PRECISE AND ACCURATE DETERMINATION OF URANIUM ISOTOPES

- **Excellent mass fractionation stability**
- **Excellent short-term IC gain stability**
- **Precise and accurate U isotope determination across a large concentration range**

A CRM U010 standard solution was introduced into the mass spectrometer in 2% HNO_3 under 'dry plasma' conditions, using an Aridus-II Desolvating Nebuliser System with a 100 µL/min glass concentric nebuliser and the Enhanced Sensitivity interface (see Nu Instruments Application Note AN27).

Data was collected using static analysis, with ^{235}U and ^{238}U measured in Faraday cups, ^{234}U and ^{236}U measured in ion-counting electron multiplier detectors IC1 and IC0, respectively. No deceleration filter was used. Each analysis consisted of one block of 40 integrations of 10 s on-peak measurements of U. The analysis duration was ca. 7 minutes. A sequence of 10 repeat analyses was performed, equating to approximately 70 minutes of data collection. Baselines were obtained by a 60 s 'on-peak' blank measurement of a 2% HNO_3 solution at the beginning of each analysis sequence. U oxide levels were measured by monitoring ^{238}U and $^{238}U^{16}O$ using dynamic analysis before and after each sequence, the observed $^{238}U^{16}O/^{238}U$ ratio was below 0.2% in all cases. The instrument was initially tuned for maximum sensitivity, no further tuning was made once a sequence had started. The experiment was repeated on three different U concentrations: 50 ppb, 5 ppb and 1 ppb, each performed on a different day with the plasma being switched off in between.

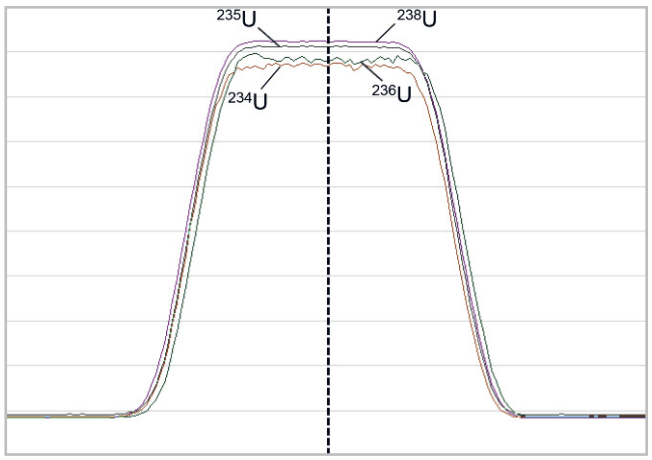

Fig. 1: U isotopes ^{234}U, ^{235}U, ^{236}U and ^{238}U in coincidence. The center of the flat peaks were chosen as the mass analysis position.

The zoom optics maintain good peak shapes (Fig 1) for both ^{235}U and ^{238}U on the Faradays, as well as for ^{234}U and ^{236}U on the ICs, allowing precise isotope measurements of U.

The U beam intensities and backgrounds measured of the 50 ppb, 5 ppb and 1 ppb U010 solutions are presented in Table 1.

Table 1: Mean U beam intensities and background of each set of 10 repeat analyses at 3 different concentrations.

Concentration (ppb)	^{235}U (V)	Total U (V)	U Blank (mV)	Blank Contribution (‰)
50	0.46	46.8	1.2	0.03
5	0.05	5.0	1.0	0.20
1	0.01	0.94	1.0	1.06

No hydride correction or tail correction was applied on the measured ^{236}U beams. Internal normalization was applied on the measured $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios using the certified reference value of $^{235}U/^{238}U = 0.01014$ for U010. IC gain corrections were applied on the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios using the gain values measured prior to each set of analyses. The corrected $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios are reported in Table 2 for each concentration, in comparison with the certified reference values. In all cases, the corrected values agree with the certified values within measurement errors.

Table 2: Fractionation and IC gain corrected $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios measured for the U010 standard solution at 3 different concentrations, in comparison with the certified reference values. All errors are 1RSD. Certified values (averages only) obtained from the U.S. DOE database, measurements performed on a thermal ionization mass spectrometer.

Concentration (ppb)	$^{234}U/^{238}U$ (corrected)	$^{234}U/^{238}U$ (certified)
50	0.00005465 ± 0.035%	0.00005465
5	0.00005461 ± 0.050%	
1	0.00005470 ± 0.094%	
Concentration (ppb)	**$^{236}U/^{238}U$ (corrected)**	**$^{236}U/^{238}U$ (certified)**
50	0.00006866 ± 0.037%	0.00006870
5	0.00006870 ± 0.042%	
1	0.00006872 ± 0.097%	

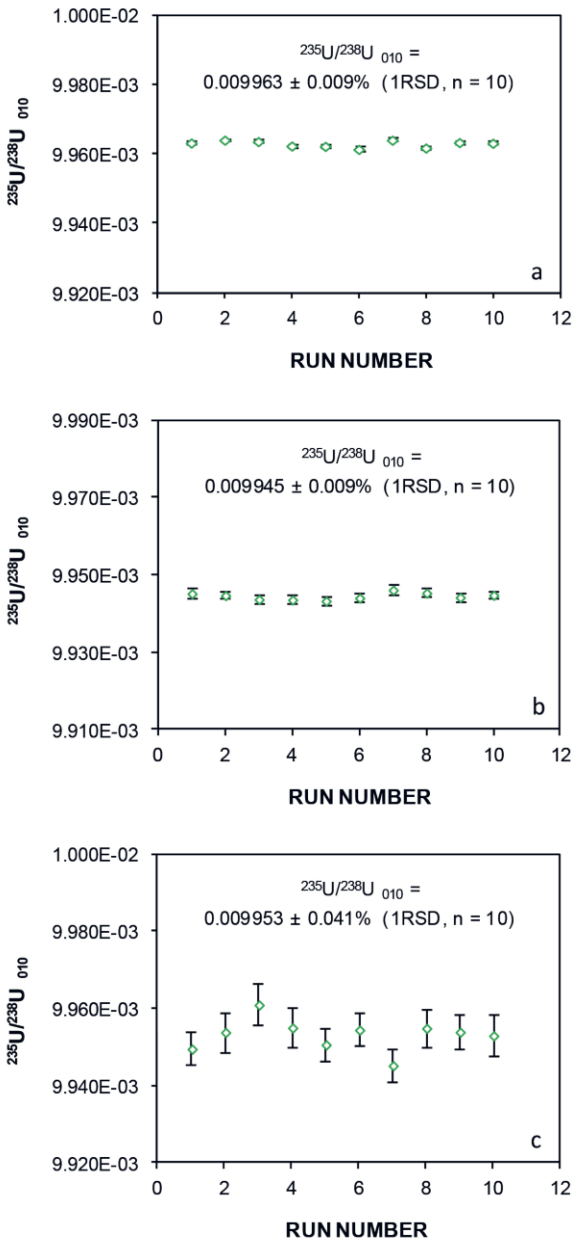

Fig. 2: Uncorrected $^{235}U/^{238}U$ ratios of the a) 50 ppb, b) 5 ppb, c) 1ppb U010 measurements, each set of 10 repeat analyses obtained over the course of 70 minutes. Error bars are 2SE.

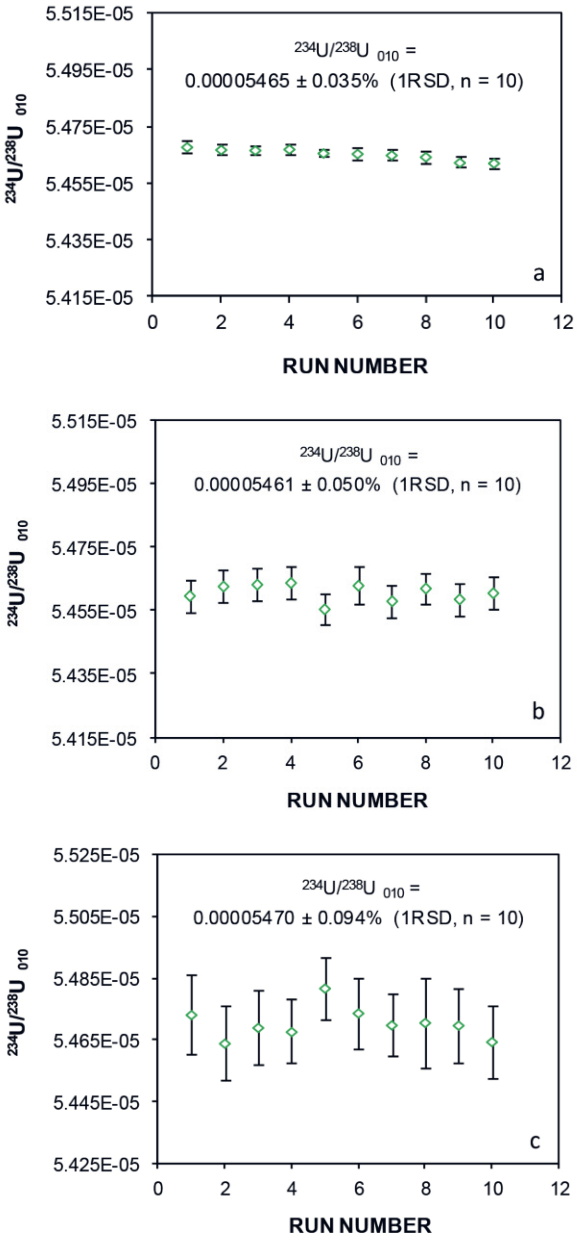

Fig. 3: Fractionation and IC gain corrected $^{234}U/^{238}U$ ratios of the a) 50 ppb, b) 5 ppb, c) 1ppb U010 measurements, each set of 10 repeat analyses obtained over the course of 70 minutes. Error bars are 2SE.

As shown in Fig 2, the external precisions of the uncorrected $^{235}U/^{238}U$ ratios of 10 repeat analyses were better than 0.01% (1RSD) for both the 50 ppb and 5 ppb measurements, exhibiting excellent stability of the plasma conditions and minimal mass fractionation drifts. Measurement uncertainties increased as signal-to-noise ratios decreased for lower concentrations. For the 10 repeat analyses of the 1 ppb solution, the ^{235}U beam intensity was ca. 10 mV, approaching the Faraday baseline. A much larger contribution of the noise resulted in much larger uncertainties of the uncorrected $^{235}U/^{238}U$ ratios.

Fig 3 and 4 show the fractionation and IC gain corrected $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios of the 50 ppb, 5 ppb and 1 ppb U010 measurements. The external precisions of both ratios were better than 0.1% (1RSD, n = 10) for all 3 concentrations, exhibiting very good short-term IC gain stability. Similar to the Faradays, measurement uncertainties on the ICs increased at lower concentrations.

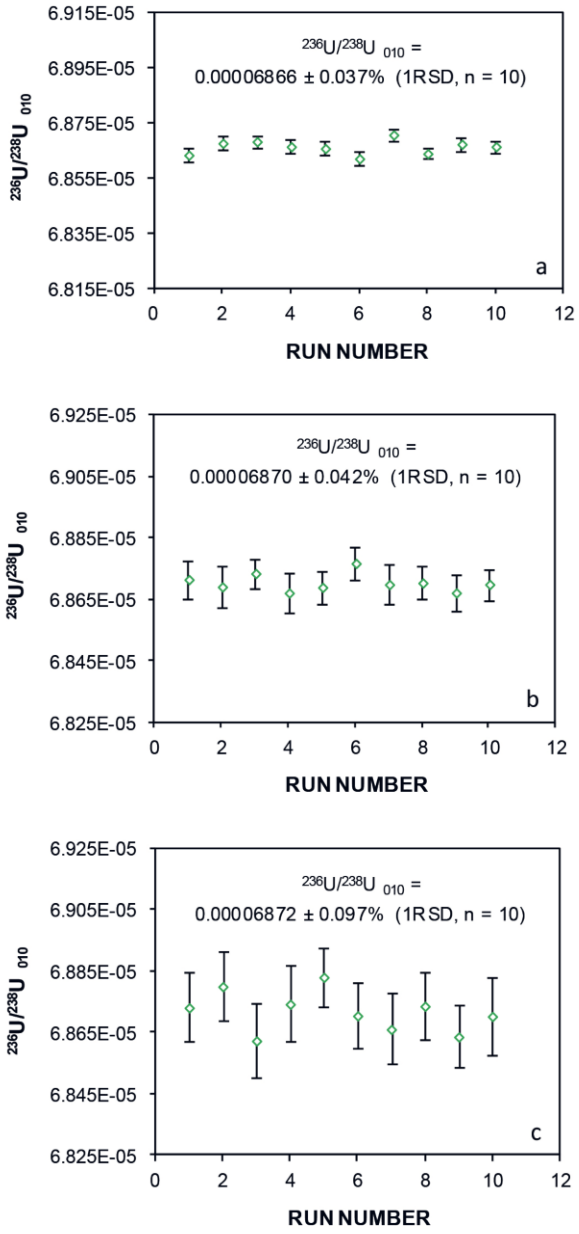

Fig. 4: Fractionation and IC gain corrected $^{236}U/^{238}U$ ratios of the a) 50 ppb, b) 5 ppb, c) 1ppb U010 measurements, each set of 10 repeat analyses obtained over the course of 70 minutes. Error bars are 2SE.

The concentration of the U010 solution used in this study ranged from 1 to 50 ppb, with count rate from 2500 to 130000 cps for ^{234}U, and 3200 to 167000 cps for ^{236}U. The good reproducibility of the corrected ratios $^{234}U/^{238}U$ (1RSD = 0.096%, n = 30) and $^{236}U/^{238}U$ (1RSD = 0.072%, n = 30) demonstrates the excellent linear response of the ICs.

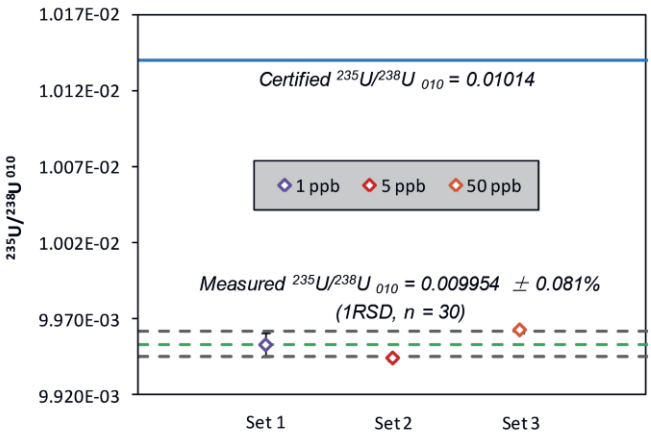

Fig. 5: Uncorrected $^{235}U/^{238}U$ ratios of the 50 ppb, 5 ppb and 1 ppb U010 solutions. Each data point represents the mean of 10 repeat analyses at one concentration, error bars are 2SD (n = 10). Dashed lines represent the mean (green) of the uncorrected $^{235}U/^{238}U$ ratios of all 3 concentrations with 1SD error (grey, n = 30), blue solid line represents the certified reference value of $^{235}U/^{238}U$.

Fig 5 summarises the $^{235}U/^{238}U$ ratios measured at all 3 concentrations. These uncorrected ratios may slightly differ due to mass fractionation shift in the plasma source between different days. The shift was, however, small across a large concentration range, potentially broadening the application range of the sample-standard bracketing method. The observed mass fractionation of U was approximately 0.6% per amu.

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