

## SIMS Uranium Isotope Analysis of NIST Standard Glasses to Determine Detection Limits

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**Introduction:** Secondary Ion Mass Spectroscopy (SIMS) is an analytical method that is utilized to determine uranium isotopic signatures of samples in nuclear forensic investigations. Understanding SIMS detection limits is critical in establishing what samples can be measured reliably. In this study, we analyzed three NIST Standard glasses with varying concentrations of depleted uranium: NIST 610 (461.5 ppm U), NIST 613 (37.38 ppm U) and NIST 617 (0.0721 ppm U). By comparing the measured uranium isotope ratios to their reference values [1], we were able to determine the effects of an incremental decrease in uranium concentration on the accuracy of the achieved ratio.

**Samples and Methods:** All samples were analyzed with the LANL Cameca IMS 1280 Large Geometry Secondary Ion Mass Spectrometer (LG-SIMS) with a primary O<sup>-</sup> ion beam generated from a duoplasmatron source. Uranium isotope signals were measured simultaneously with five electron multiplier (EM) detectors, with <sup>234</sup>U on detector L2, <sup>235</sup>U on L1, <sup>236</sup>U on C, <sup>238</sup>U on H1 and <sup>238</sup>U<sup>1</sup>H on H2. Hydride interference at mass 236 was corrected using methods from [2]. Each measurement was collected with a 25 μm raster size, a field aperture width of 4000 μm, an entrance slit width of 122 μm, a contrast aperture width of 400 μm and an energy slit width of 50 μm. The primary beam current used was 50 nA to ensure maximum signal while retaining a focused beam. With these settings, each sputtered analysis pit was approximately 50 microns in diameter. All other secondary ion optics and ion detector parameters were optimized to maximize count rates and produce a mass resolving power of ~1800. <sup>238</sup>U signal on each of the samples was as follows: 3.2e4 cps for NIST 610, 6.7e3 cps for NIST 613 and 4.4e0 cps for NIST 617.

**Results and Discussion:** As the uranium concentration decreases from 461.5 ppm in NIST 610 to 37.38 ppm in NIST 613, we begin to see abnormally high <sup>234</sup>U/<sup>238</sup>U and <sup>236</sup>U/<sup>238</sup>U with bias corrected values of 1.50e-5 and 4.70e-5 (**Table 1**) respectively, compared to reference values of 1.00e-5 and 4.31 e-5, respectively (instrument biases were determined from NIST 610 analyses). Analysis of NIST 617 (0.0721 ppm U) yields dramatic increases in <sup>234</sup>U/<sup>238</sup>U and <sup>236</sup>U/<sup>238</sup>U (bias corrected values of 1.26e-3 and 1.15 e-3 respectively) as well as an increase in <sup>235</sup>U/<sup>238</sup>U (bias corrected value of 5.14e-2 compared to reference value of 2.40e-3).

Examination of the mass scan from NIST 610 shows additional peaks that are lower in mass than those of the <sup>234</sup>U, <sup>235</sup>U, <sup>236</sup>U and <sup>238</sup>U<sup>1</sup>H signal peaks (**Figure 1**). We hypothesize these peaks are non-uranium molecular interferences, and that their tails may contribute to the overall uranium signal. When the uranium concentration in the sample is high enough to produce adequate signal, the contributions from these molecular interferences are trivial and have no effect on the uranium isotope ratios. However, as the uranium concentration, and therefore signal, decreases, the molecular interference has a greater influence on the overall signal and skews the uranium isotope ratios to appear uncharacteristically elevated.

If assuming that deviations in measured isotope ratios are due to background signal (and assuming that the background relative to the  $^{238}\text{U}$  signal is negligible), we can estimate the background concentration at each uranium isotope mass using the following equation: [(measured ppm  $^x\text{U}/^{238}\text{U}$  \*  $^{238}\text{U}$  ppm reference concentration) - ( $^x\text{U}$  reference concentration)], where “x” is 234, 235 or 236 uranium. These calculations yield an estimated background for NIST 613 of 216 ppt at mass 234, 373 ppt at mass 235 and 302 ppt at mass 236, and for NIST 617 of 95 ppt at mass 234, 3.5 ppb at mass 235 and 86 ppt at mass 236.

Using the calculated backgrounds from the NIST 613 and NIST 617 data, we can also mathematically constrain the minimum total uranium concentration needed to achieve an accurate isotope measurement (defined here as being within 10% of the real value). For our measurement setup, the data from NIST 613 predict that accurate measurements of  $^{234}\text{U}/^{238}\text{U}$ ,  $^{235}\text{U}/^{238}\text{U}$ , and  $^{236}\text{U}/^{238}\text{U}$  require 216 ppm, 1.6 ppm, and 70 ppm total U concentrations, respectively. The data from NIST 617 predict accurate  $^{234}\text{U}/^{238}\text{U}$ ,  $^{235}\text{U}/^{238}\text{U}$ , and  $^{236}\text{U}/^{238}\text{U}$  ratios require 95 ppm, 15 ppm, and 20 ppm total U concentrations, respectively. The differences in the minimum total U concentrations predicted from the NIST 613 and NIST 617 data stem from their different background concentrations for a given mass.

**Conclusions:** The characterization and treatment of data presented here provide an informative assessment of the influence of background signal, and the minimum total U concentrations needed to determine accurate isotope compositions by SIMS. As the NIST glasses characterized here have depleted uranium compositions, they represent a worst case scenario, in terms of the total U concentration required for accurate isotope ratio measurements. Qualitatively, higher abundances of  $^{234}\text{U}$ ,  $^{235}\text{U}$ , and  $^{236}\text{U}$  in materials would mean that accurate measurements could be attained with lower total U concentrations; quantitatively, the minimum concentrations required could be calculated using the methods presented here.

<b>NIST 610 (461.5 ppm U)</b>	$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$	$^{236}\text{U}/^{238}\text{U}$	Total CTS $^{235}\text{U}$	Total CTS $^{238}\text{U}$
<b>Average</b>	1.06E-05	2.42E-03	4.69E-05	1.20E+04	4.96E+06
<b>2SE</b>	3.43E-06	4.83E-05	5.51E-06		
<b>Bias</b>	1.056	1.007	1.089		
<b>Bias Corrected</b>	<b>1.00E-05</b>	<b>2.40E-03</b>	<b>4.31E-05</b>		
<b>Reference Value</b>	<b>1.00E-05</b>	<b>2.40E-03</b>	<b>4.31E-05</b>		

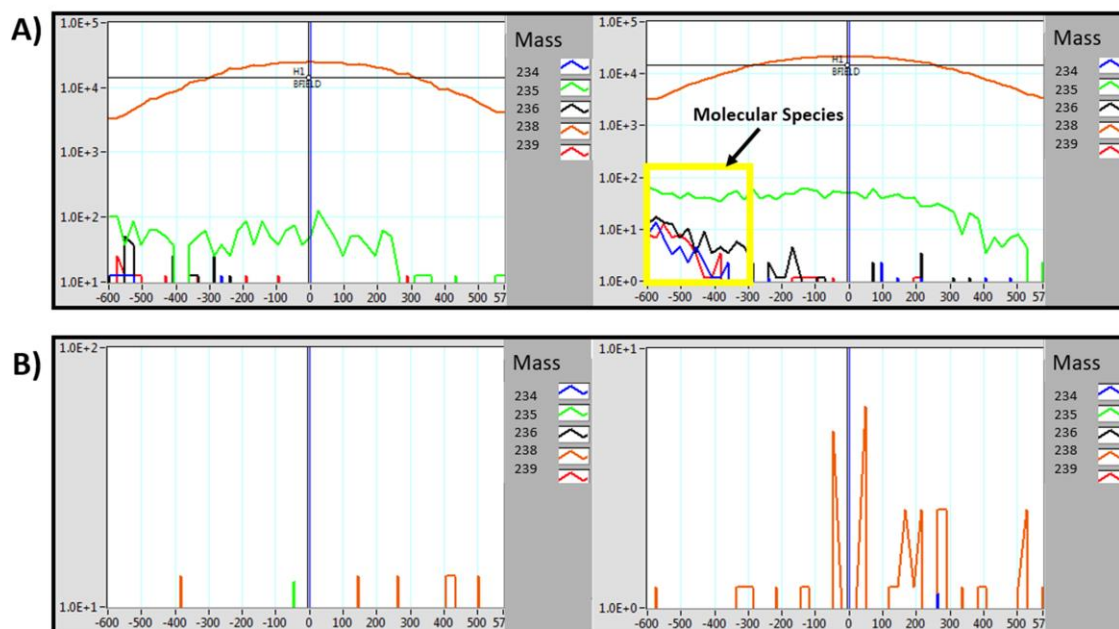
  

<b>NIST 613 (37.38 ppm U)</b>	$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$	$^{236}\text{U}/^{238}\text{U}$	Total CTS $^{235}\text{U}$	Total CTS $^{238}\text{U}$
<b>Average</b>	1.58E-05	2.41E-03	5.12E-05	3.14E+03	1.30E+06
<b>2SE</b>	6.65E-06	5.61E-05	9.22E-06		
<b>Bias Corrected (NIST 610 bias)</b>	<b>1.50E-05</b>	<b>2.39E-03</b>	<b>4.70E-05</b>		
<b>Reference Value</b>	<b>1.00E-05</b>	<b>2.40E-03</b>	<b>4.31E-05</b>		

<b>NIST 617 (0.0721 ppm U)</b>	$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$	$^{236}\text{U}/^{238}\text{U}$	Total CTS $^{235}\text{U}$	Total CTS $^{238}\text{U}$
<b>Average</b>	1.33E-03	5.18E-02	1.25E-03	2.97E+01	5.69E+02
<b>2SE</b>	1.62E-03	2.21E-02	2.92E-03		
<b>Bias Corrected (NIST 610 bias)</b>	<b>1.26E-03</b>	<b>5.14E-02</b>	<b>1.15E-03</b>		
<b>Reference Value</b>	<b>1.00E-05</b>	<b>2.40E-03</b>	<b>4.31E-05</b>		

**Table 1:** Average uranium isotope ratios from the NIST 610, 613 and 617 SIMS analyses compared to their respective reference values. Biases were calculated from the NIST 610 analyses and were used to bias correct the NIST 613 and 617 ratios. Total counts of  $^{235}\text{U}$  and  $^{238}\text{U}$  are also included for reference.



**Figure 1:** SIMS mass scans for A) NIST 610 and B) NIST 617. Blue lines represent mass 234, green lines represent mass 235, black lines represent mass 236, orange lines represent mass 238 and red lines represent mass 239. Mass is scanned over a 1200 bit range. The right scan represents counts per second on the sample; the left scan represents the signal accumulated for 2 minutes. The yellow highlighted region on the accumulated signal for NIST 610 shows the presence of a molecular species to the left of the uranium peaks.

#### References:

- [1] Zimmer M.M., Kinman W.S., Kara A.H. and Steiner R.E. (2014) Evaluation of the Homogeneity of the Uranium Isotope Composition of NIST SRM 610/611 by MC-ICP-MS, MC-TIMS, and SIMS. *Minerals* 4, 541-552.
- [2] Simons D.S. and Fassett J.D. (2017) Measurement of uranium-236 in particles by secondary ion mass spectrometry. *J Anal At Spectrom* 32(2) 393-401.