LA-UR-15-24319
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Author(s): Havrilla, George Joseph
Gonzalez, Jhanis

Intended for: Report

Issued: 2015-06-10

Demonstration of femtosecond laser ablation inductively coupled plasma mass spectrometry for uranium isotopic measurements in U-10Mo nuclear fuel foils

George J. Havrilla[1], Jhanis Gonzalez[2]

[1] Los Alamos National Laboratory, Chemistry Division, Los Alamos, NM 87544
[2] Applied Spectra Inc., 46661 Fremont Blvd., Fremont, CA 94538

ABSTRACT
The use of femtosecond laser ablation inductively coupled plasma mass spectrometry was used to demonstrate the feasibility of measuring the isotopic ratio of uranium directly in U-10Mo fuel foils. The measurements were done on both the flat surface and cross sections of bare and Zr clad U-10Mo fuel foil samples. The results for the depleted uranium content measurements were less than 10% of the accepted U235/238 ratio of 0.0020. Sampling was demonstrated for line scans and elemental mapping over large areas. In addition to the U isotopic ratio measurement, the Zr thickness could be measured as well as trace elemental composition if required. A number of interesting features were observed during the feasibility measurements which could provide the basis for further investigation using this methodology. The results demonstrate the feasibility of using fs-LA-ICP-MS for measuring the U isotopic ratio in U-10Mo fuel foils.

INTRODUCTION
The Reactor Conversion program funded by the DOE/NNSA Office of Material Management and Minimization has developed a U-10Mo fuel foil as a low enriched uranium (LEU) fuel replacement. As such the LEU fuel requires the U235 content to be below 20 wt% to qualify as LEU. In order to insure the LEU requirement is met, an alternative method for measuring the uranium isotope ratio is being considered for rapid, accurate and quantitative measurement of this critical parameter for the U-10Mo fuel. [1] This alternative method is femtosecond laser ablation inductively coupled plasma mass spectrometry (fs-LA-ICP-MS). This method utilizes ultrashort pulses (femtosecond, 10^{-18}s) of laser light to ablate material from the surface of a sample. The ablated material is carried into the inductively coupled plasma where the nanoparticles are combusted and excited into ions, which are then swept into the mass spectrometer detector. [2,3] The mass spectrometer is an ideal means to measure isotopic composition. When coupled with the femtosecond laser ablation sampling, accurate compositional analysis is feasible. The primary attribute of the femtosecond laser ablation process is the generation of nanoscale particles of the material under analysis. These nanoscale particles are more efficiently transported into the ICP where they undergo more efficient combustion and creation of elemental ionic species insures a more accurate sampling of the sample as well as more accurate quantification. This report demonstrates the feasibility of using fs-LA-ICP-MS for measuring the uranium isotopic ratio for U-10Mo fuel foils. While this is feasibility demonstration used only depleted uranium, the application to the LEU fuel range from 1 to 19% U235 is within the capabilities of the method.

EXPERIMENTAL
The fs-LA-ICP-MS instrumentation used in these measurements is commercially available. The system is supplied by Applied Spectra Inc. of Fremont, CA. The fs-LA-ICP-MS instrument

consists of an integration of 2 instruments: a femtosecond laser for ablating the sample and an inductively coupled plasma mass spectrometer for measuring the elemental composition of the ablated material. The femtosecond laser ablation instrument is the Model fs-J200, from Applied Spectra, Inc. using a wavelength of 1030 nm and a pulse duration of less than 480 fs. A laser spot size of 18 μm was used throughout these measurements. A repetition rate of 100 or 1000 Hz was used along with a carrier gas rate of helium of 0.30 L/min and the argon make-up gas rate of 0.70 L/min to introduce the ablated material into the ICP torch. The ICPMS is an Aurora Elite instrument (formerly Bruker Daltronics, Billerica, MA) now available through Jena Analytik (Jena, Germany). The settings for the ICPMS operation are the following: the plasma was operated at a flow of 18 L/min, sheath gas flow of 0.80 L/min, sampling depth of 5.50 mm, power 1.40 kW.

The samples were bare and Zr clad (~25 μm thick) U-10Mo foils ~0.3 mm thick, 10 x 10 mm and 5 x 10 mm. The smaller foils were used for cross section measurements. The samples were analyzed as received both on the flat surface for bulk isotopic composition and on the cross section of the thinner foil. The 235 and 238 uranium isotopes were monitored along with Zr90, Mo95 as well as a number of other elements. The instrument was set to correct for known isotopic interferences

The raster scans were setup to do single and multiple passes, each raster line length 0.8 mm, with a raster speed of 0.05 mm/sec. The depth of the laser ablation lines in the sample was measured with a White Light Interferometer Microscope from Zygo, (model New View 200, Middlefield, CT).

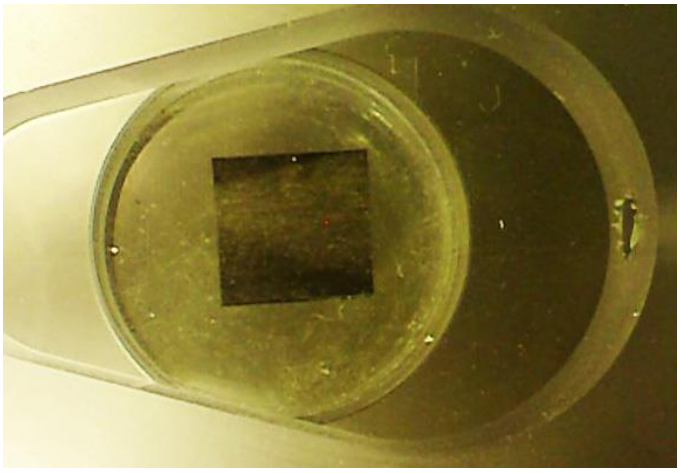

Figure 1. Picture of bare U-10Mo sample in laser ablation chamber.

RESULTS

The first sample characterized was 13K-657-C-A which was a bare U-10Mo foil. Figure 1 shows the foil in the laser ablation sample chamber. Figure 2 is a picture of the same foil after several laser ablation runs. Even though the ablation scars are visible within the red circle, the amount of material removed is quite small due to the small spot size used and the femtosecond laser ablation duration. Several different raster scans were done on the sample surface, this included a

single line-single pass, single line-multiple passes, multiple lines-single pass and multiple lines-multiple passes. In all cases the results were quite similar. Figure 3 shows an image of the mass

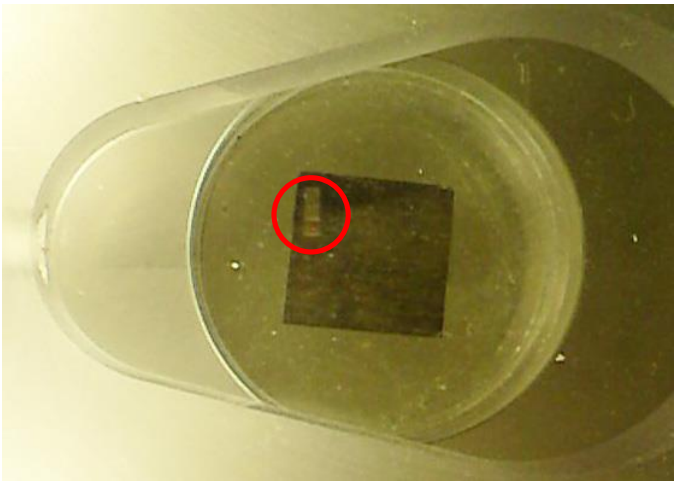

Figure 2. Picture of U-10Mo sample after several ablation runs. The red circle indicates the ablated area in the upper left corner of the foil.

spectrum signal of the uranium 238 (red), molybdenum 95 (green) and zirconium 90 (blue) isotope signals as the laser is rastered over the surface of the bare U-10Mo sample in 5 passes over a single line. Several interesting features are visible in Figure 3. First the uranium and molybdenum traces are relatively unchanged in each of the passes. Zirconium is present even though this is supposed to be a bare U-10Mo sample with no cladding. The zirconium signal decreases with repeated passes over the same line. This indicates the zirconium is not bulk but a

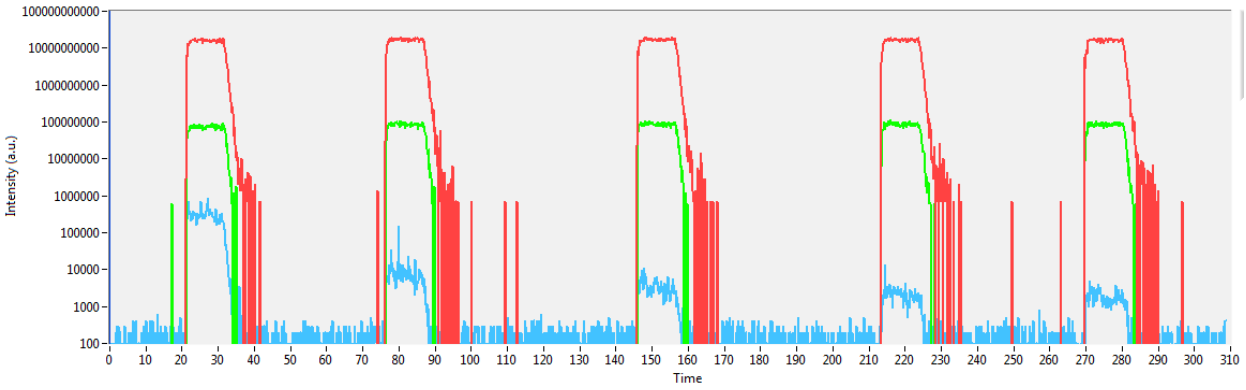

Figure 3. Image of 5 passes, single line, of laser ablation mass spectrometer signals for U238 (red), Mo95 (green) and Zr90 (blue). Note Zr signal decreases with successive laser passes.

contaminant. Further discussion of this contaminant will be reserved for the discussion section. In Table 1 the isotopic ratios for the 235/238 U signals for 5 successive passes over a single line are shown. The columns on the left in Table 1 shows the expected isotopic composition for both depleted and natural uranium, 0.0020 and 0.00725 respectively. The average measured 235/238 U ratio for the 5 passes is 0.00216 with a standard deviation of 0.00007 and a 3% RSD for the 5 measurements. When compared with the expected 235/238 ratio for depleted uranium there is a calculated bias of 8% for these 5 measurements. Table 2 shows the measured 235/238 ratio measurements for an expanded raster scan of 10 lines with 3 passes on each line. In this instance

there is improvement on the %RSD, each one is less than the previous 3%, and the standard deviation is less than half the previous value in Table 1. The calculated bias is a little worse in the Table 2 results, being greater than the expected value of 0.00200. The improved precision of the Table 2 measurements is good and even though the bias is slightly higher, it is quite acceptable for this feasibility demonstration.

Table 1. Uranium 235/238 isotopic ratio results from 5 successive passes over the same line on the bare U-10Mo sample.

	235	238	Ratio	Pass1	Pass2	Pass3	Pass4	Pass5
Depleted	0.2	99.8	0.00200	0.00209	0.00219	0.00209	0.00223	0.00220
Natural	0.72	99.27	0.00725					
235/238	**%Bias**	**8**			**Avg**	**std dev**	**%RSD**	
					0.00216	0.00007	3	

Figure 4 is a picture of 3 laser ablation lines for 1, 2 and 3 laser passes per line on the bare U-10Mo specimen. Each line is visibly wider than the next line. These ablation lines were used to measure the depth of the ablated channel. Figure 5 is a screen capture image of the measured laser track in the surface for the 3 pass line at the bottom. The line in the image shows the line profile scanned by the surface profiling instrument. The depth of the ablated line is shown in

Table 2. U 235/238 ratio measurements for bare surface U-10Mo specimen with 10 lines, 3 passes each line.

	Pass 1	Pass 2	Pass 3
Line1	0.00222	0.00221	0.00221
Line2	0.00219	0.00226	0.00215
Line3	0.00218	0.00224	0.00221
Line4	0.00218	0.00225	0.00217
Line5	0.00219	0.00222	0.00222
Line6	0.00216	0.00217	0.00217
Line7	0.00215	0.00216	0.00217
Line8	0.00224	0.00219	0.00216
Line9	0.00216	0.00222	0.00216
Line10	0.00219	0.00230	0.00220
avg	**0.00219**	**0.00222**	**0.00218**
std dev	**0.00003**	**0.00004**	**0.00002**
%RSD	**1**	**2**	**1**
%Bias	**9.5**	**11**	**9**

Figure 6. The measured depth of the laser ablation channel is around 7 μm. This gives an average

laser ablation depth of around 2.3 μm removed per laser ablation raster. This demonstrates that very little material is removed using the femtosecond laser ablation at these particular settings. Earlier we made the observation of the Zr contamination of the U-10Mo bare surface. This was confirmed by the plot the of the Zr intensity versus the number of laser raster scan line passes for the 5 pass laser ablation measurements shown in both Figure 3 and Table 1. Figure 7 shows a

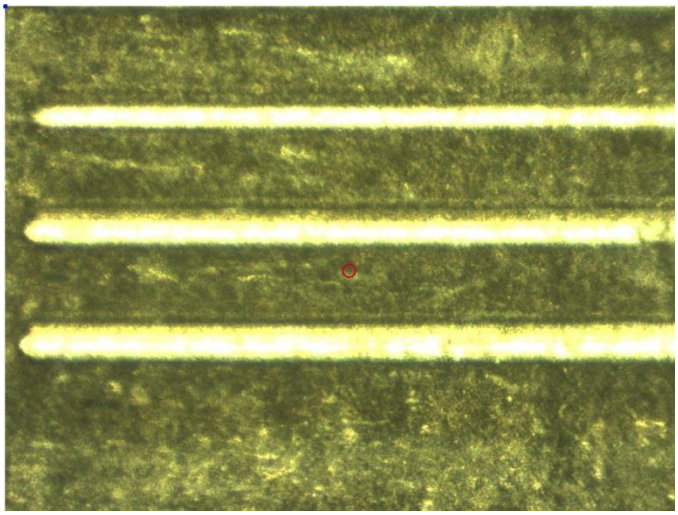

Figure 4. Picture of 3 laser ablation lines with successive passes of 1, 2 and 3 passes per line from top to bottom. Each line was measured with the Zygo surface instrument.

plot of the Zr intensity for successive laser ablation measurements indicating about 2 orders of magnitude decrease in the Zr signal as a function of depth. Based on the depth profile measurements, the 5 successive passes produces a line depth of around 11.5 micrometers. The Zr

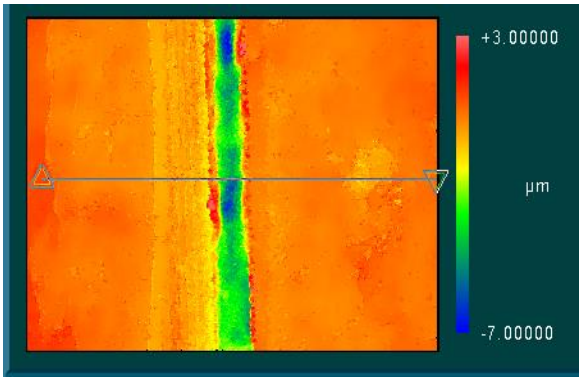

Figure 5. Screen capture image from the Zygo surface profile instrument. The green feature in the center is the laser ablation crater. The line across the middle indicates the profile measurement shown in Figure 6.

is still present at this depth. Further measurements into the bulk of the U-10Mo sample showed Zr present even at a depth of nearly 60 micrometers (30 laser ablation rasters). The source of the Zr is unclear as is the extent of the Zr contamination. Further investigation of the Zr contamination is left for another time.

The sample was turned on edge to sample the cross section. The cross section measurements would provide insights into the bulk composition compared with the measurements on the surface of the specimen. Figure 8 shows a plot of the uranium 235/238 ratio of the U-10Mo specimen cross section. The individual U235/238 ratio measurements indicates a variation in the isotopic distribution within the bulk of the U-10Mo foil. The average ratio is the depleted value of 0.0020, but we do measure both high and low ratio values. Again, this is an observation that is left for further investigation as to the distribution of the U isotopes in these foil materials.

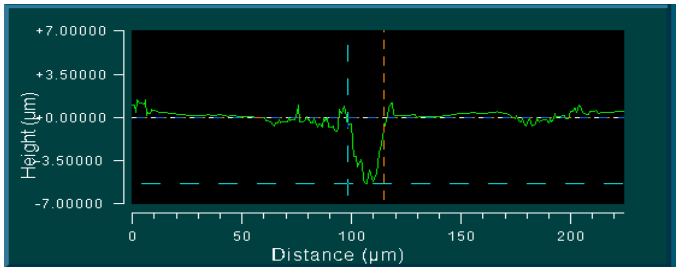

Figure 6. Screen capture image from Zygo surface profile instrument. The green trace shows the surface profile across the laser ablation crater. The depth is nearly 7 micrometers for 3 laser passes.

The cross section measurements were done on a similar sample although the size was smaller (10 x 5 mm) compared to the surface sample (10 x 10 mm) so that the sample could be turned on edge. We used several different laser raster scans on the cross section. The raster scans included moving the laser left to right, right to left and maintaining the raster scan within the cross section

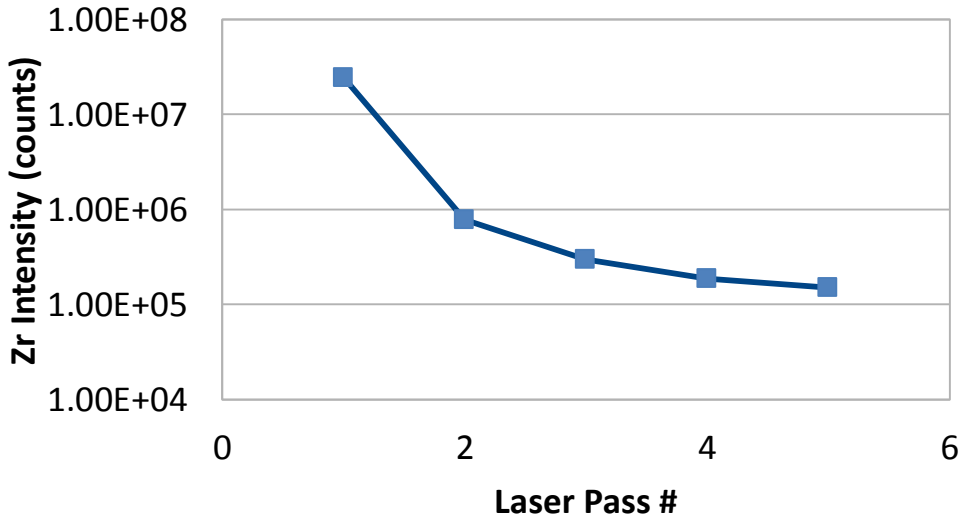

Figure 7. Plot of Zr intensity as a function of depth from successive laser ablation passes.

of the specimen. The first two raster scans allowed the laser to move off the sample into the putty holding the sample on edge. This created some artifacts in the measurements since the sample was apparently not completely perpendicular to the laser beam. This results in sampling the surface of the specimen in the direction of the laser scan when the sample is tilted in the direction of the scan.

A single line scan across the cross section from right to left is shown in Figure 9 for the Zr intensity. This is an interesting plot since it shows a relatively constant Zr distribution on the cross section of the sample. The presence of the Zr in the cross section could be explained by the shearing process used to cut the samples. However, an intense Zr signal from an apparent Zr

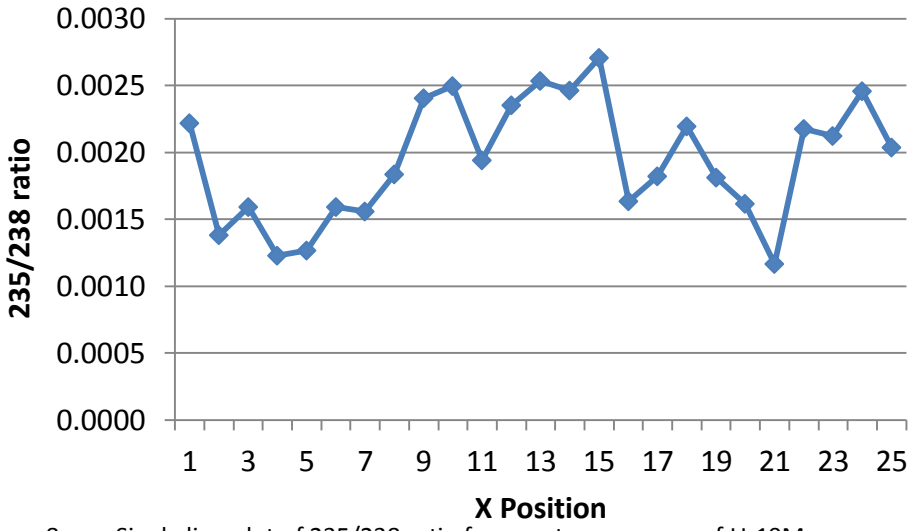

Figure 8. Single line plot of 235/238 ratio from raster scan area of U-10Mo cross section.

inclusion raises additional questions regarding the depth of the Zr contamination within the cross section. Repeated laser ablation within the cross section failed to observe any decrease in the Zr contamination to a depth over 60 micrometers. This indicates yet another issue for detailed study

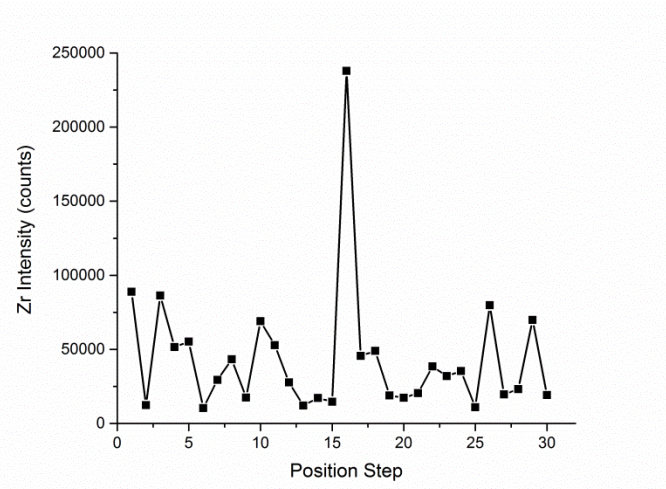

Figure 9. Plot of raw Zr intensity counts as a function of position along the cross section of the bare U-10Mo sample as laser is scanned right to left.

to discern the level of Zr contamination. One possible approach would be to machine the sheared edges to remove any Zr contamination due to the shearing process, perhaps a millimeter on each edge. This would certainly remove any shearing contamination from the edge and allow for clear

evaluation of the Zr contamination of the bulk of the U-10Mo foil. Figure 10 shows a plot of the Zr intensity when the laser is scanned from left to right.

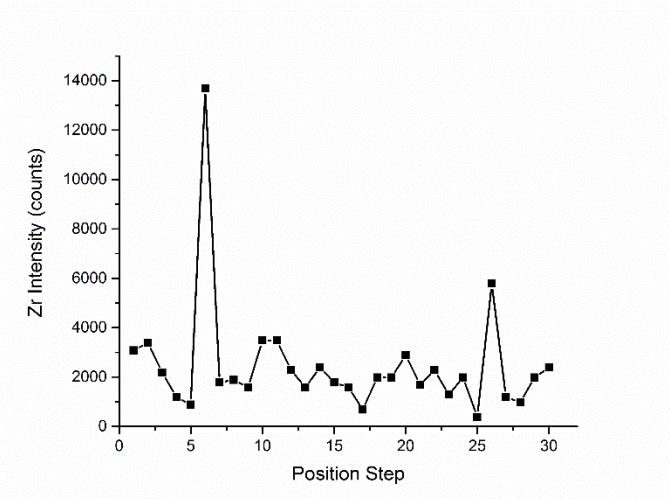

Figure 10. Plot of raw Zr intensity counts as a function of position along the cross section of the bare U-10Mo sample as laser is scanned left to right

The Zr clad U-10Mo foil sample 656-C-C was measured next. In this case we did not measure the surface U ratio since the Zr cladding would not provide any useful information for these feasibility measurements regarding the U 235/238 ratio. The Zr clad U-10Mo foil is shown in

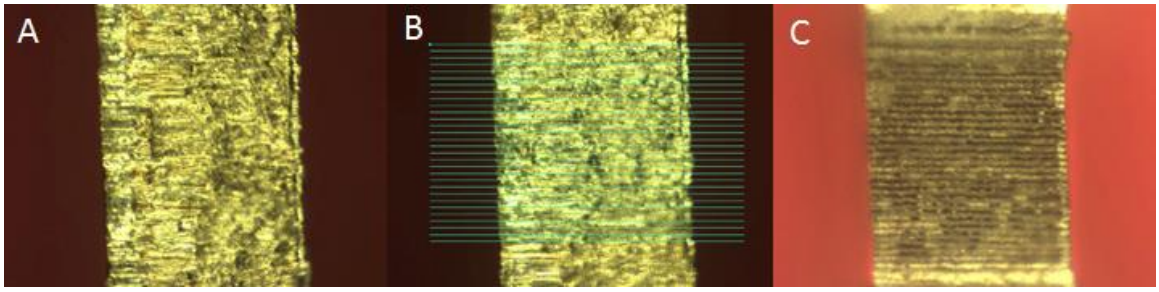

Figure 11. Magnified pictures of Zr clad U-10Mo foil. A) magnified cross section, B) magnified cross section with programmed laser raster lines, C) magnified cross section after laser ablation.

Figure 11 embedded in putty (pink) to hold it upright in the sample chamber. A similar arrangement for the bare U-10Mo foil cross section was used. Figure 11A shows a magnified image of the Zr clad U-10Mo specimen cross section and Figure 11B shows the programmed lines for laser scanning and the area after laser ablation in Figure 11C. The uneven burn pattern in the after ablation image in Figure 11C raises some issues as to the reason for these visible differences. Again, this is an area for subsequent investigation as to the underlying reason for these apparent differences in the ablation occurring in these locations.

A single line scan shown in Figure 12 plots the raw intensities of U238, Mo95 and Zr90 as a function of position. The intensities are normalized to show the relative responses across the cross section of the Zr clad U-10Mo foil. The U238 and Mo95 plots show the expected elemental response, although the apparent regular features in the cross section are interesting. These

features could be due to the shearing action of the cutting process. Again, more issues to pursue with additional testing. The Zr profile however shows some intriguing features. The Zr trace exhibits an initial high pulse, followed by a roll off in the Zr signal. The valley of the Zr intensity plot actually has nearly a million counts across the bottom of the valley, not zero, this is an

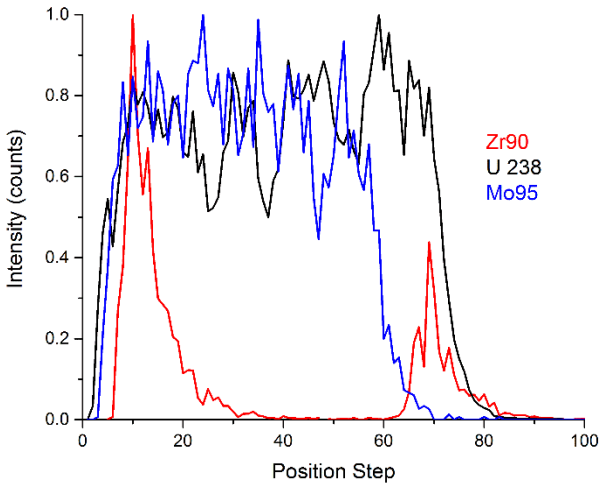

Figure 12. Single line scan across Zr clad U-10Mo cross section. Red trace is zirconium, blue is molybdenum and black is uranium

artifact of the normalization used to plot the data. This supports the earlier observation of the bare U-10Mo cross section Zr presence where the Zr appears to be incorporated across the cross section and nearly 100 micrometers into the bulk of the cross section. That was without any Zr cladding. In the case of the current Zr clad sample, it is evident the Zr is smeared across the cross section by the shearing action to cut the sample, yet there may still be Zr in the meat of the foil. The remainder of the Zr profile shows the left side of the foil cladding is thicker than the right side. The spike in Zr intensity on the left side is picking up some of the Zr on the surface cladding as well, which most likely accounts for the Zr spiked signal. The Mo profile indicates the Mo actually disappears (the Mo raw intensity values are actually zero) from about position step 70 until the end of the specimen, where the U and Zr stop. This is yet another feature for more detailed study. Is this a void of Mo in the U-10Mo foil? Additional information on this possibility will be shown later.

The cross section plots are have many features to explore, however the multiple line rasters offer the ability to create images of the elemental distributions. These images offer a more comprehensive look into the elemental spatial distributions over a much larger area than the single line raster of the laser. In Figure 13, the U235/328 ratio is plotted as a function of X and Y position across the cross section. While a majority of the cross section shows a ratio of the expected depleted uranium of 0.002, there are some spots with higher ratios and lower ratios. These variations in 235/238 ratio should be examined to determine what the relative concentrations of U isotopes exist in these areas and how extensive are these high and low spots. Figure 14 shows the same area for the Zr intensity. In this plot we see confirmation that the left side of the Zr cladding is indeed thicker than the right side. Calibration of the scanning speed with distance would enable measurements of the thickness of the Zr cladding to confirm the foil meets the Zr cladding thickness specification of 1 mil (0.001 inches or 25 micrometers of Zr).

Earlier we mentioned the possibility of observing a void in the Mo distribution in the U-10Mo foil. We have confirmation of this possibility in the form of several images of a section of the Zr

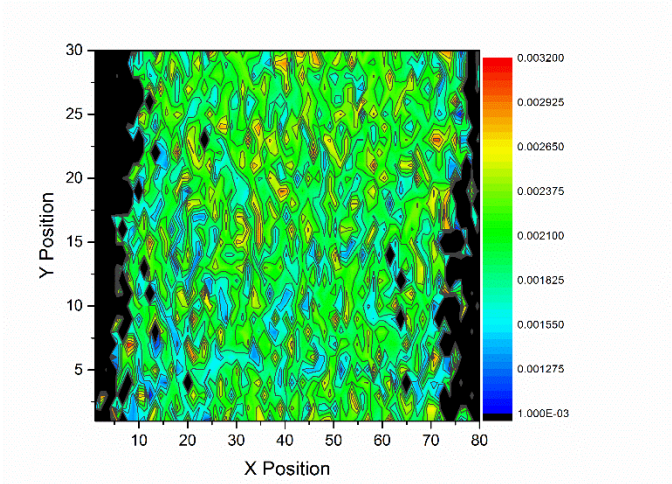

Figure 13. Uranium 235/238 intensity ratio plot across cross section of Zr clad U-10Mo cross section.

clad cross section. This is shown in Figure 15 for U238, Mo95 and Zr90 raw intensity images. The U238 image fills the cross section and the Zr90 appears on the edges of the U image indicating the Zr cladding. The image to focus on is the Mo95 (center), which does not track the

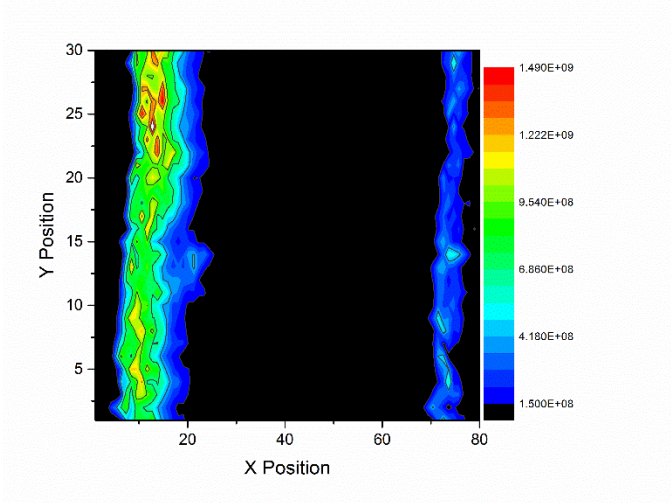

Figure 14. Zirconium intensity ratio plot across cross section of Zr clad U10Mo cross section. The images of the Zr shows the differences in Zr cladding thickness.

U image. This indicates a possible void of Mo in this area. This is another item which is left for further investigation.

Stainless steel

Stainless steel was run as a test sample. The stainless steel was a demonstration of the elemental analysis capability of the fs-LA-ICP-MS instrument. Figure 16 shows the magnified cross section of the stainless steel sample. Figure 17 is several elemental images of the cross section

showing carbon, chromium, iron and manganese. These images illustrate the effect of the sample not being perpendicular to the laser. The high intensity for all elements on the left side is indicative of the sample leaning away from the laser and the laser sampling the surface of the

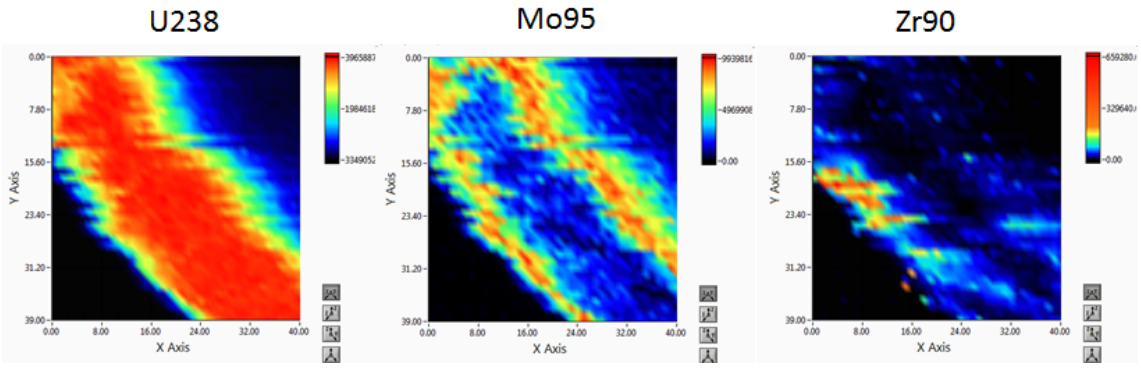

Figure 15. Images of raw elemental intensities for U238, Mo95 and Zr90 of Zr clad U10Mo cross section.

specimen as it rasters over the leading edge of the cross section from left to right. The one interesting feature of the elemental cross section images is the carbon. It is not uniform within the cross section, while the chromium, iron and manganese all exhibit the same image profiles.

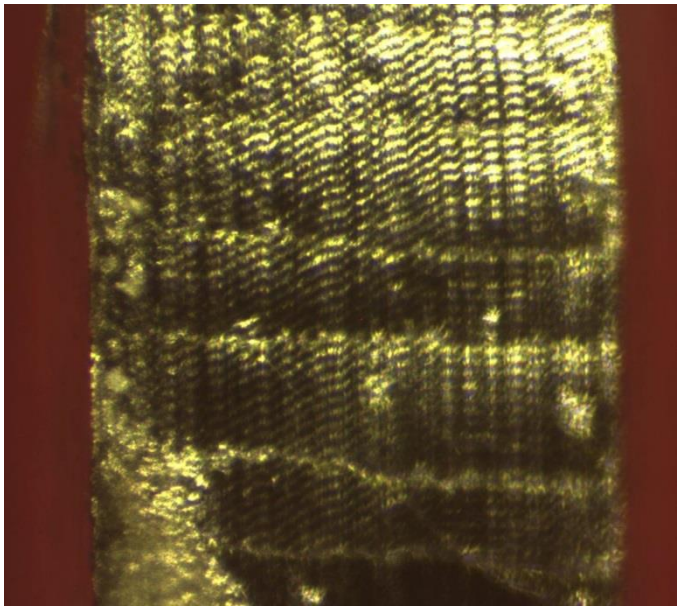

Figure 16. Magnified image of stainless steel cross section sample.

DISCUSSION

The feasibility of using femtosecond laser ablation ICPMS has been demonstrated. The results clearly demonstrate the capability of this instrumentation to provide the necessary accuracy and precision for the U 235/238 ratio needed for tracking uranium content within the production process.

In addition a number of issues have been identified which require additional study in order to determine their source. While these samples were not actual production these issues need to be

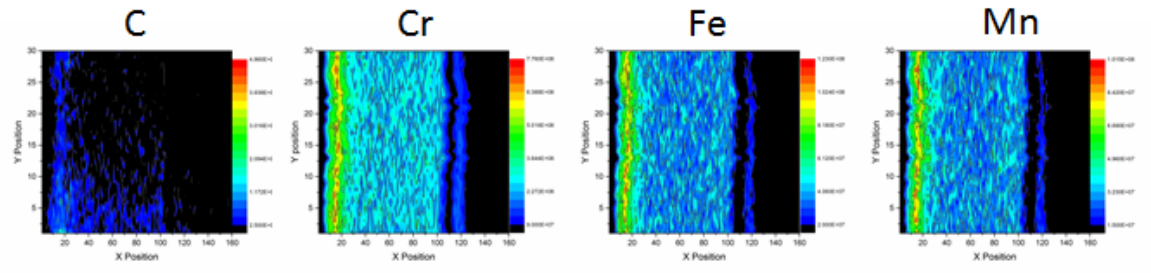

Figure 17. Elemental images of stainless steel cross section for carbon, chromium, iron and manganese.

addressed as to whether they affect the quality and performance of the U-10Mo fuel. These issues include:

- Zirconium presence both on the surface and cross section of the samples. This could be from the rolling of the master alloys on the same roller mills used to mate the zirconium cladding to the foils. Is this Zr merely a contaminant from the rolling mills or has it infiltrated into the bulk of the U-10Mo foils? Will this Zr affect the U-10Mo performance?
- The Mo profiles indicate possible Mo composition voids in the U-10Mo foils. Are these voids real and how big are they in volume?
- The Zr profile across the Zr clad foil shows differences in Zr thickness. Can we develop a measurement approach using fs-LA-ICP-MS to obtain accurate Zr thickness and correlate with XRF measurements?
- Are the high and low spots of U235/238 ratio real and how large are these features? What impact will these variations in isotopic ratio affect the performance of the fuel? This issue may become more important with incorporation of enriched uranium into the U-10Mo fuel foils.

In addition to the isotopic ratio measurements demonstrated here, there are additional capabilities which would be useful for the program. This includes identification and measurement of impurities and distribution of these impurities. The Zr thickness could be measured with appropriate calibration of the raster speed providing corroboration of the XRF Zr thickness measurements.

The capability of the fs-LA-ICP-MS instrument has been demonstrated for the measurement of the isotopic ratio of uranium in the U-10Mo foils. These measurements were not optimized. There remains significant method development to fully exploit the capabilities of this instrument as applied to the CONVERT U-10Mo fuel and the needs of the program.

Overall it appears the fs-LA-ICP-MS instrument would be a useful tool in the production of the CONVERT U-10Mo fuel.

ACKNOWLEDGEMENTS
The authors would like to thank Kester Clarke, Velma Lopez and Kathryn McIntosh for their assistance in obtaining the samples used in these measurements. Funding for this work was provided DOE/NNSA Office of Material Management and Minimization.

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