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Further improvement in the precision of ^{233}U measurements by accelerator mass spectrometry at the Lawrence Livermore National Laboratory.

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Summary

In response to sponsor interest in October 2005 we proposed two methods for enhancing the precision of ^{233}U accelerator mass spectrometry (AMS) capabilities at the Lawrence Livermore National Laboratory (LLNL). In a previous report we evaluated the first method and demonstrated that by increasing sample loading by a factor of four coupled with performing four replicates of each sample, we could achieve measurement precision of ~1%. Recent modifications to our system have enabled us to test the second proposed method. By changing our setup to normalize ^{233}U ions counted in a gas ionization chamber to ^{238}U measured as a current in an off-axis Faraday cup we were able to attain 1% precision without the need for replicate analysis. This method could be further refined to achieve 0.5% precision in samples of interest.

1. Introduction

Established protocols for the measurement of ^{233}U by AMS rely on the direct measurement of the intrinsic ^{233}U/^{236}U ratio. Both of these species are measured as count rates in a gas ionization detector and as a result, electronic dead-time limits the maximum amount of each that can be loaded into an AMS target to ~10^{11} atoms. The expected ~10^{-4} ^{233}U/^{236}U atom ratio in the samples of interest implies that typical AMS targets will contain ~10^{7} atoms ^{233}U. Since our measurement error is dominated largely by Poisson counting statistics, this presents a fundamental limit of ~5% in the precision of our system under established protocols.

In response to expressed sponsor interest, we proposed two methods for improving the precision of our ^{233}U measurement capability. The first method consisted of modifying our established protocols to allow for greater sample loading as well as performing replicate analysis of samples. Our established protocols call for loading 500 ng of U into AMS target holders but we determined that sample loading can be increased to 2 μg in order to increase the number of ^{233}U atoms and therefore the counts obtained in our detector. Beyond 2 μg, errors associated with dead-time correction of the ^{236}U count rate begin to dominate so there is no advantage to increasing sample loading above this level. However, a further increase in ^{233}U counts was obtained by performing four

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replicate analyses of each sample. These two changes enabled us to improve our measurement precision from 5% down to ~1%.

We have since evaluated the second proposed method for precision enhancement of our AMS system. This method involved changing the setup of our system so that ^{233}U would be normalized to ^{238}U current measured in an off-axis Faraday cup rather than ^{236}U ions counted in the gas ionization chamber. This approach eliminates the constraints of count rate limits on the normalizing isotope and therefore allows us to load more of the ^{233}U atoms of interest into our AMS targets. Initially, we were unable to evaluate this method because ^{238}U currents were insufficient for our existing current measurement system. Through work supported by the Department of Energy (DOE) Office of Basic Energy Research (OBER) and LLNL, we have upgraded our measurement system and now have a robust capability for measuring ^{238}U currents in the samples of interest. We have independently measured a limited set of test samples to demonstrate the improved precision of this "^{233}U counts vs. ^{238}U current" method.

2. Evaluation tests of the "^{233}U counts vs. ^{238}U current" AMS setup

We prepared a series of test samples to evaluate the increased precision of the proposed method. These samples consisted of ~1 mg of natural U (in the form of New Brunswick Laboratory CRM 112-A) to which a known spike of ^{233}U (Isotope Products Laboratories 7233(1172.06)) was added. Duplicate samples were prepared at spike levels of 10^{10} and 10^7 atoms of ^{233}U as well as blanks with no ^{233}U added. The samples were processed using our standard chemical procedure that involves purification by ion exchange and extraction chromatography followed by co-precipitation with iron and oxidation in a muffle furnace. The resulting oxide powder is mixed with Nb metal and packed into our AMS target holders.

We configured our system to test this method by installing an off-axis Faraday cup on the high-mass side of our high-energy analyzing magnet. The cup was positioned so that ^{238}U ions were collected while ^{233}U ions were transmitted through to the end of our system where they were counted in our standard gas ionization chamber. Electrostatic bouncing at the low-energy side of the system was used to rapidly switch between ^{233}U (400 ms) and ^{238}U (4 ms) injected into the accelerator during each measurement cycle. The samples were measured four times with each individual measurement lasting 300 seconds or until 10,000 ^{233}U counts were obtained which corresponds to 1% counting statistics.

3. Results

The results of the test analysis are presented in Table I. The internal error for each sample refers to Poisson counting statistics while the external error is equivalent to the standard error in the mean of the four repeat measurements of each sample.

Table I. Results of the analysis of test samples for evaluating the "^{233}U counts vs. ^{238}U current" AMS method.

CAMS ID	Description	Nominal ^{233}U/^{238}U (x 10^{-12})	Measurement Time (s)	^{233}U Counts	^{238}U Current (nA)	Online Ratio (counts/nC)	Internal Error	External Error
Ac8162	1mgNatU#1	Blank	1200	8	63.8	0.114	35.9%	37.7%
Ac8163	1mgNatU#2	Blank	1200	3	81.2	0.029	58.6%	34.5%
Ac8166	1mgNatU10E7#1	3.942	1200	315	82.0	3.16	5.7%	11.7%
Ac8167	1mgNatU10E7#2	3.906	1200	392	97.3	3.40	5.0%	6.5%
Ac8168	1mgNatU10E10#1	3960	124.0	40193	102.8	3276	0.49%	1.3%
Ac8169	1mgNatU10E10#2	3931	329.2	40120	39.8	3139	0.51%	0.99%

As expected, both the blanks and the 10^7 spiked samples yielded sufficiently low ^{233}U count rates so that they were unable to attain 1% counting statistics within the allotted measurement time. As a result, the internal and external errors are virtually equal for all but one of these samples. By contrast, the 10^{10} spiked samples achieved 1% counting statistics for an individual measurement in less then a minute which translates into 0.5% internal error for the four combined measurements of each sample. It is important to note that for these samples the external error was larger than the internal error. All of the samples gave ^{238}U currents between 40 and 100 nA which is well above the lower limit of our current measurement system and we would expect a precision of 0.1%. This implies that there are sources of inter-measurement variability such as subtle changes in ion beam transport as the targets are consumed, temperature drifts in key system components, and others.

For all of these samples the dead-time was <5%. Based on past experience we can load up to 5×10^{11} atoms into samples, which corresponds to ^{233}U/^{238}U of 2×10^{-7}, before observing a detrimental increase in dead-time. Assuming a linear fit the measured ratio for the blank samples corresponds to a ^{233}U/^{238}U atom ratio of 3×10^{-13}. This implies that our system has a dynamic range of nearly six orders of magnitude. We could employ straightforward isotope dilution techniques in order to measure samples with ^{233}U/^{238}U greater than 2×10^{-7}.

4. Discussion and Conclusions

The results from the analysis of the test samples demonstrate that the "^{233}U counts vs. ^{238}U current" method can achieve 1% precision in samples of interest. These results also show that this method could be further refined to attain a precision of <1%. In this initial evaluation of the method we attained Poisson counting statistics of 0.5% but the overall precision was limited by inter-measurement variations. Past experience with AMS of other isotopes suggest that these sources of inter-measurement variation can be eliminated through systematic investigations and incremental improvements to the setup of the system. For example, ^{14}C is routinely measured by AMS at LLNL with a typical measurement precision of 0.5%. The ^{14}C AMS system has been steadily refined so that the measurement precision is limited only by counting statistics and similar efforts could be employed to improve our ^{233}U AMS system.

In addition to refining our ^{233}U AMS system to eliminate inter-measurement variations and achieve the 0.5% precision predicted by counting statistics, there are major upgrades to the system that could push the precision even lower. We are currently performing internally funded work to redesign the ion source we use for ^{14}C AMS with the goal of improving its ionization efficiency. This increased efficiency will enable us to achieve 0.1% measurement precision for ^{14}C. Once the efficacy of this new ion source design has been demonstrated, we could make similar modifications to the ion source we currently use for ^{233}U. This capability would represent the state-of-the-art for measurement of ^{233}U and would be unique within the DOE complex.