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Application Brief G10712

Mass Fractionation behaviour of U isotopes during Thermal Ionization, the potential for mass fractionation correction using double spike.

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Introduction

Until recently it was assumed that the terrestrial ^{235}U/^{238}U was 137.88. However high precision ^{235}U/^{238}U measurements using ICP multi collector mass spectrometers[1] as well as double spiked TIMS have shown small variations in ^{235}U/^{238}U at the 1- 2 per mil level. In uranium ores these variations are possibly due to changes in environmental redux conditions[2]. Variations in terrestrial minerals of >5 per mil have also been reported[3], the reasons for these variations is not known.

Whilst TIMS can detect these small variations in ^{235}U/^{238}U a very high quality correction of instrumental mass fractionation is required. Many elements e.g. Sr and Nd possess stable isotopes of known ratio which can be monitored during TIMS analysis and used to correct the radiogenic ratio for the effects of mass fractionation. Unfortunately U (as well as Pb) does not possess a stable isotope pair and mass fractionation must be corrected using an external correction factor, by totally evaporating the sample[4,6,7], or by using a double spike method[2,5].

In the case of total evaporation, small residual mass biases can still exist at the 0.01% level. Analytical reproducibilty is ~0.02 to 0.03% 1RSD (0.2 to 0.3 per mil), which is too large to resolve terrestrial variations.

The alternative is to use a double "spike" of known isotopic composition to correct for mass fractionation. For example a ^{233}U/^{236}U double spike has been shown to correct ^{235}U/^{238}U to a precision of 0.02% 2RSD[5].

This work uses ^{234}U/^{238}U to fractionation correct ^{235}U/^{238}U in SRM U500 in a series of measurements on a Phoenix Thermal Ionization mass spectrometer. This is the reverse of the traditional method where the major isotopes ^{235}U/^{238}U are used to fractionation correct ^{234}U/^{238}U and ^{236}U/^{238}U[6].

Method

2 micrograms of SRM U500 was loaded on one side filament of a triple rhenium filament assembly. Following ion focussing an ion beam of 2e^{-11} A was maintained during the analysis. Data was collected in the static mode in ten blocks of twenty, 10 second integrations. The sample was not analysed to exhaustion.

Results

1. Mass Fractionation during analysis and fractionation correction using ^{234}U/^{238}U.

The results for one analysis are shown in Table 1. During the analysis the ^{235}U/^{238}U ratio reduces as would be expected (see also Figure 1). The ratio approximates the NBS value of 0.9997 by the 5th block. The precision of each block also improves to between 10 and 20ppm 1rse.

The ^{234}U/^{238}U data also shows a reduction in ratio after the first 2 blocks of data. The precision of each block of data is approximately 0.015%. This precision is entirely consistent with counting statistics. For example the ^{234}U ion beam is 2 x 10^{-13} A (20mV). The noise associated with a 0.015% error (0.06% 1RSD) on a 20mV ion beam is: 2x10^{-13} x 0.0006 = 1.2 x 10^{-16} A, which is the equivalent to the noise level of 1e^{11} ohm resistor for a 10 second integration.

We can use the ^{234}U/^{238}U ratio to fractionation correct the ^{235}U/^{238}U. This is shown in Table 1 (^{235}U/^{238}U N column*)* and Figure 1 (pink line). A value of 0.010425 was taken as the reference ratio[6], and using an exponential correction a mean ratio of 0.99973 +/- 0.016% 1RSD is obtained for the 10 blocks of data. This is identical to the certified value. The precision is 4 times better than the uncorrected ^{235}U/^{238}U (1.00013+/-0.06%). The precision of each block of the normalized data is

Block	^{235}U/^{238}U	%1se	^{234}U/^{238}U	%1se	^{235}U/^{238}U N	%1se
1	**1.001670**	0.0070	**0.010453**	0.015	**0.999672**	0.008
2	**1.000427**	0.0033	**0.010436**	0.020	**0.999618**	0.013
3	**1.000059**	0.0014	**0.010428**	0.013	**0.999859**	0.009
4	**0.999975**	0.0014	**0.010433**	0.011	**0.999402**	0.008
5	**0.999730**	0.0013	**0.010426**	0.010	**0.999635**	0.008
6	**0.999629**	0.0008	**0.010424**	0.010	**0.999675**	0.008
7	**0.999761**	0.0012	**0.010424**	0.011	**0.999868**	0.009
8	**0.999966**	0.0016	**0.010427**	0.015	**0.999852**	0.011
9	**1.000084**	0.0011	**0.010428**	0.012	**0.999897**	0.009
10	**1.000043**	0.0016	**0.010429**	0.018	**0.999779**	0.013
MEAN	**1.00013**		**0.010431**		**0.99973**	
1SD	**0.00058**		**0.000009**		**0.00016**	
%1RSD	**0.06%**		**0.08%**		**0.016%**	

Table 1. *Variation in isotope composition during a single analysis of CRM U500.*

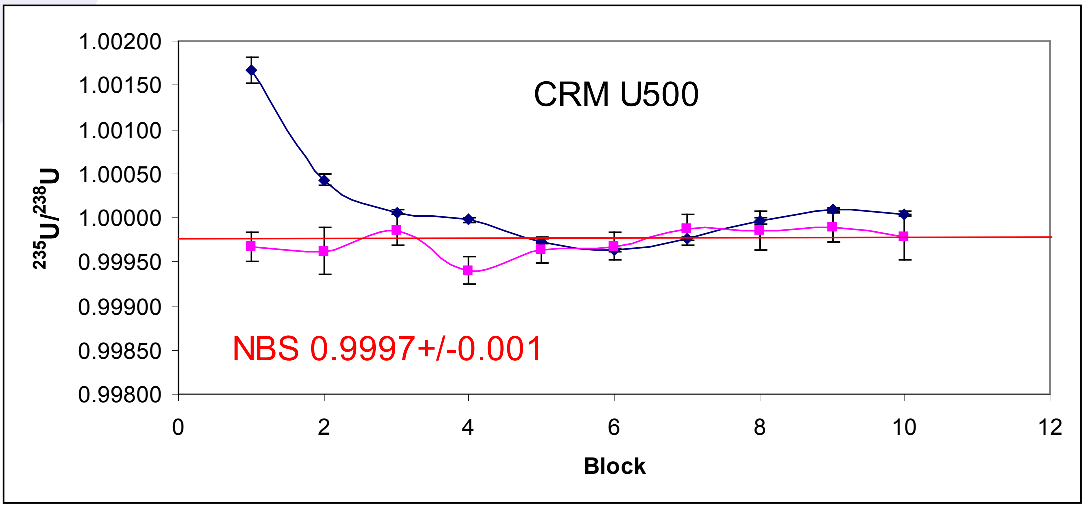

Figure 1. *Variation in ^{235}U/^{238}U of U500 during thermal ionization (not taken to exhaustion). The raw ratios are in blue. The ^{235}U/^{238}U fractionation corrected with ^{234}U/^{238}U=0.010425 are shown in pink. The reference ratio of 0.9997 is shown in red. Note that the certificate has an error of 0.1%.*

worse than the raw ratio, because the largest source of error is the precision of the ^{234}U/^{238}U ratio, i.e. the counting statistics on the ^{234}U measurement.

2. Robustness of this method.

Table 2 shows the results of 16 analyses of U500 using the same analysis protocol. For each analysis the data are presented as the mean of each 200 ratio analysis and the errors are the percentage standard error. For the 16 different filaments the mean ^{235}U/^{238}U without fractionation correction is 1.00016 +/- 0.03%. This is higher than the certified value of 0.9997. The data is comparable to total evaporation data on 500ng loads which gave a ratio of 1.00014 +/-0.02%[7]

Figure 2, is a plot of ^{235}U/^{238}U and ^{234}U/^{238}U expressed as a ppm variation in the isotope ratio with the first measurement as the reference. A mass dependent fractionation would define a linear array with a slope of 1.33. The data define a linear array with a slope of 1.4 which is within error of this value, consequently ^{234}U/^{238}U can accurately correct the ^{235}U/^{238}U, despite the two orders of magnitude difference in isotope abundance between ^{234}Uand ^{238}U. The fractionation corrected ^{235}U/^{238}U is 0.999586+/-0.009% 1RSD. The ratio is slightly lower than the certified value but is more precise by an order of magnitude than the certification (0.1%). An improvement in precision by a factor of 3 over the uncorrected data is achieved, and an accuracy relative to the certificate of 0.01%.

Figure 3 shows what happens to the ^{235}U/^{238}U with different values of the normalizing ratio. There is a linear relationship between ^{235}U/^{238}U N and the ^{234}U/^{238}U ratio chosen as the normalizing ratio. In this work a ^{234}U/^{238}U of 0.010425 (Richter et. al. 2011) yields ^{235}U/^{238}N of 0.999584+/-0.00018 2RSD. Using the certified value of ^{234}U/^{238}U 0.010422 would result in a ^{235}U/^{238}U of 0.99937 which is not within error of the certified value. The data would therefore support the ^{234}U/^{238}U of Richter et. al 2011 as being correct, though a ratio of 0.0104265 would yield the precise value of the CRM ^{235}U/^{238}U of 0.9997

3. Comparison with isotopic composition determined with double spike

Condon et. al 2010[5] used IRMM 3636 (^{233}U-^{236}U) double spike to measure ^{235}U/^{238}U in CRM U500 from two different laboratories and two different TIMS instruments. The ^{235}U/^{238}U was 1.00022+/-0.00016 2RSD. Our uncorrected values of 1.00016+/-0.00060 2RSD is identical within error to this, though both are within error of the CRM (+/-0.1%).

There appears to be a significant difference between the double spiked value of 1.00022+/-0.00016 and our value of 0.99958+/-0.00018.

One possible reason for this could be that peak tailing from ^{235}U on our measurements could result in an over correction of the ^{234}U, (lower ^{234}U/^{238}U). This can be rejected as the abundance sensitivity at -1amu was <2ppm of the major isotope. For a 2e^{-11} A ion beam the uncorrected peak tail of ^{235}U on ^{234}U would be 4e^{-17} A which is less than the Faraday noise for a 10 second integration. A lower measured ^{234}U/^{238}U would result in a normalized ^{235}U/^{238}U which was higher than 0.99958.

An interference under the ^{234}U or uncorrected peak tail, would result in a higher measured ^{234}U/^{238}U, producing a larger correction and hence a lower ^{235}U/^{238}U. This can be rejected because the measurements were made over several filaments and Figure 2 shows a significant correlation without outliers.

Our data are consistent with those of Richter et.al. 2011. We therefore do not understand at the moment why the double spiked data is different from our data.

Conclusions

1. **Internal mass fractionation correction of $^{235}U/^{238}U$ in NBS U500 using $^{234}U/^{238}U=0.010425$ improves the precision of $^{235}U/^{238}U$ by a factor of 3 to <0.01% 1RSD, despite the large $^{234}U/^{238}U$.**
2. **The $^{235}U/^{238}U$ = 0.999586 is within 0.01% of the certificate value of 0.99968.**

Sample	^{238}U intensity (amps)	$^{235}U/^{238}U$	% 1se	$^{236}U/^{238}U$	% 1se	$^{234}U/^{238}U$	% 1se	$(^{235}U/^{238}U)_N$
1	1.9E-11	0.999814	0.001	0.001516	0.019	0.010427	0.003	0.999671
2	1.8E-11	1.000014	0.002	0.001512	0.051	0.010430	0.006	0.999687
3	1.7E-11	1.000002	0.003	0.001491	0.082	0.010429	0.005	0.999710
4	1.9E-11	1.000079	0.002	0.001507	0.023	0.010430	0.004	0.999693
5	1.8E-11	0.999740	0.003	0.001506	0.078	0.010428	0.007	0.999501
6	1.8E-11	1.000116	0.006	0.001513	0.040	0.010431	0.011	0.999705
7	1.8E-11	0.999989	0.001	0.001508	0.024	0.010431	0.004	0.999525
8	1.9E-11	1.000736	0.005	0.001520	0.021	0.010442	0.007	0.999481
9	1.9E-11	0.999832	0.005	0.001524	0.019	0.010430	0.008	0.999505
10	1.8E-11	1.000199	0.003	0.001498	0.036	0.010433	0.006	0.999633
11	1.9E-11	1.000058	0.004	0.001518	0.022	0.010432	0.006	0.999578
12	1.9E-11	1.000540	0.005	0.001524	0.022	0.010438	0.008	0.999621
13	1.9E-11	1.000009	0.007	0.001512	0.019	0.010433	0.010	0.999464
14	1.9E-11	1.000398	0.003	0.001519	0.022	0.010438	0.005	0.999497
15	1.9E-11	1.000501	0.004	0.001518	0.020	0.010439	0.007	0.999477
16	1.8E-11	1.000583	0.001	0.001520	0.023	0.010438	0.004	0.999622
mean		**1.00016**	**0.003**	**0.001513**	**0.03**	**0.010433**	**0.006**	**0.999586**
1SD		**0.00030**		**0.000009**		**0.000005**		**0.000092**
1RSD		**0.03%**		**0.60%**		**0.044%**		**0.009%**
CRM		0.9997		0.001523		0.010425		0.9997
Accuracy		0.05%		-0.66%		0.08%		-0.01%

Table 2. *Replicate analyses of CRM U500. The $^{234}U/^{238}U$ and $^{236}U/^{238}U$ of CRM U500 are from Richter et. al. 2011.*

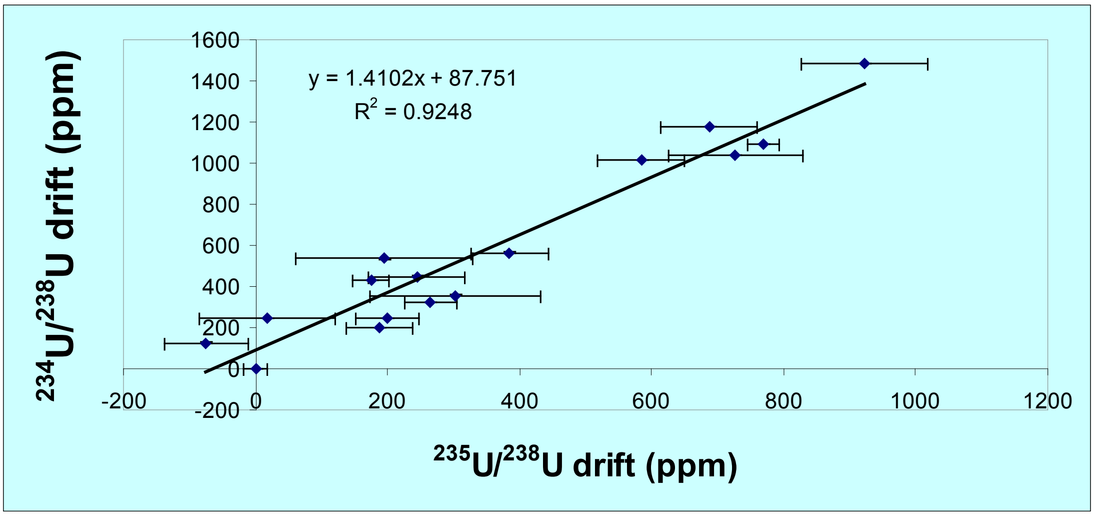

***Figure 2**. Correlation between $^{234}U/^{238}U$ and $^{235}U/^{238}U$ showing mass dependent fractionation behaviour between filaments.*

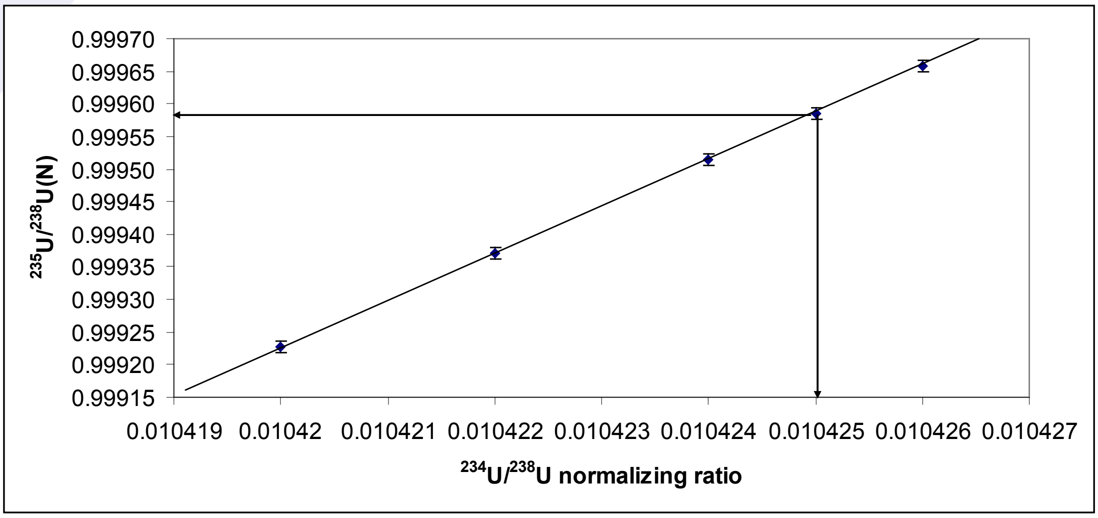

***Figure 3**. Variation in ^{235}U/^{238}U with different values of the normalizing ratio.*

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