The Ins and Outs of U and Th Isotopic Measurements Using a Nu Plasma 1700 MC-ICP-MS

Aaron J. Pietruszka[1] and Tyrone O. Rooney[1,2]

[1]Department of Geological Sciences, San Diego State University, San Diego, CA 92182, USA

[2]Department of Geological Sciences, Michigan State University, East Lansing, MI 48824, USA

Abstract

The Nu Plasma 1700 is a relatively new type of large-geometry MC-ICP-MS that offers the potential to improve the accuracy and precision of U and Th isotopic measurements compared to previous instruments (e.g., the Plasma 54-30, or P54-30). The higher resolution of the Nu Plasma 1700 translates to more than a factor of 6 improvement in the abundance sensitivity at high mass (compared to the P54-30), and virtually eliminates the necessity of a tail correction on ^{230}Th during the measurement of $^{232}Th/^{230}Th$ ratios (the major source of uncertainty using the P54-30). However, the Nu Plasma 1700 uses a discrete dynode secondary electron multiplier for ion-counting, which has a smaller dynamic range than the Daly detector used by the P54-30. This prevents the placement of a relatively large ^{235}U signal on the ion-counter, and thus, requires alternative methods to correct for the effects of instrumental mass bias. Initial efforts in our laboratory have focused on the development of standard-sample bracketing (SSB) techniques to correct for mass bias, with a careful evaluation of possible instrumental artifacts such as matrix effects, drift in the bias between the Faraday collectors and the ion-counting detector (Faraday/IC bias), and non-linearity of both the ion-counting detector and the retardation lens. Experiments with solution standards suggest that the major source of uncertainty on U and Th isotopic measurements using the Nu Plasma 1700 in SSB mode is drift in the Faraday/IC bias. Nevertheless, SSB analyses for U and Th solution standards are reproducible to ±0.3% for $^{238}U/^{234}U$ and ±0.4% for $^{232}Th/^{230}Th$ (±2σ), which is similar to the results obtained on the Plasma 54-30 (Luo et al., 1997; Pietruszka et al., 2002). So far, accuracy has been evaluated by repeatedly analyzing the UCSC Th isotopic standard against a previously characterized in-house Th isotopic standard in SSB mode. The result agrees within error of previous determinations for UCSC Th using the Plasma 54-30. Our future development work will focus on a more thorough characterization of the accuracy and precision of the SSB method and a detailed exploration of alternative techniques to correct for mass bias.

Collector Array

	IC0	Low 3	Low 2	Low 1	Axial	High 1	High 2	High 3	High 4
Thorium	^{230}Th		^{232}Th			^{235}U			^{238}U
Uranium	^{234}U	^{235}U			^{238}U				

The ^{230}Th and ^{234}U peaks are measured on an ion-counting detector (IC0). A modification of the collector block allows both the $^{232}Th/^{230}Th$ and $^{238}U/^{235}U$ ratios to be measured in a single sequence (the latter may used to correct for instrumental mass-dependent isotopic fractionation).

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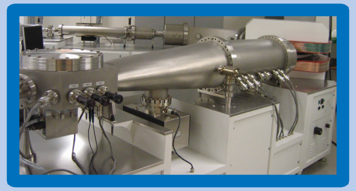
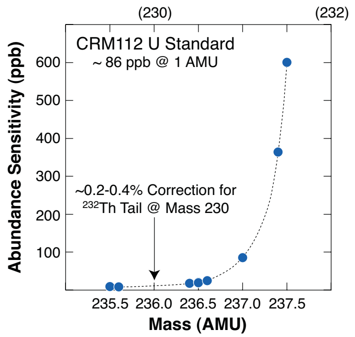
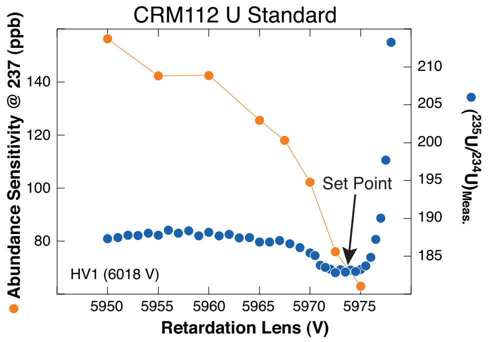


Abundance Sensitivity



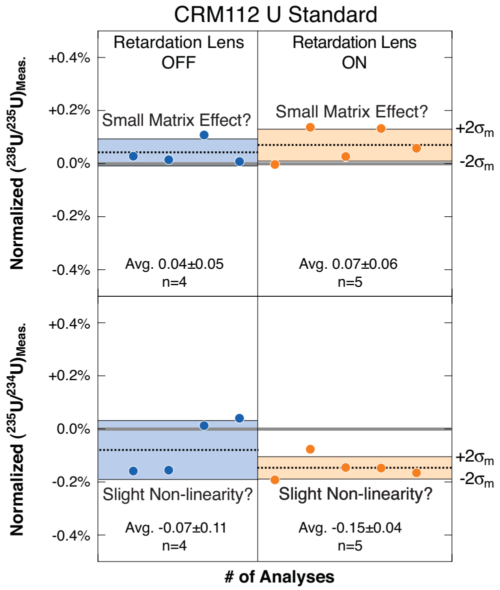
The abundance sensitivity on the Nu Plasma 1700 is ~86 ppb @ 1 AMU below mass 238 using the retardation lens. This translates to a correction of only ~0.2-0.4% for the tail of ^{232}Th below mass 230. Currently, the zeros are being measured by ESA deflection with no correction for either the magnitude or "shape" of the tail.

Retardation Lens



Early experiments using the retardation lens for $^{238}U/^{234}U$ and $^{232}Th/^{230}Th$ measurements on the Nu Plasma 1700 gave poor reproducibility. A more careful analysis of the behavior of the retardation lens showed that, beyond a certain point, a further increase in the voltage of the lens causes a rapid increase in the $^{238}U/^{234}U$ and $^{232}Th/^{230}Th$ ratios. Thus, slight variations in the lens voltage during analysis can lead to poor reproducibility. The retardation lens "profile" must be scanned before each measurement session to determine the proper setting.

Linearity and Matrix Effects

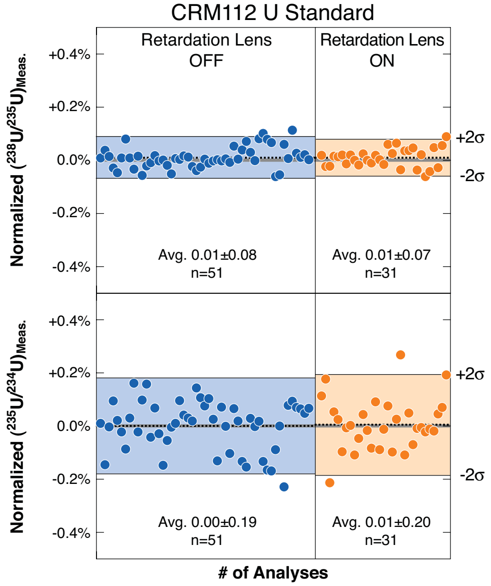


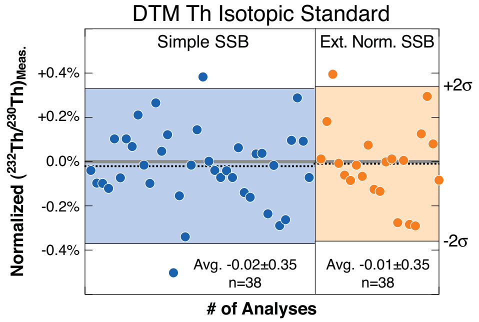
The possibility of an automatrix effect and/or non-linearity of the ion-counting detector was evaluated by running two different concentrations of the same U standard in standard-sample bracketing mode. The "bracketing" solution was run at ~16.5V of ^{238}U and the "unknown" solution was run at ~2.3V of ^{238}U. In this test, a normalized $^{238}U/^{235}U$ or $^{235}U/^{234}U$ ratio of zero indicates the absence of an automatrix effect or IC non-linearity, respectively. The test was conducted with the retardation lens off vs. on. The normalized $^{238}U/^{235}U$ ratios are slightly above zero, which may indicate the presence of a small automatrix effect for U (<0.1%). In contrast, the normalized $^{235}U/^{234}U$ ratios are slightly below zero, which may indicate a slight non-linearity on IC0 (<0.2%). Both of these issues can be dealt with by matching the concentrations (and signal intensities) of the sample and the bracketing standard.

Accuracy

Accuracy has been evaluated by repeatedly analyzing the UCSC Th isotopic standard against a previously characterized in-house Th isotopic standard in standard-sample bracketing mode. The result (172,279±622; n=5) agrees within error of previous determinations for UCSC Th using the Plasma 54-30 ($^{232}Th/^{230}Th$ = 171,657± 183).

Precision





The precision of $^{238}U/^{234}U$ measurements in standard-sample bracketing mode is ~0.2%. The reproducibility for $^{238}U/^{234}U$ seems to be limited primarily by drift in the relative bias of the Faraday detector and IC0 (given the ~3x better precision of the $^{238}U/^{235}U$ ratios). The precision of the $^{232}Th/^{230}Th$ measurements in standard-sample bracketing mode is ~0.4%. There is no improvement in the reproducibility if the $^{238}U/^{235}U$ ratio of U added to the Th standard is used to correct for instrumental mass-dependent isotopic fractionation. Thus, the reproducibility for $^{232}Th/^{230}Th$ seems to be limited primarily by drift in the relative bias of the Faraday detector and IC0.