Application Brief G30111

Determination of ^{234}U and ^{236}U in IRMM184 Uranium Standard on the Phoenix Thermal Ionization Mass Spectrometer.

GEOLOGY

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Introduction

IRMM 184 has an extremely low level of ^{236}U (0.12ppm relative to ^{238}U) and a high quality analysis of this minor isotope requires the use of an ion counting detector equipped with a retarding filter.

Application Brief G20111 describes a multi-step analysis routine combining Faraday and Daly ion-counting to measure $^{234}U/^{238}U$ and in this note we extend the analysis to include the ^{236}U isotope.

The measurements described in this note were obtained on a different spectrometer to that in G20111 highlighting the high degree of consistency between Phoenix instruments.

High Precision and Accuracy

To obtain high precision and accuracy the relative gain between the Daly and the Faradays must be measured extremely precisely. The most convenient method of achieving this is to use a multi-sequence routine where ^{235}U is measured on both Faraday and Daly detectors permitting the Faraday/Daly gain to be accurately measured in real time (Table1).

Collector	Daly	H1	H2	H3	H4
Sequence 1	234	235			238
Sequence 2	235			238	
Sequence 3	236		238		

Table 1. Analytical sequence

In the first sequence ^{234}U is measured on the Daly while ^{235}U and ^{238}U are measured simultaneously on Faraday collectors. Sequence 2 is initiated with a peak jump which places mass ^{235}U on the Daly with ^{238}U on the H3 Faraday. Once Sequence 1 and 2 are complete the Faraday/Daly gain can be determined by dividing the $^{235}U/^{238}U$ measured in sequence1 (F/F) by that in sequence 2 (F/D). The excellent linearity of the Daly means that the gain calculated for $^{235}U/^{238}U$ can also be used to correct $^{234}U/^{238}U$ and $^{236}U/^{238}U$ even though the ratios are significantly different.

Finally, a fractionation correction is calculated by comparing $^{235}U/^{238}U$ from sequence 1 with the accepted value. This is then used to fractionation correct the already gain corrected $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios.

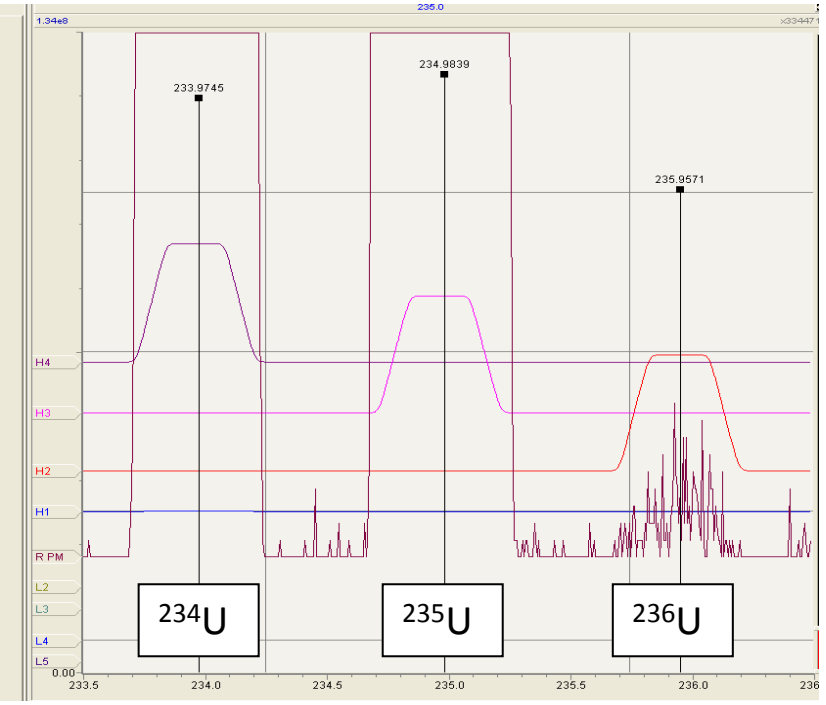

Figure 1. Mass scan showing Faraday/Daly coincidence.

Abundance Sensitivity

A scan showing ^{234}U ,^{235}U and ^{236}U on the ion-counting Daly (with WARP filter) is shown in Figure 1. The Daly trace is off-scale for ^{234}U and ^{235}U to allow visualization of the very small ^{236}U signal. The other 3 traces show ^{238}U on the H2, H3 and H4 Faradays

Note the lack of any tailing from ^{238}U on the high mass side of the ^{236}U peak. With the WARP filter activated the abundance sensitivity measured at m/z 237 with respect to ^{238}U is approximately 5e-9. At ^{236}U the ^{238}U contribution is not measurable on the Daly and so must be less than 1e-10 of the ^{238}U intensity.

IRMM184 analyses

Single microgram loads of IRMM184 were loaded onto one side filament of a triple Re filament assembly. The routine shown in Table 1 was used with each sequence taking 10 seconds to give a total of 30 seconds per ratio measurement. A total of 200 ratio measurements were taken on each bead to give a total time taken per analysis including filament warm up and focussing of around 3 hours.

The results are shown in Table 2

Bead	^{238}U (amps)	F/D gain	% 1RSE	^{234}D/^{238}F gain and fractionation corrected	%1RSE	^{236}D/^{238}F gain and fractionation corrected	%1RSE
1	2.5E-11	**1.05683**	**0.10**	**0.00005306**	**0.036**	**0.000000117**	**1.14**
2	2.2E-11	**1.04633**	**0.02**	**0.00005308**	**0.035**	**0.000000119**	**0.74**
3	2.3E-11	**1.03992**	**0.02**	**0.00005306**	**0.040**	**0.000000121**	**0.84**
4	2.3E-11	**1.04896**	**0.02**	**0.00005312**	**0.042**	**0.000000116**	**0.82**
5	2.2E-11	**1.03667**	**0.02**	**0.00005307**	**0.036**	**0.000000120**	**0.74**
6	2.2E-11	**1.04774**	**0.01**	**0.00005310**	**0.038**	**0.000000124**	**1.05**
7	2.2E-11	**1.04215**	**0.03**	**0.00005321**	**0.044**	**0.000000127**	**0.97**
8	2.2E-11	**1.04197**	**0.04**	**0.00005312**	**0.044**	**0.000000124**	**0.77**
9	2.2E-11	**1.04071**	**0.04**	**0.00005306**	**0.034**	**0.000000121**	**0.82**
10	2.3E-11	**1.04911**	**0.10**	**0.00005305**	**0.033**	**0.000000116**	**0.92**
11	2.3E-11	**1.05352**	**0.03**	**0.00005308**	**0.045**	**0.000000118**	**0.81**
MEAN		**1.04581**	**0.04**	**0.00005309**	**0.04**	**0.000000120**	**0.9**
1SD		**0.00614832**		**0.00000005**		**0.000000004**	
1RSD %		**0.59%**		**0.09%**		**3.00%**	
IRMM				0.00005314		0.0000001245	
(+/-)				0.00000003		0.0000000002	

Table 2. Data from 11 consecutive beads loaded with 1µg of IRMM184

F/D Gain Correction

The RSD of the Faraday/Daly gains measured across all 11 beads is 0.59%. However, the mean of the 'within run' gains is an order of magnitude better at 0.04%. This difference is most likely due to the varying position of the sample on each filament leading to differences in focus conditions and so a change in F/D gain. Once an individual bead is focussed and running the gain is very stable. This highlights the importance of using the within-run gain cancelling method as it automatically calculates the gain for each filament rather than assuming that a value calculated on one filament is equally applicable to others.

Results

The mean value for the gain and fractionation corrected ^{234}U/^{238}U is 0.00005309 +/- 0.09%. This compares well with 0.00005310+/-0.09% which was obtained on a second Phoenix instrument and matches closely with the certified value.

The ^{236}U/^{238}U is 1.20e-7 +/- 3.0%. For a sample with this ratio, a ^{238}U ion beam of 2.2e-11A would result in ^{236}U count rate of around 10cps. The theoretical error on this small ion beam calculated from counting statistics is around 3% which closely matches the RSD recorded here. This is a powerful demonstration of the stability of the Phoenix ion-counting Daly.

Summary - A multi-static analysis routine which combines Faraday and ion counting Daly detector produces sub per mil ^{234}U/^{238}U data by online correction of the Faraday/Daly gain. The ^{236}U can be accurately measured with a WARP filter removing the peak tail from the ^{238}U

Further Reading: For related information see Isotopx Application Brief G20111 - Determination of ^{234}U in IRMM184 Uranium Standard on the Phoenix Thermal Ionization Mass Spectrometer.