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Development and Qualification of Tungsten Reference Materials for LA-ICP-MS

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Power Exhaust & Particle Control

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ABSTRACT

Reference materials have been developed to provide areal density measurements of tungsten that is deposited on graphite when using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Several reference materials of varying areal densities have been produced using a magnetron sputtering, thin film deposition technique. With multiple reference materials that have varying areal densities, a calibration curve has been developed for translating the detector response of an ICP-MS into a quantitative measurement. These results provide the opportunity to make calibrated comparisons across graphite samples that were exposed to tungsten transport experiments for nuclear fusion research. In addition, these methods may be applied to provide individual areal density measurements for the five unique isotopes of tungsten. It is found that areal density measurements via LA-ICP-MS agree with characterization for the same samples when using the more traditional Rutherford backscattering ion beam technique. Qualification of these reference materials was completed using ion beam laboratories at the University of Tennessee, Knoxville and Massachusetts Institute of Technology, and Sandia National Laboratory.

1. INTRODUCTION

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) offers many attractive features for sample characterization. Little to no sample preparation is required when compared to the digestion and serial dilution that is essential to aqueous ICP-MS sample introduction techniques. Samples that will be characterized by LA-ICP-MS most often simply require mounting within an ablation cell along with any reference materials (RM) that are used for quantitative determination of the sample composition. Unfortunately, a wide variety of RMs are not readily available for the laser ablation sample introduction methods. Matrix matching is one of the key characteristics of an appropriate RM that is used to calibrate the detector signal, but many times these can require significant effort for preparation when using laser ablation sample introduction [1]. Herein we present a simple method for providing LA-ICP-MS areal density measurements [W atoms/cm^2] of tungsten (W) deposits on a carbon (C) substrate using a RM that has been developed in-house. While the results presented here are specifically for a sample comprised of W deposited on a C substrate, the technique may be applied to a wide variety of elemental and isotopic combinations. Therefore, this method has broad application to those interested in characterizing trace levels of materials on the surface or even within a sample.

Within the field of fusion energy science, material transport and the resulting deposition is a key area of interest. Material erosion from plasma material interactions (PMI) is a concern for future fusion reactors due to the resulting degradation of plasma-facing components (PFCs) and the introduction of harmful impurities into the plasma core. Therefore, we must study the PFC erosion and ensuing material transport that eventually results in the deposition of the eroded particles in the device. When isotopically unique materials are used as a particle source for PMI studies, these liberated particles can be uniquely identified wherever they deposit in the device and therefore act as isotopic tracer particles [2]. In order to enable these more complex tracer experiments, there remains the open issue of developing standards for calibrating isotopic deposition measurements. This holds true particularly for cases that require high sensitivity due to very low areal density of deposited material [3]. Other surface characterization techniques for determining the isotopic nature and areal density of the deposited material often requires the use of multiple analytical methods in order to obtain both the elemental areal density and isotopic ratios with high spatial resolution [4]. Both issues are addressed through this work. With the use

of LA-ICP-MS, isotopic ratios may be obtained simultaneously with areal density measurements when proper RMs are available.

During the first Metal Rings Campaign (MRC) at DIII-D, an experimental fusion device operated by General Atomics, graphite collector probes were inserted into the edge plasma region of the device. As their name implies, these collector probes were used to *collect* eroded material entrained within the flow of the edge plasma. These eroded materials of interest were sourced from isotopically unique W metal rings that were installed in the lower divertor of the device [5]. One of the rings was created using natural W while the other ring was isotopically enriched with 93% ^{182}W. The high-Z W depositing on the low-Z C collector probes made Rutherford backscattering spectrometry (RBS) an ideal tool for assessing the elemental or 'total-W' areal density. However, isotopic measurements and sub-millimeter resolution mapping of the collector probe surface are unavailable using this method. LA-ICP-MS offers a complementary characterization method for providing sub-millimeter resolution 2-D surface maps of the individual isotopic W profiles as well as qualitative elemental W profiles across the collector probe surface [4]. Unfortunately, RMs for this analysis of W on graphite are not commercially available. Many RMs that are available on order, such as the NIST standard reference materials (SRM), are often limited to bulk silicon samples that have been spiked with known levels of impurities [6]. The use of these standard RMs is appropriate for tuning the LA-ICP-MS system prior to an analysis run. However, when used to develop a point for detector response calibration, they are only appropriate for samples that match the matrix of the standards. While these are easily accessible, literature still emphasizes the importance of matching the RM matrix to that of the sample being characterized [7]. Since this study focuses on W that has been deposited onto a graphite substrate, in-house reference materials have been created for developing a LA-ICP-MS calibration curve. This calibration is used to translate the ICP-MS detector response to the laser-ablated W into a quantitative measurement of both isotopic and elemental W areal density.

2. REFERENCE MATERIAL PREPARATION

Table 1. List of parameters applied to the AJA Magnetron Sputtering Tool during the development of W on C coupon reference materials.

Voltage	Current	Pressure	Power	Argon Flow	Sample Rotation
323 V	31 mA	9 mTorr	10 W	18.5 sccm	90 rpm

In order to properly develop a calibration curve, multiple reference material samples were prepared using an AJA International ATC Orion-5 confocal magnetron sputtering system for depositing thin W films onto one-inch diameter graphite coupons. This system directs an argon plasma onto a material target material surface. The argon plasma sputters this target material, and the ejecta is then collected on the C coupon in order to grow a thin W film. Kurt J. Lesker targets with a diameter of 2 inches, thickness of 0.25 inches, and purity of 99.95 % W were used as the deposition target material. With the parameters fixed as presented in Table 1, the growth rate of the W thin film is proportional to the exposure time. In order to optimize the uniformity of the thin film, low power of 10 W, high sample rotation at 90 rpm, and a maximized distance between sputtering target and sample within the thin film deposition chamber were implemented.

The thin films were grown on sample coupons that were cut to 1 mm thickness from an Alfa Aesar rod of graphite stock material (Chemical Abstracts Service number 7782-42-5) using

an Allied TechCut low speed saw. No further surface modification was completed prior to thin-film deposition; however, it is suggested that they be cleaned via plasma etching in future iterations. Surface roughness measurements via profilometry or other techniques were not available prior to deposition. However, characterization of this parameter would be useful in qualifying the surface prior to deposition and ensuring consistency.

Once cut, each coupon was then placed into the magnetron sputtering system in order to grow W thin films. During deposition, the parameters listed in Table 1 were used. While three samples were created using the parameters in Table 1, each graphite wafer was exposed to the thin film deposition tool for different amounts of time. This resulted in three samples with unique areal densities. The sputtering times used included 1, 5 and 10 seconds in order to create enough samples for a three-point calibration curve. These samples will be referred to as W-1, W-5 and W-10 respectively. These times and sputtering tool parameters were chosen after a series of samples were created. Each series was tested to encompass the observed detector count range that resulted from initial collector probe LA-ICP-MS measurements of deposited W from the transport experiments.

After development, the RMs were then sent to two separate ion beam facilities in order to determine the areal density of W upon the graphite wafer surface. The two facilities located at the University of Tennessee, Knoxville (UTK) and the Massachusetts Institute of Technology (MIT) were chosen in order to perform a comparative analysis of the RMs.

3. RBS ANALYSIS

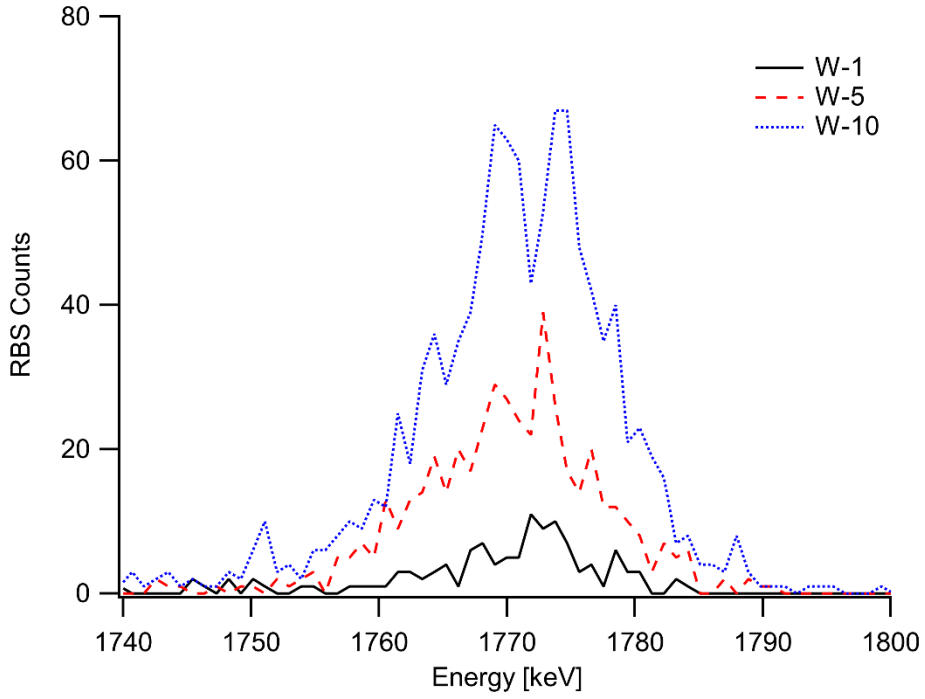

Figure 1. Presented are RBS spectra for each RM depicting the variation in sample thickness due to change in deposition time. The plot is fixed on the W peak position and is plotted versus detector counts. Higher counts correspond with a greater W areal density.

RBS spectrum results from the Ion Beam Materials Laboratory at UTK are overlaid in Figure 1 for a single measurement on each of the three RMs. During sample analysis, a 2 MeV He^4 analysis beam was used. Long acquisition times of 30 minutes were employed on each reference material due to the expectation of low W signal. The figure is honed in on the energy range that is correlated with the W thin films. Each spectrum was analyzed using SIMNRA in order to determine the measured W areal density [8]. Calibration for SIMNRA was generated using gold and silicon-nitride upon a silicon surface. Measurements at multiple locations were taken for each sample. The average of these multiple measurements for a single RM is presented along with the associated standard deviation in Table 2.

RBS analysis was repeated by the ion beam laboratory at the MIT. Instead of measurements at multiple locations across the RM surface, multiple beam energies were used on each RM. Initial measurement at 2 MeV were followed by a 2.745 MeV ^4He analysis beam. The averages of these multiple measurements are presented along with the standard deviation of the measurements in Table 2.

Table 2. Areal density measurements for each sample. Units are 10^{15} W atoms / cm^2.

Laboratory	W-10	W-5	W-1
UTK	0.2564 ± 0.0008	0.1084 ± 0.0008	0.0270 ± 0.0008
MIT	0.2269 ± 0.0110	0.0914 ± 0.0049	0.0235 ± 0.0034
Average	0.2417 ± 0.0091	0.0999 ± 0.0035	0.0252 ± 0.0025

Through these multiple measurements, it is found that the areal density measurements for each of these calibration measurements are in close agreement with one another. Average values for measurements between the two facilities may be calculated and used as an areal density value in future sections and analysis.

4. LA-ICP-MS ANALYSIS

The laser ablation tool used for introducing samples into the ICP-MS is a UP-213 YAG laser ablation system from New Wave Research, Inc. This tool is equipped with a 6 x 6 x 1 inch large format cell (LFC) which utilizes helium as the carrier gas with a flow rate of 800 sccm during analysis. Collector probe samples and the RMs are all mounted into this cell in preparation for analysis via LA-ICP-MS. With the RMs, the goal is to determine the LA-ICP-MS detector response to each of the RMs listed in Table 2. Considering we know the areal density of each RM from RBS, we can then develop a calibration curve when we know LA-ICP-MS detector response to a given areal density. The equation of the calibration curve may then be used to provide *calibrated* measurements of areal density across the collector probe surface for both elemental and isotopic W deposition. The settings used during analysis with this tool are presented in Table 3. These specific settings were chosen in order to ablate all W within the crater produced by the tool without flaking of the surface or any crater overlap. Once the sample is ablated, the released material is passed from the LFC to the ICP-MS by the helium carrier gas. In order to produce a stable plasma within the ICP-MS, an additional 700 sccm of argon gas is mixed with the helium prior to reaching the ICP-MS torch.

Table 3. Laser ablation tool settings for W on graphite reference materials

Spot size	Repetition rate	Fluence	Scan speed
50 μm	10 Hz	7.75 J/cm^2	500 μm/s

The ICP-MS is an Agilent 7700X which ionizes elements and uses the mass to charge ratio for each ion in order to sort the ions before counting them with a detector. The ICP operating conditions are optimized for sensitivity and stability using a NIST 612 SRM prior to each sample analysis. The glass NIST 612 is doped with known concentrations of elements. During the initial tune, we first check for ^{29}Si. Considering the primary component in the SRM is glass, Si is the 'filler' material in the sample. Therefore, one should expect the counts to be high on the detector. Values will vary depending on the parameters and individual system, but this is something that a user should have a good sense for when using the technique on a regular basis. Any detector response that greatly varies from the average could be an indicator for an issue with the system or methods. Next, we check for sensitivity in addition to mass balance through the ^{45}Sc, ^{175}Lu, and ^{238}U isotopes. The system response for these isotopes should be lower than those for the Si, but fairly even with one another considering they are all in approximately equal concentrations throughout the SRM. This matching of the response for each mass is what is referred to as mass balance. Next, we typically check for the oxide ratio of masses 248/232. This will yield a measurement of the oxygen levels within the LFC. Lower is better. Oxygen comes from the atmosphere and is introduced when loading samples. We want to evacuate and purge until these oxygen levels are low. Ratio values of less than 0.7% are a good indication of when it is acceptable to begin sample analysis. However, even lower numbers are preferable. This is a game against time. The longer you are willing to wait, the more stable this value will become. The oxide ratio typically stabilizes around 0.35%, but this can take up to two hours to achieve. Following the oxide ratio, we also check the null mass at 220. This mass does not exist, so the detector response should be fluctuating near zero. Any significant detector response on this mass is an indication of the electron multiplier being overly sensitive. The vendor can help resolve this issue. Finally, one can monitor any masses that they are interested in during sample analysis. This can provide an idea of what to expect as an inherent background sensitivity within the system. Here we check for tungsten in order to ensure there is little to no sample history from previous runs. Once the system is tuned and no issues are found, sample analysis may begin.

During sample analysis, the five isotopes of W are monitored with 0.1 seconds of integration time. With five isotopes, at an integration time of 0.1 seconds each, we then have 0.5 seconds required to develop the total or *elemental* W signature at a particular position along a laser ablation scan. Considering then that the scan or laser raster speed is set to 500 μm/s, the resolution for the elemental signature is 0.25 mm using this LA-ICP-MS method. Therefore, we have a new elemental W signature every 0.25 mm along the ablation path. This is all variable. Lower scan speeds will slow down analysis, but provide even higher resolution measurements. More masses will increase total integration times and decrease the frequency of individual isotopic measurements. Higher scan speeds and lower total number of isotopes provide an efficient analysis scheme.

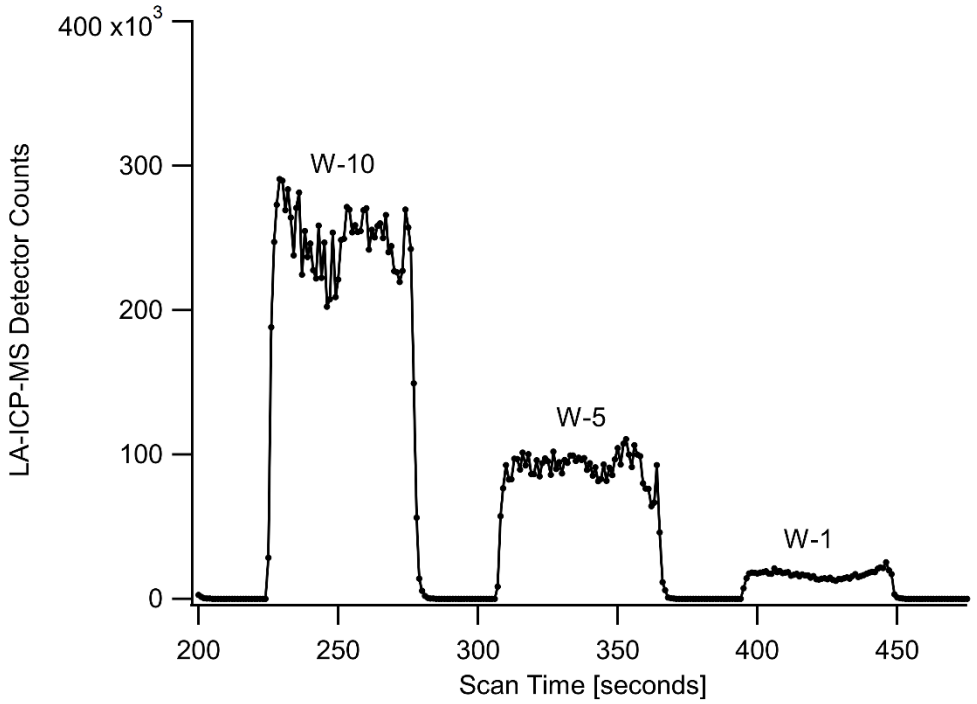

Figure 2. LA-ICP-MS detector response showing the variation in signal stability across each RM. Deposition times are listed on the plot in order to identify each scan plateau.

With the samples and RMs mounted in the LFC and the tuning process complete, RM analysis may begin. Again, the objective is to determine the LA-ICP-MS detector response for each of the three RMs. The three unique RM samples were measured with LA-ICP-MS across the full radial extent of the RMs in order check for surface uniformity as a result of the deposition process. Results from these radial scans are shown in Figure 2. These three radial scans are results of time resolved analysis (TRA) mode using the LA-ICP-MS method. In TRA mode, the detector response is measured over time using the laser ablation tool settings in Table 3. The scans are taking during a single sample acquisition time of 500 seconds. Each unique RM is marked by a plateau in signal while the troughs between these samples indicated time taken to move from one RM to the next. A plateau in the TRA scan marks consistent areal density across the sample surface. As is clearly shown in the figure, there is a difference in detector response for each RM. The higher the deposition time on the RM, the more counts the LA-ICP-MS technique detects. This is expected. Each RM has a relative standard deviation of 10 - 15 % across the flattop portions of the scan. This is sufficient for calibrating the W content on the graphite collector probes. One can then take an average over the plateau for each of the three RMs in order to obtain an average ICP-MS detector response for a given areal density. These two numbers together can be fit to a linear trendline in order to obtain the calibration curve that is presented in the next section.

5. RESULTS

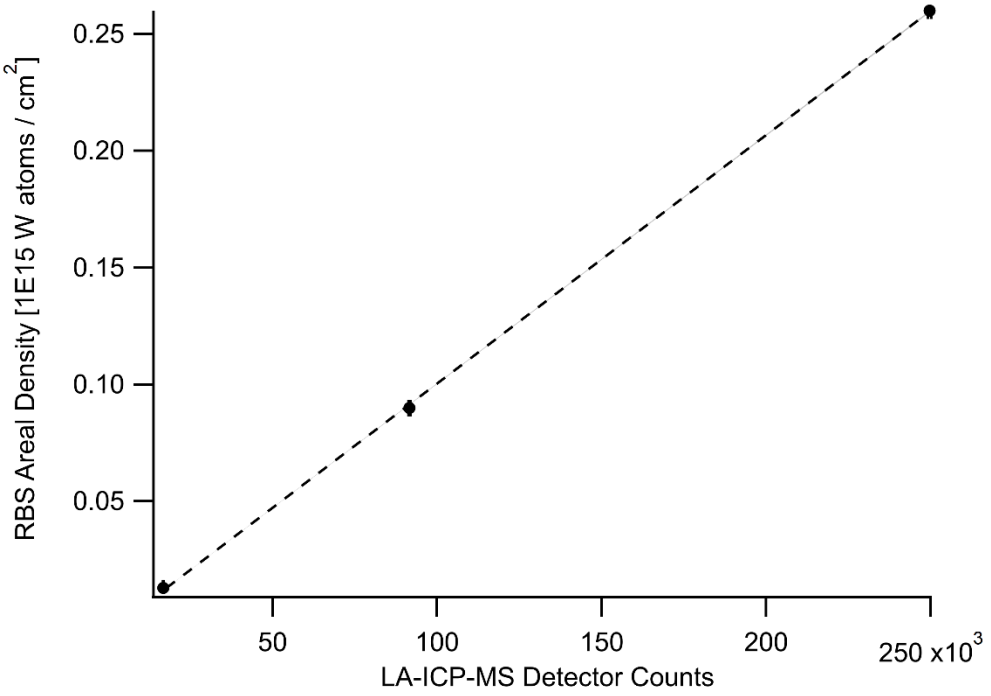

Figure 3. Three-point calibration curve for converting LA-ICP-MS detector counts to areal density. The three points are fit with a dashed trendline, that is forced to zero y-intercept, in order to produce the equation $y = (1.033 * 10^{-6})x$ with an R^2 value of 0.9986.

With the calibration curve shown in Figure 3, a line equation is generated from a linear trendline fit of the RM data. The equation for the dataset presented herein is forced to zero and results in the Equation 1. Note that a new trendline should be gathered prior to sample analysis. This will account for any variation in the ICP-MS response. The trendline shown here was obtained directly prior to collector probe analysis.

$$y = (1.033 * 10^{-6})x \tag{1}$$

While simple in nature, the equation is an accurate fit to the data with an R^2 value of 0.9986 and is also effective in translating counts into a useful quantity. The equation from the fit is utilized to convert the collector probe measurements of W into areal density measurements across the collector probe surface. LA-ICP-MS counts of the total W upon the collector probe surface may be plugged into the equation at each point along the ablation scan. The resulting values then provide a *quantitative* profile of the elemental W across the probe surface in terms of areal density. In order to validate these measurements, the Sandia National Laboratory ion beam facility has provided areal density measurements of the graphite collector probes in 5 mm increments down the centerline of the diagnostic's collection surface. LA-ICP-MS was then used to recreate the measurement using the discussed calibration technique. Both results are plotted in Figure 4 for comparison.

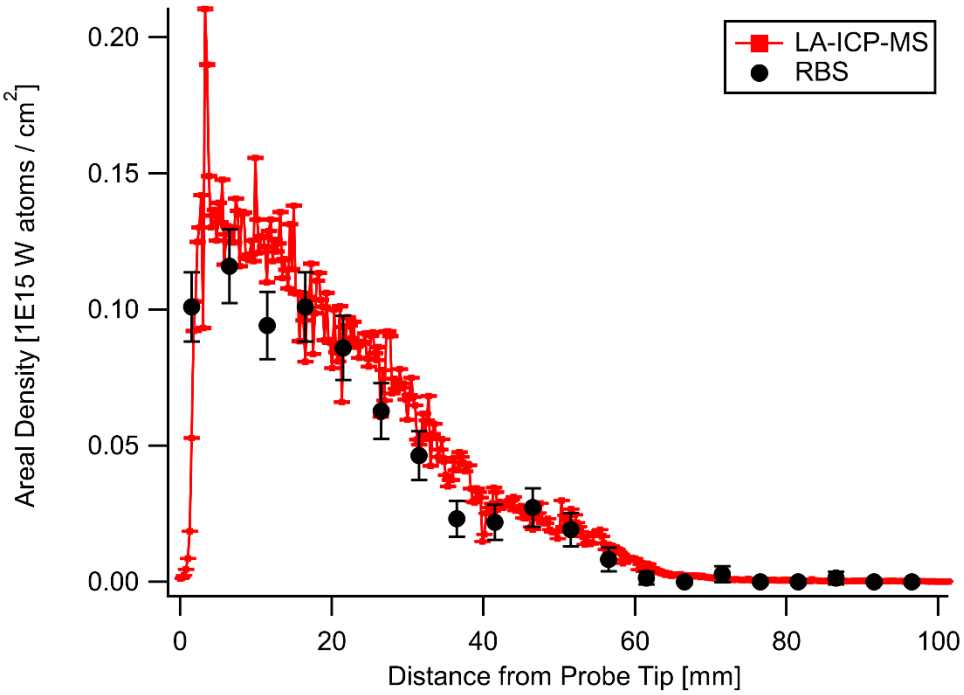

Figure 4. Calibrated measurement comparison between LA-ICP-MS and RBS techniques for W areal density across the collector probe centerline.

In Figure 4, we find agreement between LA-ICP-MS and RBS measurements for a centerline W deposition measurement of a collector probe. Error for LA-ICP-MS is based on detector counting statistics and result in small error bars that are approximately the size of the square marker. RBS has larger error bars due to the standard deviation calculation. Barring two data points, the two quantitative data sets match both in trend and areal density. These results yield confidence in our methods, and they prove the viability of using a thin film deposition technique in order to generate RMs for calibrating LA-ICP-MS measurements. The profiles have provided valuable information in regards to the plasma physics occurring within a fusion experiment, especially in understanding of impurity transport throughout the edge plasma. With the probe tip closer to the plasma core, a higher concentration of tungsten is seen in this region. Following the areal density peak, a fall off is observed in tungsten profile down to approximately zero. This correlates with a portion of the probe that is expected to be exposed to less W. Closest to the probe tip, the low counts are due to a shadowing effect from the housing unit that was employed during the experiment. These fine resolution details are made possible due to the development of the methods using LA-ICP-MS. With calibrated measurements, we can now compare collector probes exposed to different conditions with quantitative results rather than qualitative profiles. This enables a host of new studies that will be presented in future publications.

While the elemental signatures are useful, areal density measurements of each isotope are also now available when using the presented methods. The collection parameters used in generating the elemental signatures are simply the addition of each isotopic signature. Therefore, we can break up that total into its constituents in order to see the areal density of each isotopic signature across the collector probe surface as depicted in Figure 5. As presented in separate

publications, these results provide quantitative values for deposition that are valuable in determining the material evolution processes in the fusion environment [2, 9].

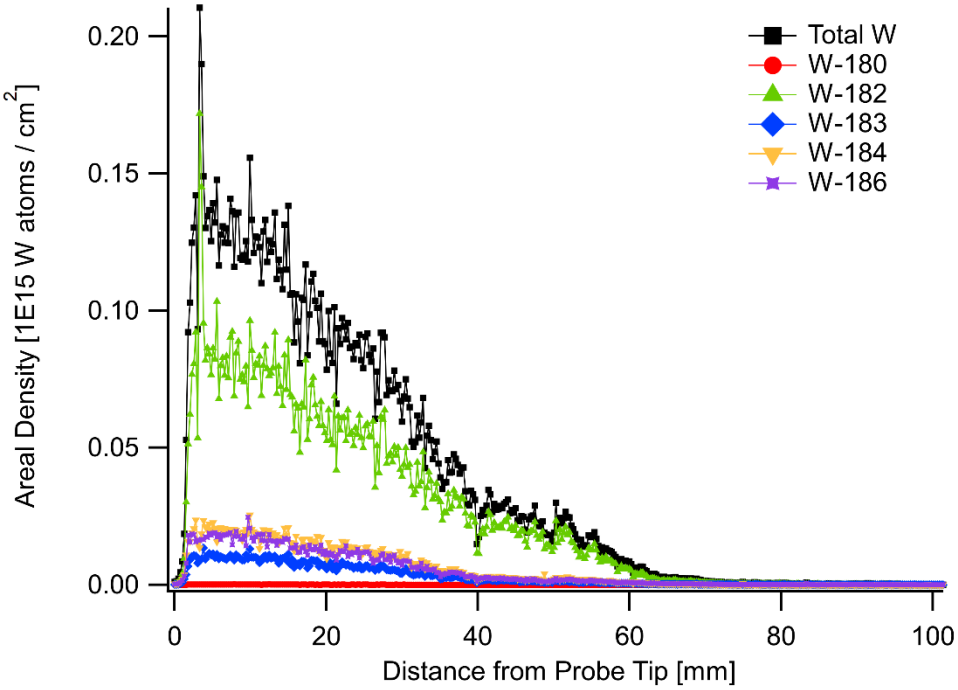

Figure 5. Each line is the isotopic contribution of each W species that contributes to the total elemental signature shown in previous figures.

6. CONCLUSIONS

Isotopic ratios and high-resolution quantitative measurements of material surfaces are instrumental in material transport studies for fusion energy research. In order to enable studies of isotopic W transport, reference materials have been developed using a thin film deposition technique. The reference materials have been qualified by ion beam analysis using Rutherford backscattering in order to determine the areal density and uniformity from the deposition process. The low areal density reference materials are consistent across the full radial extent of the wafer surface and show sequential areal density that is necessary for calibrating LA-ICP-MS measurements. The resulting reference materials have provided a calibration curve for determination of the W areal density across a collector probe surface used for fusion material transport studies. This method improves upon previous capabilities and increases the efficiency for completing these studies. With the methods for producing the reference materials in hand, it is expected that the same processes and procedures may be used with new elements and sample surface combinations. Therefore, this method of calibrating thin film ablation results for LA-ICP-MS is expected to have a wide range of application to weathering, erosion, deposition, and many other surface experiments that are interested in quantitative isotopic analysis.

7. ACKNOWLEDGEMENTS

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