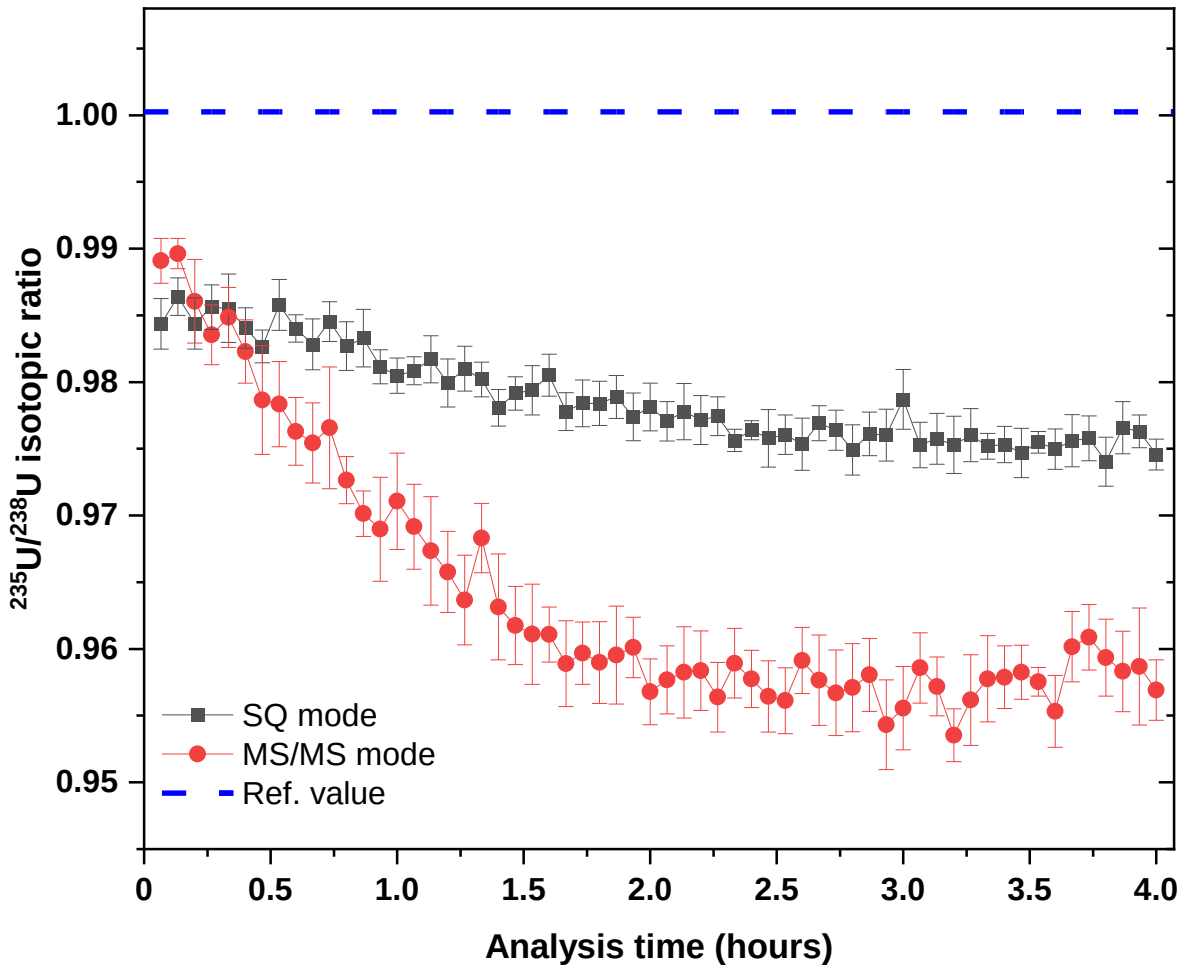

Figure S2. Repeated measurements (n = 60) of $^{235}U/^{238}U$ isotopic ratio (not mass bias corrected) in a uranium standard reference solutions (IRMM-074/1; ~0.75 µg L^{-1} total U) using the first installed Agilent 8900 ICP-MS/MS instrument. Measurements were carried out in SQ mode and MS/MS mode. Default start-up tuning parameter values and automatically lens tuning, with standard resolution settings for Q1 and Q2. Each value represents the average of 10 replicates with error bars representing combined standard uncertainty with coverage factor k = 2. Dashed line represents the certified reference value of 1.00025 ± 0.00015 (k = 2).

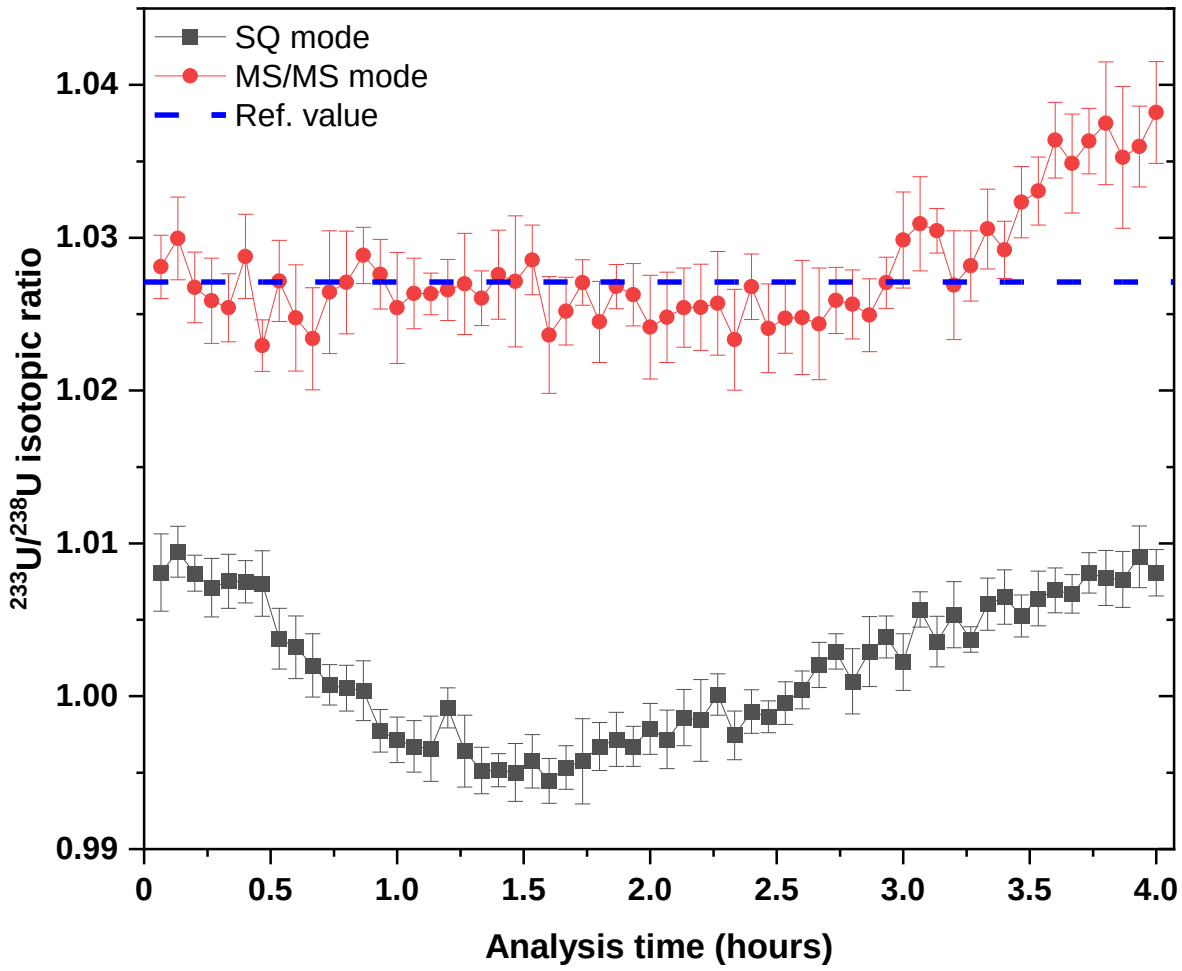

Figure S3. Repeated measurements (n = 60) of $^{233}U/^{238}U$ isotopic ratio (not mass bias corrected) in a standard reference solutions (IRMM-074/1; ~0.75 µg L^{-1} total U) using the second Agilent 8900 ICP-MS/MS. Measurements were carried out in SQ mode and MS/MS mode in the same batch. Default start-up tuning parameter values and automatically lens tuning, with standard resolution settings for Q1 and Q2. Each value represents the average of 10 replicates with error bars representing combined standard uncertainty with coverage factor k = 2. Dashed line represents the certified reference value of 1.02711 ± 0.00026 (k = 2).

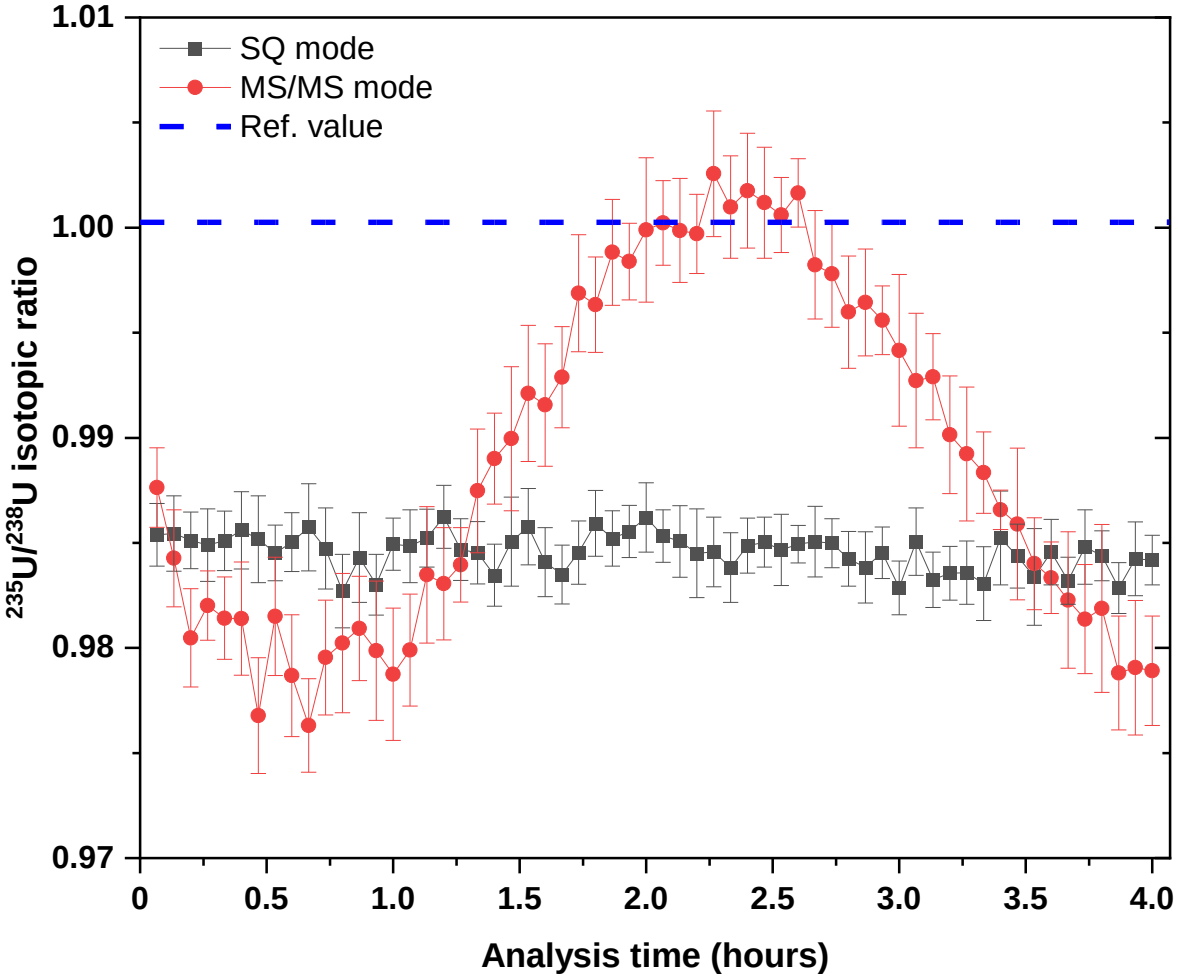

Figure S4. Repeated measurements (n = 60) of $^{235}U/^{238}U$ isotopic ratio (not mass bias corrected) in a standard reference solutions (IRMM-074/1; ~0.75 µg L^{-1} total U) using the second Agilent 8900 ICP-MS/MS. Measurements were carried out in SQ mode and MS/MS mode in the same batch. Default start-up tuning parameter values and automatically lens tuning, with standard resolution settings for Q1 and Q2. Each value represents the average of 10 replicates with error bars representing combined standard uncertainty with coverage factor k = 2. Dashed line represents the certified reference value of 1.00025 ± 0.00015 (k = 2).

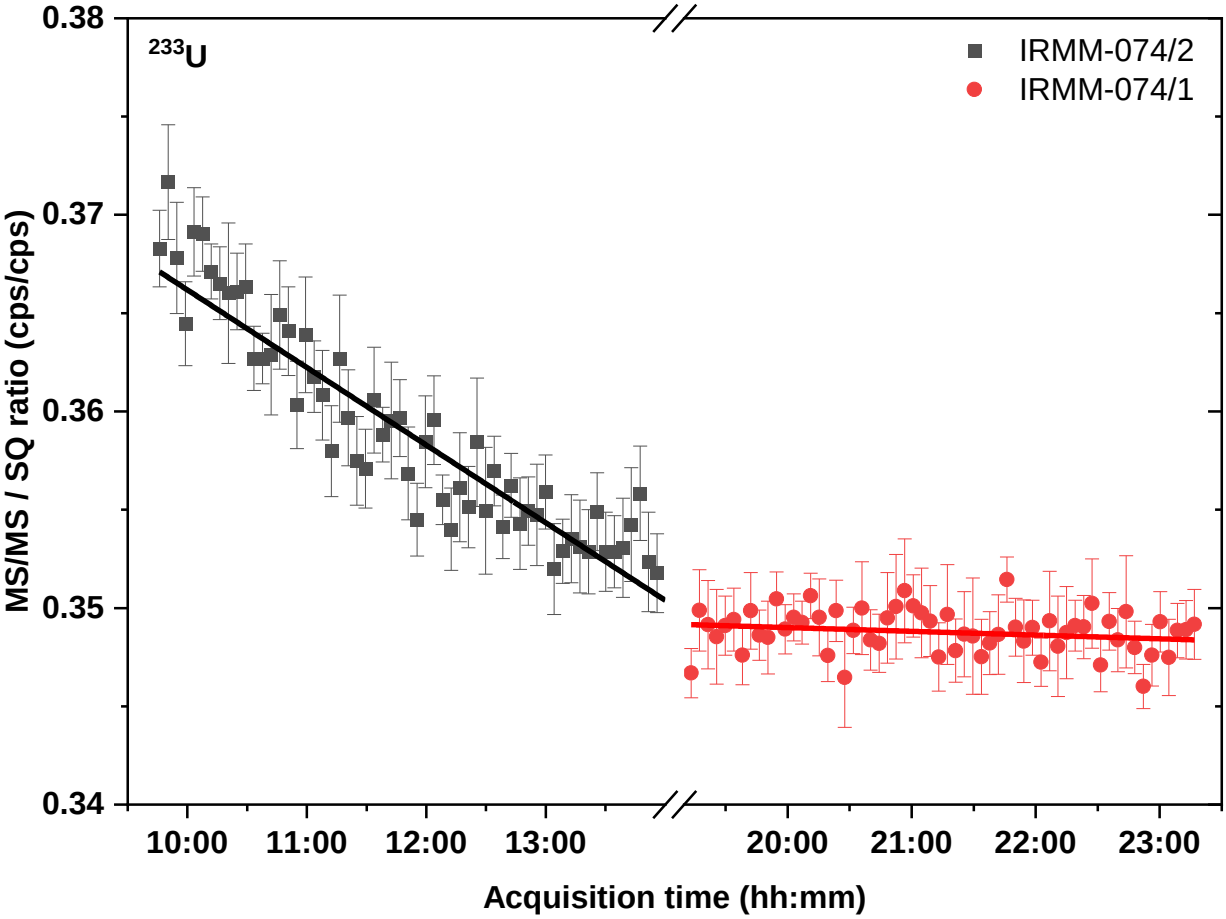

Figure S5. Ratios between signal (cps) in MS/MS mode and signal (cps) in SQ mode for ^{233}U measured in two sequential measurement batches of diluted IRMM-074/2 (■) and IRMM-074/1 (●) using an Agilent 8900 ICP-MS/MS. Measurements were carried out in SQ mode and MS/MS mode. Default start-up tuning parameter values and automatically lens tuning, with standard resolution settings for Q1 and Q2. Each measurement represents the average of 10 replicates with the error bars representing the standard uncertainty with coverage factor k = 2.

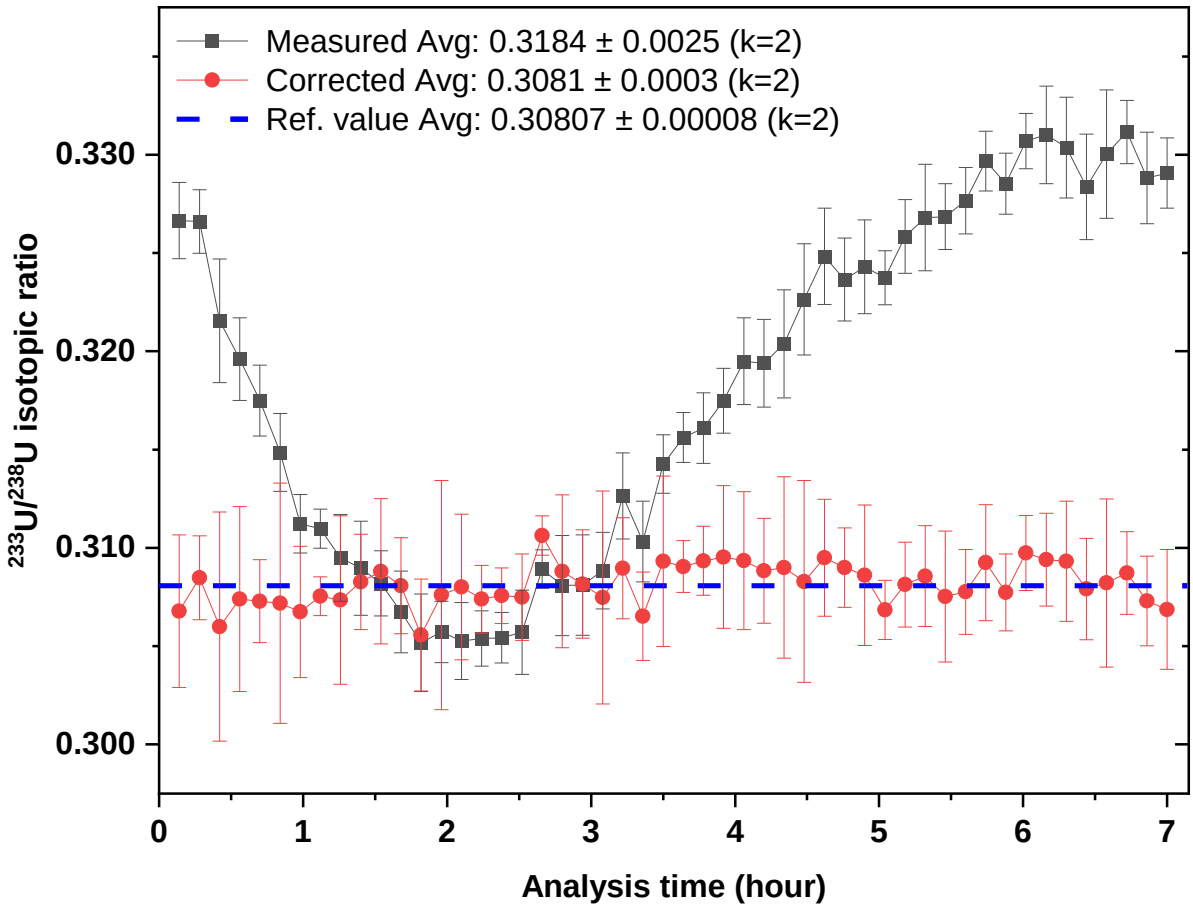

Figure S6. Comparison of measured and corrected $^{233}U/^{238}U$ isotopic ratios using the sample standard bracketing (SSB) approach. Analyses are carried out with every other repeated measurements of IRMM-074/1 (n = 51) and IRMM-074/2 (n = 50) standard solutions in MS/MS mode with standard operating conditions and narrow resolution settings. Each measured value represents the average of 10 replicated with error bars representing combined standard uncertainty with coverage factor k = 2. Dashed line represents the certified reference value of IRMM-074/2.

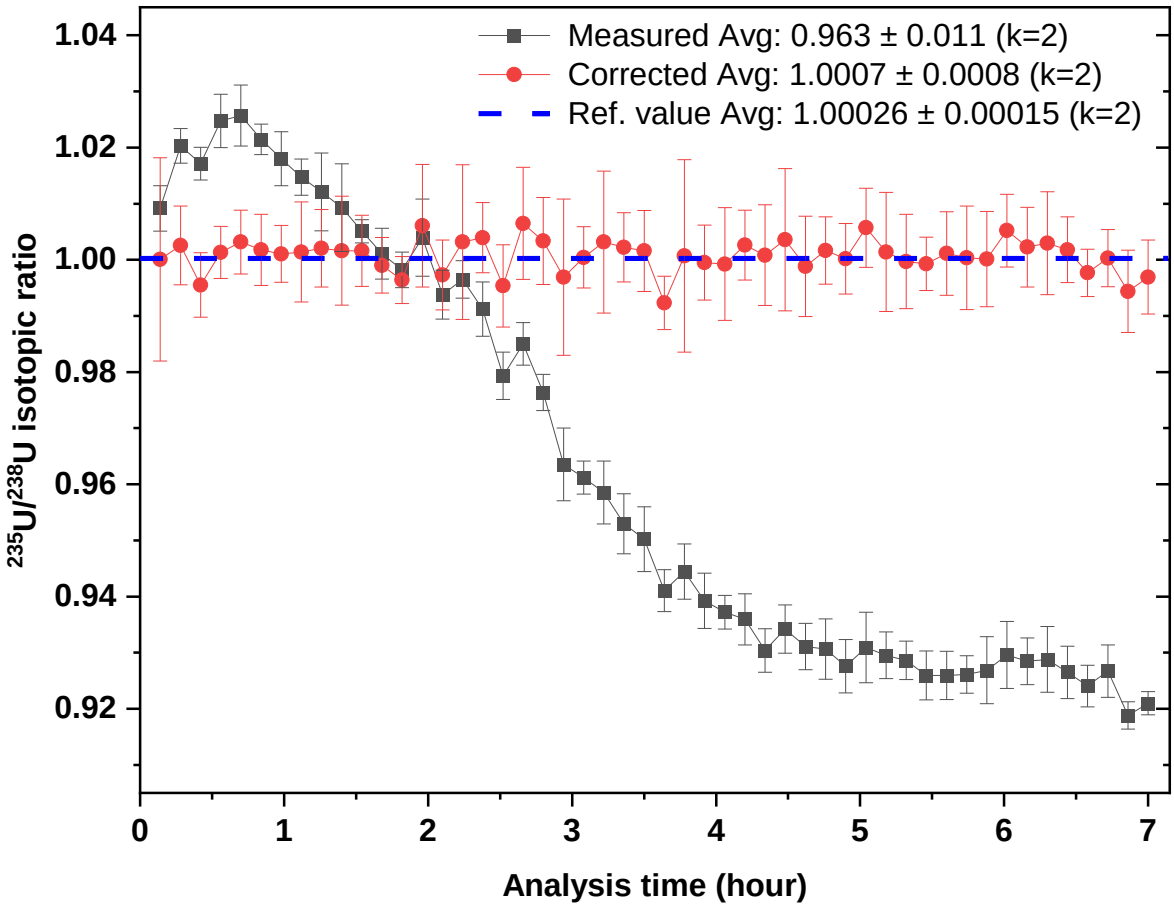

Figure S7. Comparison of measured and corrected $^{235}U/^{238}U$ isotopic ratios using the sample standard bracketing (SSB) approach. Analyses are carried out with every other repeated measurements of IRMM-074/1 (n = 51) and IRMM-074/2 (n = 50) standard solutions in MS/MS mode with standard operating conditions and narrow resolution settings. Each measured value represents the average of 10 replicated with error bars representing combined standard uncertainty with coverage factor k = 2. Dashed line represents the certified reference value of IRMM-074/2.

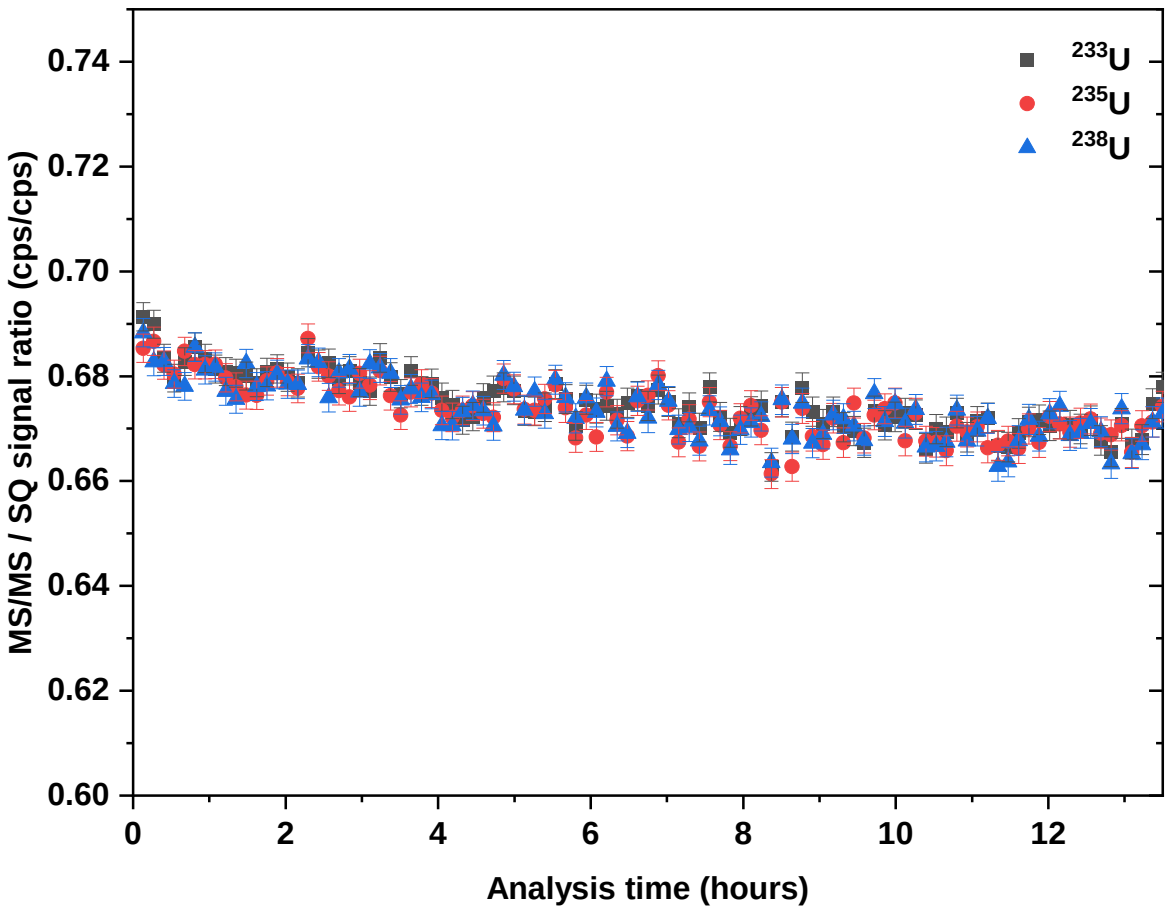

Figure S8. Ratios between signal (cps) in MS/MS mode and signal (cps) in SQ mode for ^{233}U, ^{235}U, ^{238}U measured in in a diluted IRMM-074/1 standard reference solution (~0.75 µg L^{-1} total U) using an Agilent 8900 ICP-MS/MS. Standard operating conditions with broad peak resolution settings. Error bars representing combined standard uncertainties with coverage factor k = 2.

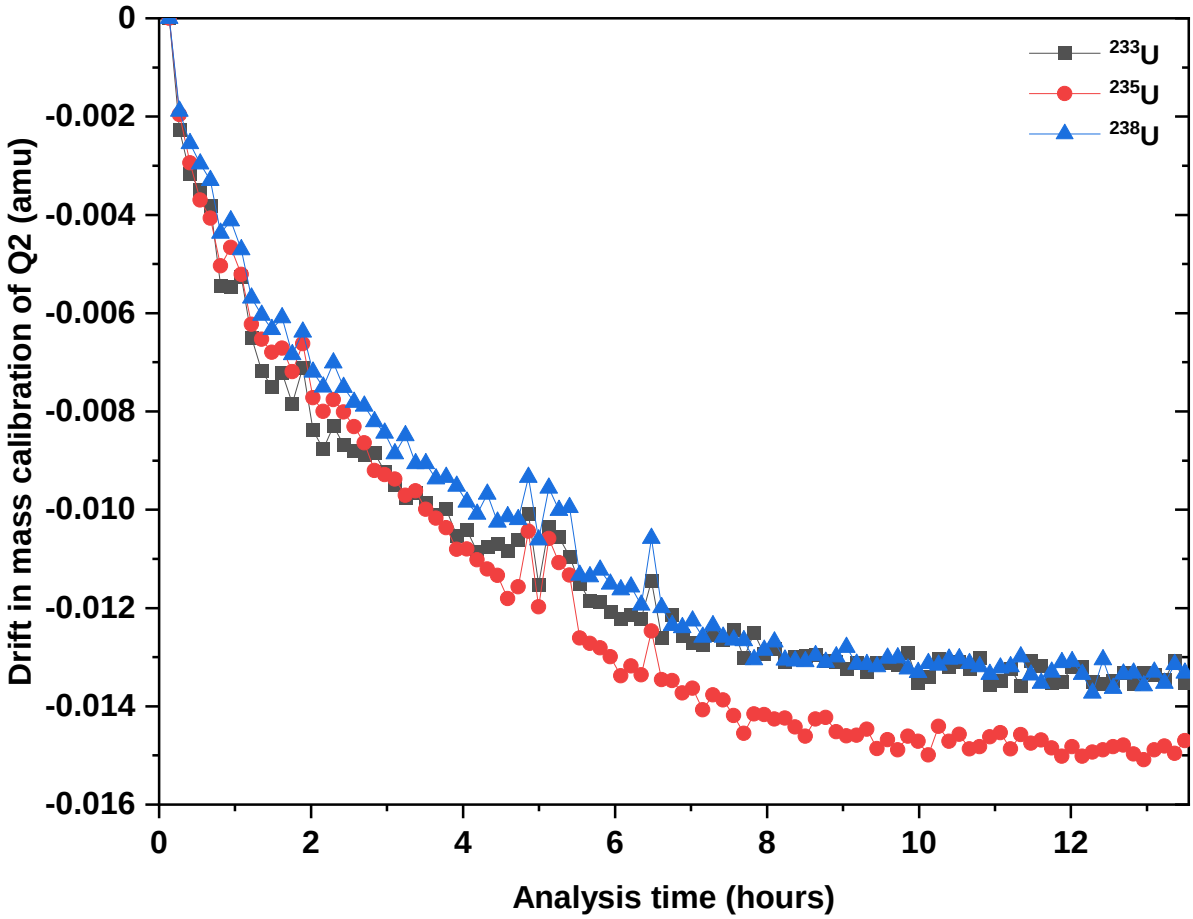

Figure S9. Estimated temporal mass calibration drift in Q2 for ^{233}U, ^{235}U and ^{238}U analysed by repeated measurements (n = 100) in a diluted IRMM-074/1 standard solution (~0.75 µg L^{-1} total U) in SQ mode and full spectrum peak profile (20 points). Standard operating conditions with broad peak resolution settings for Q2.

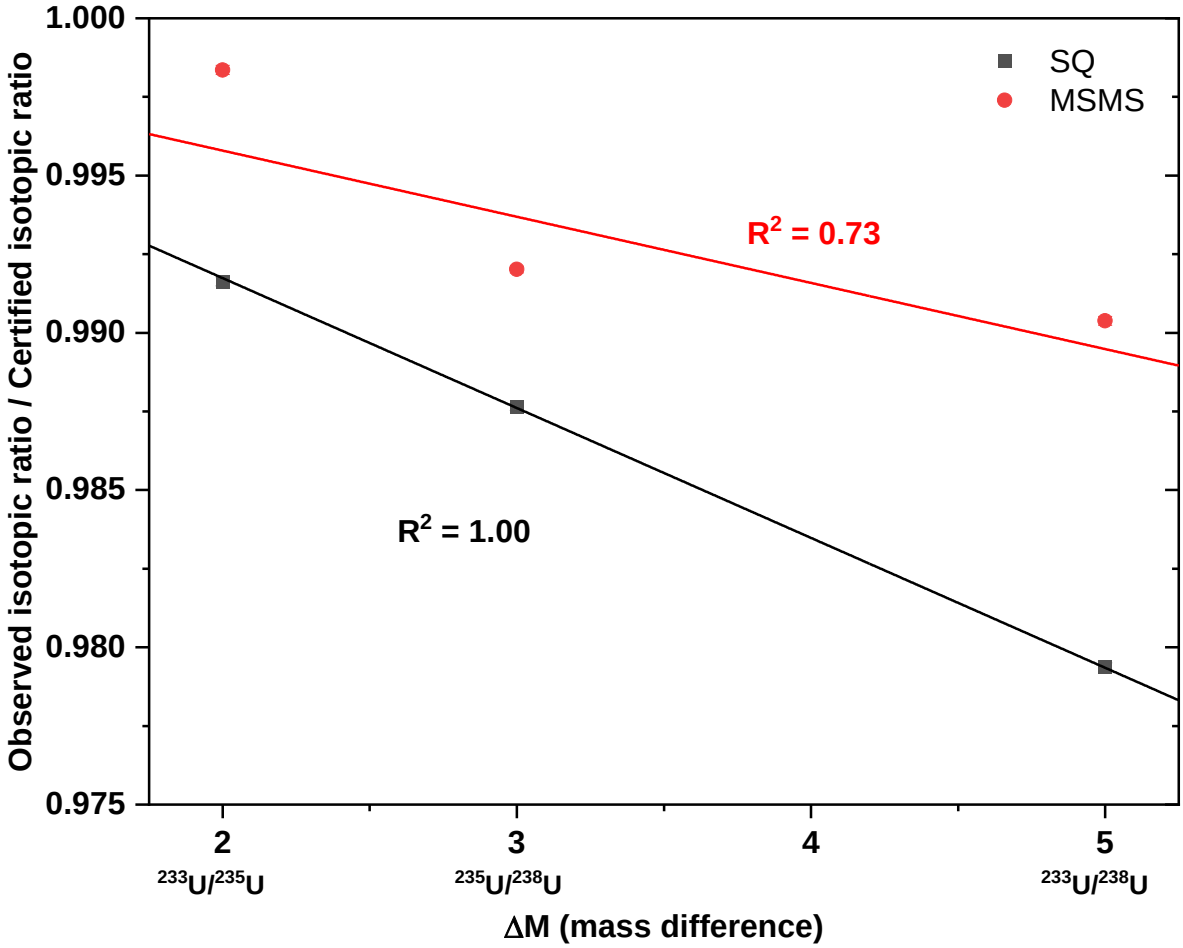

Figure S10. Ratios of observed U isotopic ratios to certified U isotopic ratios plotted against mass difference for SQ mode and MS/MS mode using Agilent 8900 ICP-MS/MS. Each U ratios represent the average of 130 measurements with error bars representing the standard uncertainties with coverage factor k = 2. The lines represent the linear fitting with equation y = a + bx.

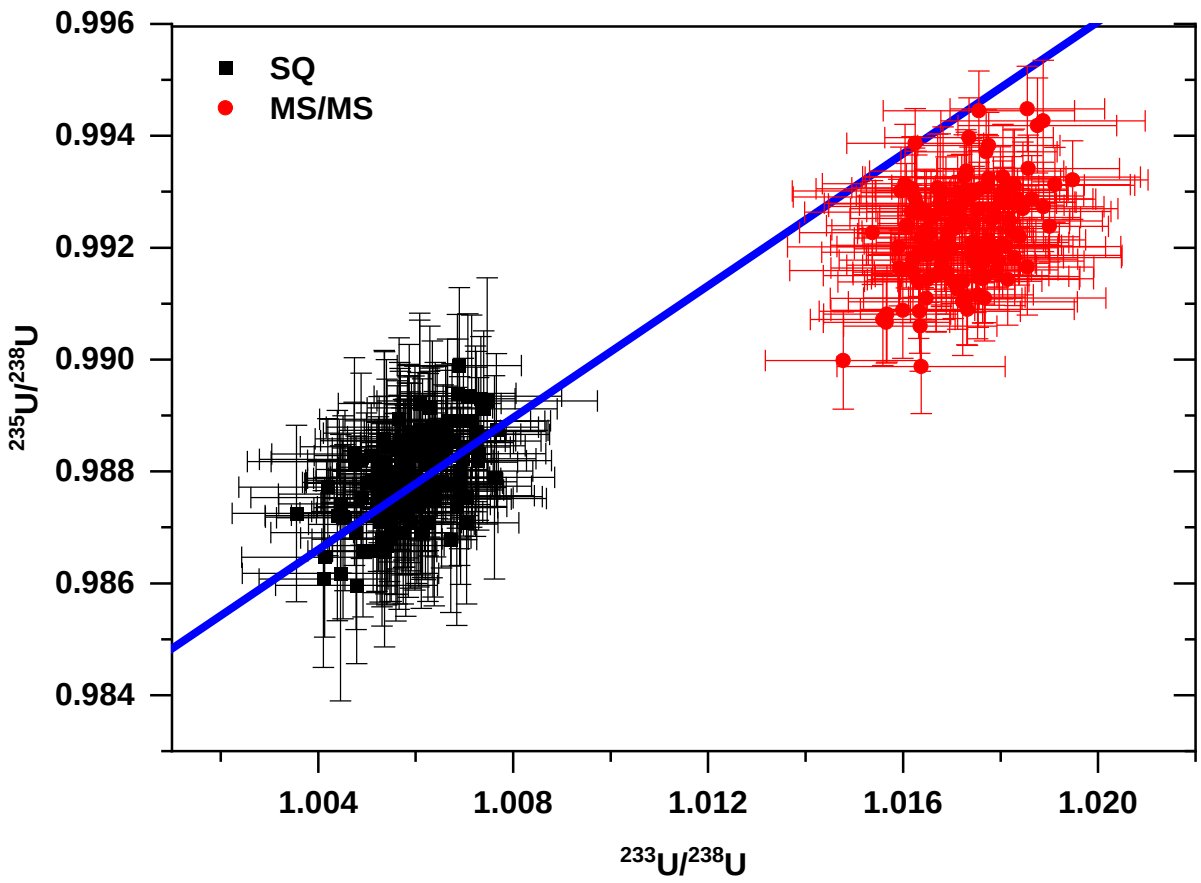

Figure S11. Observed $^{235}U/^{238}U$ isotopic ratios as a function of observed $^{233}U/^{238}U$ isotopic ratios for repeated measurements (n = 130) of an IRMM-074/1 standard reference solution (~0.75 µg L^{-1} total U) using Agilent 8900 ICP-MS/MS in SQ mode and MS/MS mode. Analyses were performed using broad peak resolution settings for Q1 and Q2. Uncertainties of the ratios are expressed as the combined standard uncertainties with coverage factor k = 2. The blue solid line represents the linear mass bias model.

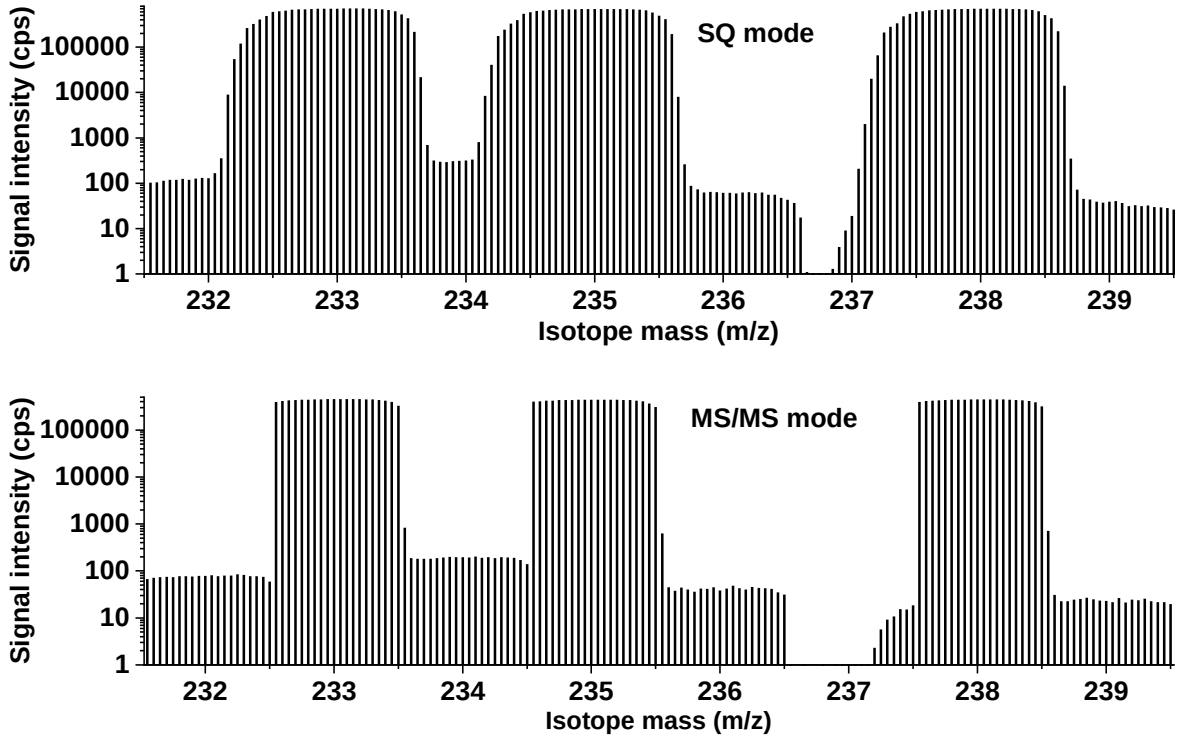

Figure S12. Spectra of a diluted IRMM-074/1 reference solution (~0.75 µg L^{-1} total U) measured in SQ mode and in MS/MS mode. Standard operating conditions with broad peak resolution settings for Q1 and Q2.