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# Multiple ion counting ICPMS double spike method for precise U isotopic analysis at ultra-trace levels

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**Abstract**

Of the various methods for the measurement of the isotopic composition of U in solids and solutions, few offer both sensitivity and precision. In recent years, the use of ICPMS technology for this determination has become increasingly prevalent. Here we describe a method for the determination of the $^{235}U/^{238}U$ ratio in very small quantities ($\leq$350 pg) with an accuracy of better than 3‰. We measured several terrestrial standard materials and repeated analyses of the U960 isotopic composition standard. We used a $^{233}U/^{236}U$ double spike, with multiple ion counting on an unmodified Nu Instruments multicollector ICPMS and a non-standard detector configuration that allows an approximately 20-fold sensitivity gain over the best conventional techniques. This technique shows promise for the detection of isotopic tracers in the environment (for example anthropogenic $^{238}U$) at very extreme dilutions, or in cases where the total amount of analyte is necessarily limited.


*Keywords:* Double spike method; Isotope ratio measurements; Multicollector inductively coupled plasma mass spectrometry; Uranium

## 1. Introduction

The isotopic composition of the long-lived isotopes of U is constant in nature. Since the ratios of the decay constants of $^{235}U$ and $^{238}U$ are fixed, the ratio of the two to one another is fixed at any given point in time for terrestrial materials. Terrestrial variations in $^{235}U/^{238}U$ are primarily due to anthropogenic modification for the purpose of inducing nuclear fission. However, there are natural processes that can also affect this isotopic ratio including: (1) environmental mass dependent fractionations (in principle); (2) regions of natural nuclear fission [1]; and (3) in principal, cosmochemically-derived deviations due to the decay of $^{247}Cm$ during nucleosynthesis [2,3].

The precise measurement of the $^{235}U/^{238}U$ ratio has a long history, being a motivating force driving much of mass spectrometry in the early part of the preceding century. This was of course due to the need to measure enrichment grades of fissile $^{235}U$ in concentrates derived from ores with a natural $^{235}U/^{238}U$ ratio of 0.007253. Currently, there are a variety of techniques for this determination, which vary remarkably in their sensitivity and accuracy. These include counting-based nuclear spectroscopy, TIMS (thermal ionization mass spectrometry) and ICPMS (inductively coupled plasma mass spectrometry). Of the mass spectrometric techniques utilizing an ICP ion source, there is the further distinction between quadrupole, and magnetic/electrostatic types, of which there are commercially available models with single and multiple collectors (MC-ICPMS). Each of these ICPMS configurations delivers progressively more precise and sensitive results.

While each of the above techniques has a particular application, many methods developed for them rely upon the assumption that there is a nearly unlimited amount of available sample. Although large sample amounts are often available, this is not often the case when it comes to biological, environmental and cosmochemical samples. Recognizing sample limitations such as these, we wanted to develop a method that consumes a limited amount of sample yet can yield good

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isotopic precision. Here, we report a new method of determining the $^{238}U/^{235}U$ ratio in solutions using dynamic multiple ion counting.

## 2. Methods

### 2.1. Chemistry and sample preparation

Solutions of $^{960}U$ isotopically natural standard reference uranium were prepared with a concentration of 100 pg U/g in 1% $HNO_3$. These solutions were spiked with an isotopic tracer containing well-characterized equal-atom $^{233}U$ and $^{236}U$ previously prepared for this purpose for TIMS measurements [3]. We prepared the standard solutions such that the $^{238}U/^{236}U$ ratio was ∼10.

To test the efficacy of our method on natural samples, we selected three terrestrial Standard Reference Materials [GS-N (ANRT granite), MA-N (CRPG granite), and MICA-Fe (CRPG biotite mica)]. We dissolved each sample using ultrapure reagents ($HF/HNO_3$) under clean-room conditions, and removed a small aliquot (∼5%) for U quantification. We spiked the remaining dissolved material so that the $^{238}U/^{236}U$ ratio was ∼10. This provides adequate precision while conserving spike. After drying down and re-dissolving to ensure sample-spike equilibration, we used standard (e.g. [4] and references therein) column purification procedures to isolate uranium from the matrix of the SRMs for U for isotopic analysis.

### 2.2. Instrumentation and measurement

We measured the solutions on a Nu Instruments MC-ICPMS using a CETAC Aridus desolvating nebulizer with the operating conditions shown in Table 1. The mass spectrometer is equipped with an electrostatic zoom lens that creates a variable dispersion at the collector end. In its default configuration the machine utilizes unit mass dispersion (Fig. 1a), resulting in a mass separation between the ion counters of 2 for the mass range near uranium. This configuration is not optimal for the determination of our low-concentration double-spiked isotope ratios because the masses of interest ($^{235}U/^{238}U$ and $^{233}U/^{236}U$) are three mass units apart rather than two. Measuring the large $^{238}U$ beam in a Faraday cup and the small $^{235}U$ beam in an ion counter would make sense, and is commonly done. However, for very small amounts of U, the signal strength is low enough that the inherent dark noise of the Faraday cup limits the precision of the analysis. Additionally, the $^{233}U/^{236}U$ ratio would not be well determined, since both isotopes tend to be small for reasonable sample/spike ratios. Using larger amounts of spike is not desirable, since the spike itself is costly.

For this study, we set the zoom optics of the mass spectrometer to a mass dispersion factor of 1.5 (Fig. 1b and Table 1). The three-mass difference between masses 238 and 235 then corresponds exactly to the spacing between the ion counting systems, so that both the $^{235}U/^{238}U$ ratio and the $^{233}U/^{236}U$ ratio can be statically ion counted. In the first cycle of the multidynamic sequence we can therefore monitor masses 235 and 238 then with the second cycle masses 235 and 236 (see Table 1). Our configuration could be easily accomplished with other multiple ion counting systems where the ion counters are appropriately spaced.

Table 1
Nu Instruments MC-ICPMS operating conditions

| | |
|---|---|
| Plasma | |
| RF power | 1300 W |
| Reflected power | ≤5 W |
| Ni sampling cone | 1.1 mm diameter |
| Ni skimmer cone | 0.6 mm diameter |
| Nebulizer setup | |
| Ar sweep rate | 3.8 l min$^{-1}$ |
| $N_2$ | 0 l min$^{-1}$ |
| Uptake rate | 0.05 ml min$^{-1}$ |
| Optics | |
| ESA | 230 V |
| Mass resolution | 400 at $^{208}Pb$ |
| Zoom optics | |
| Quad 1 | −25 V |
| Quad 2 | +140 V |
| Quad 15 | As necessary[a] |
| Quad 16 | As necessary[a] |
| Integration times | |
| Magnet settle | 2 s |
| Magnet setting 1 (235,238) | 15 s |
| Magnet setting 2 (233,236) | 10 s |
| Total integrations | 3 blocks of 5 (∼10 min) |

[a] See text.

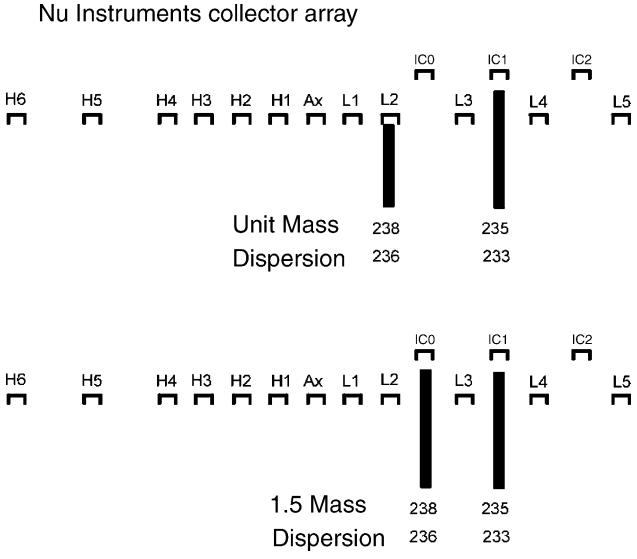


Fig. 1. Mass dispersion used for U isotopic analysis. The convention for relative mass dispersion in this context is the mass separation between two adjacent detectors. The Nu Instruments MC-ICPMS achieves variable dispersion via ion optics between the magnetic sector and detectors.

### 2.3. Multidynamic U calculations

Writing the power-law expressions for a forward model of the fractionation and gains operating on the two isotope pairs involved is quite simple:

$$\left(\frac{^{238}U}{^{235}U}\right)_M = \left(\frac{^{238}U}{^{235}U}\right)_T (1+f)^3 \left(\frac{G_0}{G_1}\right) \quad (1)$$

$$\left(\frac{^{236}U}{^{233}U}\right)_M = \left(\frac{^{236}U}{^{233}U}\right)_T (1+f)^3 \left(\frac{G_0}{G_1}\right) \quad (2)$$

where $f$ is the power-law fractionation factor and $G_0$ and $G_1$ are the gains on collectors $IC_0$ and $IC_1$, respectively. The cubic exponents refer to the three mass-unit difference between the isotopes. Dividing Eq. (1) by Eq. (2) and solving for the true $^{238}U/^{235}U$ ratio gives:

$$\left(\frac{^{238}U}{^{235}U}\right)_T = \frac{(^{238}U/^{235}U)_M (^{236}U/^{233}U)_T}{(^{236}U/^{233}U)_M} \quad (3)$$

Eq. (3) shows that both mass-dependant fractionation and collector gain are cancelled out using this data reduction. This is the same reasoning commonly used for multidynamic Sr and Nd isotopic data reduction (cf. [5]). The difference between the power law and other possible fractionation laws is not significant at the level of precision used here.

## 3. Results

Two sigma results of replicate measurements on our natural-ratio U960 standard and the three terrestrial Standard Reference Materials are presented in Table 2. Typical internal precision for our standards ranges from 0.5 to 1.5‰ while using between 200 and 350 pg per analysis for a total of ~1 ng of U for four replicate analyses. The relationship between typical individual measurements and the mean results in Table 2 are shown in Fig. 2 and discussed in the next section.

Table 2
$^{235}U/^{238}U$ isotopic results of standard materials

| Sample | $N$ | $\delta^{235}U$ (‰) | $2\sigma m$ error (‰) | Total U (ng) |
|---|---|---|---|---|
| U960 standard 25-8-03 #1 | 1 | −0.99 | 1.36 | 0.35 |
| U960 standard 26-8-03 #1 | 1 | +0.61 | 1.34 | 0.35 |
| U960 standard 08-9-03 #1 | 1 | −0.46 | 1.14 | 0.35 |
| U960 standard 25-7-03 #1 | 1 | +0.63 | 1.09 | 0.35 |
| GS-N (ANRT granite SRM) | 4 | −1.04 | 1.98 | ~1 |
| MA-N (CRPG granite SRM) | 4 | −0.33 | 1.70 | ~1 |
| MICA-Fe (CRPG mica SRM) | 4 | −0.97 | 1.42 | ~1 |

External reproducibility based on all $^{960}U$ standard measurements: $N = 58$, mean = 137.87, $2\sigma m = 0.045$, $2\sigma$ reproducibility = 2.25‰.

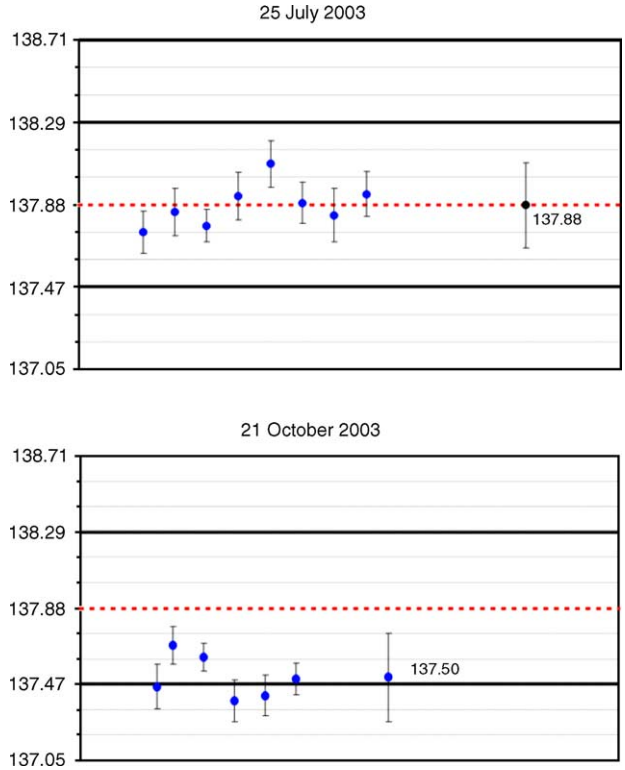


Fig. 2. Intraday reproducibility of $^{960}U$ isotopic measurements without bracketing. Major grid lines are at 3‰ spacing.

### 3.1. Reproducibility

Over about 6 months of measurement, the mean intraday $2\sigma$ reproducibility was 1.5‰ for samples with less than about 350 pg of U per analysis. This is illustrated in Fig. 2, showing a single measurement series and accompanying average. On other days, while the reproducibility remained the same, the mean value of the analyses of $^{960}U$ varied by as much as 3‰. This effect seems to be influenced by the settings of the quadrupole zoom optics of the Nu Instruments mass spectrometer. The deviations can be controlled to some extent by carefully adjusting the Q15 and Q16 quadrupole focus (Table 1) until the peak shape is optimized. The overall $2\sigma$ reproducibility determined without prior standardization was 2.25‰ using individual sample sizes of under 350 pg ($8.8 \times 10^{11}$ U atoms). This figure improves to 1‰ or better by bracketing of unknowns with $^{960}U$ and renormalizing.

### 3.2. Sensitivity

The term sensitivity generally refers to the ability to detect an element at a given concentration. In this case, we refer to the sensitivity of the method to refer to the ability to measure an isotopic ratio with a given precision at a given concentration. So defined, the sensitivity of the method is very good when compared to other methods. In Fig. 3 we show the analytical precision plotted as a function of total U for various isotopic analysis techniques. The tradeoff between precision

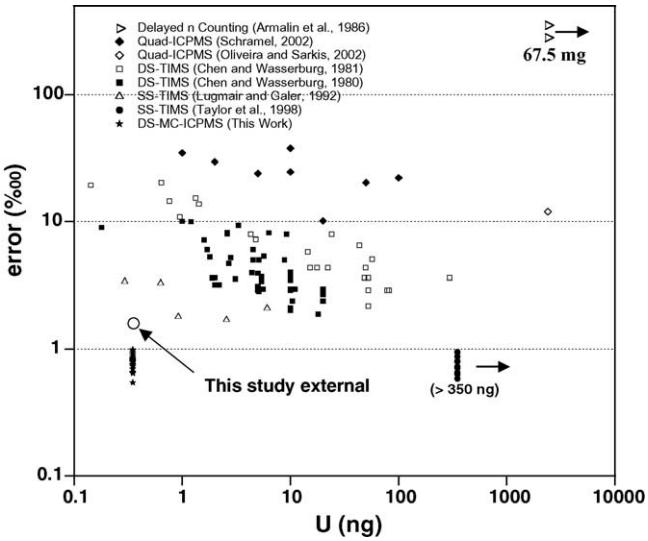


Fig. 3. Sensitivity and precision compared with other methods. Circle is the external reproducibility, stars are the internal precision in $^{238}U/^{235}U$ is plotted as a function of total U consumed during the analysis. Literature data from [2,6,8–12].

and sensitivity is reflected in results sloping downward from upper left to lower right in this diagram, due in large part to simply to counting statistics. Shifting to better sensitivity produces a parallel array with a lower precision for a given amount of U. The single-spike analyses of [6] showing better precision than previous double spike measurements (e.g. [2]) is likely due to improvements in instrumentation in the intervening time. Our double spiked MC-ICPMS measurements using the ion counters is substantially more sensitive for the U isotopic analysis compared to conventional TIMS analysis and about factor 5 compared to quadrupole analysis (Fig. 3).

The internal precision is better, even with bracketing, than the external precision. This may be due to instabilities in the peak shape. The peak shape on the Nu Instruments is quite good, however, at this very extreme setting of the zoom optics some care was required to get good results. Another possibility is detector nonlinearity. This is a known problem of ion counting detectors, which is why precision of better than 1‰ are not to be expected using such detectors. Detector saturation was not an issue, as count rates were kept well below 1 MHz.

## 4. Discussion

This technique has been developed in order to try to detect isotopically anomalous U that may be incorporated into certain components of certain meteorite classes during nucleosynthetic processes. This reflects the type of application that this technique should in principle be useful for small analyte quantities.

Another potential application would be in the detection of mass-dependent fractionation of U isotopes by natural redox processes in the near-surface environment. While U does have a number of oxidation states, the normalized mass difference ($\Delta m/m$) of 1.2% is small compared to other metals currently under study for environmental fractionations. At the same time, U is plentiful for this type of measurement, so that mass spectrometric techniques yielding higher precision (with more U) would be a more appropriate choice.

This technique is especially useful in the case where the total amount of analyte is extremely restricted. For example, in tracer studies of U transport in organisms or humans, it may be valuable to use very small doses to avoid the metal toxicity of U in the test subjects. At the same time, this technique should permit the detection of a U tracer (for example anthropogenic depleted $^{238}U$) in the environment at very high dilution factors.

Recent events have resulted in releases of isotopically anomalous U (nearly pure $^{238}U$) into the environment in several countries. Detecting and monitoring the spread of munitions-derived U in the environment is a significant and important task for which this method may find use. In the immediate vicinity of a targeted detonation there is likely to be sufficient U present for other methods to be used.

As a test for anthropogenic depleted U in regions proximal to sources (i.e. war zones), this technique is hampered by being labor intensive, expensive and time consuming. In the immediate vicinity of a weapons impact, other less expensive techniques are preferable (e.g. [7]), as the amount of analyte is not restricted. However, as U spreads in the environment and in the food chain and is diluted, the application of precise and sensitive methods such as this one may become useful, for example in biological samples, where the total quantity of analyte available may be very restricted. Especially in the case of living human subjects, large quantities of tissue or body fluids are not generally available for study. It is possible to imagine situations where only a few pg of U are available for analysis (in biopsied tissue, or a child's blood) where the sensitivity of this technique would outweigh other factors.

Another example of this would be in post-conflict assessment studies, where samples that were negative for DU using other methods could be re-screened using this method (perhaps also using a higher concentration factor) in order to better quantify the spread of anomalous U in the environment. In studies of reactor releases (such as Chernobyl), this method might be similarly useful. However, adjustments would be necessary to account for the presence of $^{236}U$ and $^{234}U$ in the nuclear fuel—these isotopes are present in small negligibly small amounts in munitions with respect to the analysis, though their detection may be desirable for other reasons.

## 5. Conclusions

Our technique exploits an unusual configuration of the Nu Instruments mass spectrometer to increase the precision of small sample (<350 pg) double spike measurements of U isotopic composition about 5× over conventional TIMS measurements, and 20× over quadrupole mass spectrome-

ter methods at a given concentration. At the same time, our method combines the ease of ICPMS sample preparation (when compared to TIMS) and significantly decreases the time required for a single isotopic analysis. The applications of this method are clearly in detecting isotopically anomalous U at great dilutions, and those where analyte quantities are very limited, such as in human or other biological samples. The sensitivity of this technique may make possible new types of studies of U metabolism not previously possible. For example, most U in the bloodstream ends up in bones and kidneys. This technique might make possible detailed studies of U uptake and metabolism in a variety of tissues in vivo without incurring significant risks of heavy metal toxicity.

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