

Isotope Ratio Analysis of Low Abundance Uranium Isotopes

Key Words

- High Resolution ICP-MS
- Isotope Ratio
- Detector
- Uranium
- Low Abundance Isotopes
- Analog Conversion Factor
- Finnigan™ ELEMENT2

The rapid and reliable determination of natural ^{234}U and anthropogenic ^{236}U in environmental samples is challenging as these isotopes have very low abundances of only several ppm relative to the major uranium isotope ^{238}U . These low abundances make analyses difficult, requiring the most sensitive and stable instrumentation¹⁻⁴.

Most modern ICP-MS detection systems have two user definable detector modes to allow the measurement of low and high ion signals. In the Finnigan™ ELEMENT2 sector field ICP-MS, these detector modes are termed Counting and Analog respectively.

• Counting mode:

All the dynodes of the SEM (secondary electron multiplier) amplify electrons released by the impact of ions on the conversion dynode. These electron pulses are counted directly to give the counting signal. Because all dynodes of the SEM are used, the amplification is highest and therefore this detector mode is used for the detection of low intensities (<5 Mcps).

• Analog mode:

Only the first dynodes of the SEM are used for amplification of the electrons from the conversion dynode. The charge of this electron cloud (measured after the seventh dynode) is constantly monitored through an integrating system to give the analog signal. This mode is used for the detection of higher ion signals (max. 5 Gcps) that require a lower amplification factor.

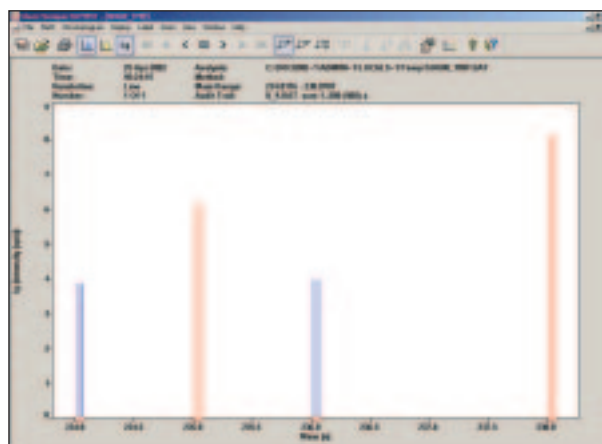


Figure 1: Spectrum of CRM NBS U010, 100 ng g⁻¹ uranium, logarithmic scale. Blue = counting, red = analog

In multi-elemental analyses a software-defined detector mode, the Both mode, is used. By selecting this mode, the choice of actual detector mode is made by the ELEMENT2

control software, freeing the user from choosing a detector mode for each analysis. For optimum isotope ratio determinations, previous ICP-MS studies⁵ have recommended the use of the same detector mode for all isotopes in order to avoid inaccuracies from cross-calibration between detector modes. For the analysis of extremely large isotope ratios such as $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ the use of the same detector mode for all isotopes is often not practical. For these analyses the more abundant isotopes have to be measured in the analog mode while counting mode is used for the least abundant isotopes (Figure 1). This analysis requires a stable and well-defined detector mode cross calibration.

In the Finnigan ELEMENT2 the cross calibration factor between the counting and analog detector modes is termed the analog conversion factor (ACF). During multi-element measurements the ACF is constantly updated, guaranteeing automatic detector mode cross calibration. Nevertheless, for high accuracy isotope ratio analyses the ACF should be established manually for the target isotope. In this study, an uranium specific ACF was obtained by acquiring 30 spectra across a ^{238}U peak of 1 x 10⁶ cps in the Both mode, giving a precise, easily definable ACF for subsequent analyses.

With these settings and an acquisition time of <4 min per sample (Table 1), excellent precision for the three isotope ratios analyzed could be obtained. Due to the high sensitivity and stability of the Finnigan ELEMENT2, isotope ratio precisions of <0.3% RSD for $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, and $^{236}\text{U}/^{238}\text{U}$ (Table 2) were achievable (100 ng g⁻¹ uranium CRM U010), although ^{234}U and ^{236}U were present only in low ppm abundance (Figure 2). The precision refers to the external reproducibility from 10 replicate analyses without any manipulation of the data (e.g. outlier rejection) except for automatic deadtime correction.

Sample introduction	Stable Sample Introduction Kit with PFA nebulizer at 0.05 ml/min, self-aspiration
Plasma	1250 W, Guard Electrode
Sample	100 ng g ⁻¹ CRM U010 in 2% HNO ₃ ("Baseline" purity, Seastar Chemicals, Canada)
Integration time & detector mode	^{234}U 100 s (counting), ^{238}U 10 s (analog), ^{236}U 100 s (counting), ^{238}U 10 s (analog)
Total number of scans	500
Total time of method	3:41 min

Table 1: Instrument settings used for the analysis of uranium isotope ratios

Ratio accuracies are also excellent, especially since the $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ ratios are more than two orders of magnitude smaller than $^{235}\text{U}/^{238}\text{U}$.

The high data quality obtained gives a clear picture of the precision and accuracy that can be obtained on a single collector instrument.

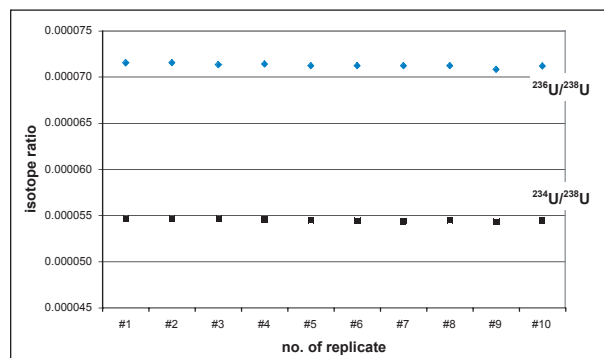


Figure 2: Stability of $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ over 40 min

RATIO:	$^{234}\text{U}/^{238}\text{U}$ [ppm]	$^{235}\text{U}/^{238}\text{U}$ [ppm]	$^{236}\text{U}/^{238}\text{U}$ [ppm]
DETECTION MODE:	C/A	A/A	C/A
#1	54.63	10137	71.54
#2	54.65	10135	71.55
#3	54.64	10127	71.32
#4	54.55	10133	71.39
#5	54.48	10136	71.22
#6	54.42	10143	71.24
#7	54.35	10159	71.22
#8	54.51	10151	71.22
#9	54.32	10140	70.82
#10	54.45	10142	71.19
Average (n=10)	54.50	10140	71.27
Stdev (n=10)	0.12	9	0.21
RSD (n=10)	0.22%	0.09%	0.29%
Standard error	0.07%	0.028%	0.09%
Certified ratio:	54.6	10140	68.7
Accuracy:	-0.2%	0.003%	3.7%

Table 2: Results from 10 replicate isotope ratio measurements of CRM U010 at 100 ng g^{-1} in Low Resolution mode.

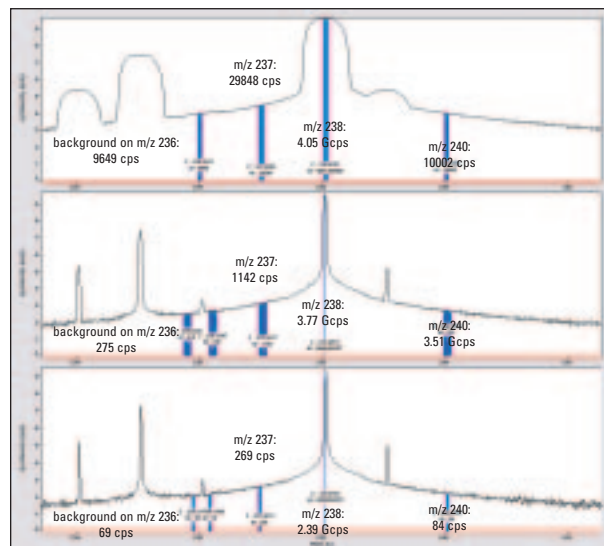


Figure 3: Abundance sensitivity of uranium on a logarithmic intensity scale. Upper pane: $2 \mu\text{g g}^{-1}$ U in Low Resolution (LR) mode; middle pane: $20 \mu\text{g g}^{-1}$ U in Medium Resolution (MR); lower pane: $100 \mu\text{g g}^{-1}$ U in High Resolution (HR)

Tips

- The precision values in Table 2 are presented as both %RSD and as a standard error. The standard error is more commonly used in multi-collector measurements and is calculated as:

$$\text{standard error} = \text{standard deviation} / \text{square root of number of values used}$$

Its meaning is simple: the more values used to generate an average, the more reliable the value (and therefore the smaller the deviation from the average).

- For the measurement of large isotope ratios, the abundance sensitivity of the instrument needs to be considered. Abundance sensitivity is specified for the Finnigan ELEMENT2 (with the optional abundance sensitivity kit) to be $< 3 \times 10^{-5}$ for 237/238; equivalent to approximately 8×10^{-6} for the analytically more important 236/238 ratio. These figures are for measurements made in low resolution (LR); however, abundance sensitivity can be increased by moving to higher mass resolutions⁶. Example spectra are shown in Figure 3, displaying the tailing of an intense uranium signal in all three available resolutions. The abundance sensitivity (236/238) for these spectra is 2×10^{-6} in LR, 7×10^{-8} in MR, and 3×10^{-8} in HR.
- Abundance sensitivity during the experiments described above was found to be 5×10^{-6} for 236/238 in LR. This means that a measured isotope ratio of 50 ppm will be displayed as 55 ppm. This error has to be corrected for mathematically.
- The contribution of ^{235}U on ^{236}U can be reduced by using a desolvating nebulizer. Nevertheless, the accurate results presented in this report were collected without desolvation.

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