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Absorbance Ratio Spectrometry (LAARS) Assay Performance Study

September 2018

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U.S. DEPARTMENT OF
ENERGY

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Richland, Washington 99352

Executive Summary

The International Atomic Energy Agency (IAEA) has a long history of testing and using laser-based technologies for a variety of safeguards applications. Notable laser-based on-site applications include: 3-dimensional laser range (3DLR) instruments, used for facility design information and verification (DIV); laser measurements to verify unique labels and detect signs of tampering; and laser spectroscopy, for non-contact process monitoring. The IAEA is also evaluating analytical laboratory instruments, such as laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) for interrogating individual particles to determine uranium isotopic ratios in collected environment samples. Recent laser technology advancements will continue to fuel future IAEA adoption of new and novel laser-based safeguards tools.

Pacific Northwest National Laboratory (PNNL) is developing one such tool, called the Laser Ablation, Absorbance Ratio Spectrometry (LAARS) technology, which is designed to provide high-fidelity $^{235}U/^{238}U$ isotope ratio measurements to support either on-site enrichment plant or off-site laboratory destructive assay (DA). Analyzing uranium hexafluoride (UF_6) DA samples on-site by LAARS could provide early indication of discrepancies with operator declarations during physical inventory verifications, so that such discrepancies could be addressed immediately, rather than after off-site analysis is completed. The IAEA is also seeking on-site DA options, because sample shipping time can be long and evolving restrictions on radioactive/corrosive material shipments may increasingly limit the IAEA's ability to easily transport UF_6 samples.

Routine on-site LAARS analysis could provide timely assay results and reduce the DA sample shipment inventory to just those needed for more definitive determination. A laboratory-based LAARS instrument could also provide rapid, cost-effective prescreening of selected DA samples shipped to the IAEA's Nuclear Materials Laboratory in Seibersdorf, Austria. PNNL has also developed a complementary UF_6 sampling technology and method, called the Single-Use Destructive Assay (SUDA) sampler to easily collect DA samples that are ideal for on-site analysis by LAARS. Combining the LAARS and SUDA sampler technologies could provide a powerful new on-site DA option for the IAEA.

The recent SUDA sampler technology advancement and UF_6 field sampling demonstrations [Anheier et. al., 2018] compelled PNNL to evaluate the LAARS assay performance with this new DA sample geometry. Two replicate studies were conducted to assess the current LAARS assay relative precision, with respect to the IAEA's International Target Values (ITV) for mass spectrometry measurement uncertainty for natural uranium (NU) and low enriched uranium (LEU) DA samples [IAEA 2010]. A replicate study refers to a statistically random sampling process used to determine repeatability, reproducibility, or relative precision, which then can be used to estimate future sampling outcomes. This approach is applied to estimate the LAARS sample-to-sample assay relative precision. The replicate experimental design incorporates random DA sample selection, assay by LAARS, and assigning that assay result as one of the replicate values. This process is repeated for all samples in the replicate study. In this context, a replicate measurement in not the same as repeated measurements of the same sample, which does not provide information relevant to the ITV measurement uncertainty.

All DA replicate samples were collected by the SUDA sampler using the preparation and exposure methods described in Section 3 of this report. The LAARS instrument design and measurement method are described in Section 2. During each day of the replicate studies, the LAARS instrument was powered on and the probe laser frequencies were locked to their respective uranium isotope transitions. Individual SUDA samples were loaded into the LAARS sample chamber, and then removed after the assay measurement was completed. At the end of the day, the LAARS instrument was powered off.

Each LAARS assay produced an assay distribution with a population around 500 estimates. The individual estimates are based on a short (20 to 40 µs) integration of each probe laser's absorbance value. The LAARS assay distribution mean for each sample is used as the replicate assay value. The final LAARS relative precision determination is reported as the replicate set standard deviation divided by the mean in percent. The LAARS assay measurements were not calibrated (a certified uranium standard was not conveniently available) for these studies, so the bias component of the total LAARS measurement uncertainty was not evaluated.

In preparation for the NU replicate study, 12 SUDA samples were prepared and exposed to natural UF_6 using PNNL's UF_6 sampling tap. Seven SUDA samples were selected and sequentially assayed, one at a time, by LAARS over a 14-day period to assess the long-term assay repeatability. The remaining three were used for initial instrument alignment and screening.

The LEU replicate study included 8 SUDA samples that were collected at the UF_6 Test Loop laboratory at Oak Ridge National Laboratory (ORNL). These samples were assayed by LAARS over a 3-day period. The same procedure used in the NU replicate study was used to collect the LAARS LEU replicate measurements. However, in this study both the LAARS short-term and long-term assay repeatability was evaluated. The short-term repeatability was estimated by sequentially assaying two different areas of the same SUDA sample. These assays were taken about 1 hour apart without removing the sample from the LAARS sample chamber. While the method did not provide two definitive replicates, it did provide useful information about the short-term measurement reproducibility.

These first assessments of the SUDA sample assays by LAARS demonstrated a new level of performance for laser-based isotope analysis. The $^{235}U/^{238}U$ atom ratio mean and standard deviation for the NU replicate study was 0.7213±0.0025% and the LAARS relative precision for NU SUDA samples was 0.35%. This precision is almost a factor of 2 better than prior LAARS replicate studies that used DA samples prepared from dried uranyl acetate solutions, and only 1.2X greater than the ITV for NU DA measurements. The LEU replicate mean and standard deviation was 4.918±0.0276%, and resulted in a LAARS relative precision of ±0.56% for LEU sample DA. This precision only 3.7X greater than the ITV goal, and is similar to best performance seen in prior LAARS replicate studies that used dried uranyl acetate solutions. The slightly better relative precision seen in NU replicate study was surprising, considering the significantly better signal levels observed in the LEU ^{235}U absorbance measurements.

These results are remarkable, considering this is the first evaluation of SUDA sample assay by LAARS. The relative precision fell just short of the ITVs; however, comparing LAARS assay performance and the deployment application with high precision mass spectrometry performance is not really appropriate for several reasons. LAARS and SUDA technologies represent a promising option for future on-site DA. Even with more than 70 years of development, mass spectrometers have not been successfully fielded for this application. Single point LAARS assay estimates are based on absorbance measurement, with only 10s of microseconds integration, using shot-noise limited optical detectors. Only a tiny uranium atom concentration in the vapor plume is sampled during each LAARS measurement. In contrast, mass spectrometry has the luxury of long signal integration (i.e., minutes) using essentially noise-free charge detectors. Finally, these studies revealed new insights about the LAARS measurement process and data analysis method that has identified several promising pathways to further improve the assay precision. Routine on-site DA that exceeds the ITV goals is a strong possibility through further refinement of the LAARS and SUDA sampler technology combination.

Acronyms and Abbreviations

3DLR	3-D laser range finder
COMPUCEA	Combined Procedure for Uranium Concentration and Enrichment Assay
DA	destructive assay
DIV	design information verification
HF	hydrogen fluoride
IAEA	International Atomic Energy Agency
ICP-MS	inductively-coupled plasma mass spectrometry
LA	laser ablation
LAARS	Laser Ablation, Absorbance Ratio Spectrometry
LEU	low enriched uranium
NML	Nuclear Material Laboratory
NU	natural uranium
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
PIV	physical inventory verification
SNR	signal-to-noise ratio
SUDA	Single-Use Destructive Assay

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1.0 Introduction

The International Atomic Energy Agency (IAEA) has successfully leveraged many laser-based technologies for safeguard applications [IAEA 2011]. The 3-D laser range finder (3DLR) is used for design information verification (DIV) during facility inspections. The 3DLR produces high-resolution, 3-D images of structural and processing systems, which can be compared to reference images to verify that the process configurations have not changed since the last inspection. Other similar laser mapping systems are used for containment tamper detection and uranium hexafluoride (UF_6) cylinder identification. These laser systems measure 'fingerprint' features that are detected as spatial surface irregularities that are unique to each container or cylinder. Several laser spectrometry measurement techniques have been identified by the IAEA, including tunable laser spectroscopy to detect hydrogen fluoride gas emissions and assay gaseous UF_6 [Poirier, 2007]. The IAEA is also implementing laser ablation (LA) sampling technique, in combination with inductively-coupled plasma mass spectrometry (ICP-MS) for environmental particle sample analysis [Kappel, et. al., 2013].

Emerging technologies and measurement methods could help address current destructive assay (DA) safeguards gaps and future verifications needs. For example, if UF_6 DA samples could be analyzed in the field, the sample shipment burden for off-site analysis could be reduced and discrepancies with operator declarations could be addressed immediately, during a physical inventory verification (PIV). The IAEA is considering the use of the Combined Procedure for Uranium Concentration and Enrichment Assay (COMPUCEA) to achieve this goal for on-site analytical measurements at uranium enrichment facilities. COMPUCEA is used by the IAEA (and Euratom) during PIV campaigns in fuel fabrication plants to determine total elemental uranium content and ^{235}U enrichment in uranium powder and pellet samples. COMPUCEA has proven to be an excellent tool for the solid samples at a fuel fabrication plant; however, implementing this method for UF_6 sample analysis at enrichment facilities may be challenging, because it requires large volume hydrolysis and dissolution chemistry, access to an on-site laboratory, and provisions for maintaining continuity of knowledge during a multiday inspection and analysis process.

The Pacific Northwest National Laboratory (PNNL) has developed a laser spectroscopy technology, called Laser Ablation, Absorption Ratio Spectrometry (LAARS) [Anheier, et. al., 20], that could provide additional options for DA sample analysis and ultimately help increase the efficiency of future DA safeguards. LAARS provides quantitative measurements of the $^{235}U/^{238}U$ atomic ratio in collected UF_6 destructive assay (DA) samples. LAARS could be applied as an on-site DA sample analysis method during PIV campaigns or, alternatively, as a laboratory-based analytical tool that provides rapid and less resource-intensive analysis of DA samples at IAEA's Nuclear Material Laboratory (NML). This report summarizes two LAARS assay replicate studies using natural and low enriched uranium (LEU) DA samples that were collected by the PNNL-developed Single-Use Destructive Assay (SUDA) sampler. The resulting LAARS assay data was then analyzed using PNNL-developed post-processing software to determine the relative precision, as compared to the IAEA target values for DA samples.

2.0 LAARS Method and Design

The LAARS instrument schematic is shown in Figure 1. LAARS couples LA with diode laser absorption spectroscopy to achieve high-precision $^{235}U/^{238}U$ atomic ratio analysis. Implementing LA has the distinct advantage of eliminating all the sample preparation steps (i.e., condensation, hydrolysis, dilution) normally associated with DA. A miniature pulsed Nd:YAG laser source vaporizes a pinpoint sample region (40 µm diameter) to form a high-temperature (~50,000 K) plasma. The laser vaporization process effectively atomizes and ionizes any uranium composition (e.g., UO_2, UO_2F_2) in this region, resulting in a dense atomic plasma. The plasma rapidly expands and cools (under ~1330 Pa argon environment in the sample chamber) into a ~3-mm-diameter hemispherical vapor plume. This plume contains ground-state uranium atoms that can be optically probed to produce measurement signals that are proportion to the ^{235}U and ^{238}U atom concentrations in each plume. LAARS uses two fiber-coupled, wavelength-stabilized diode lasers that emit wavelengths near 640 nm (^{238}U laser) and 683 nm (^{235}U laser), which are resonant with strong ^{238}U and ^{235}U isotope transitions (i.e., 468631.22 GHz and 439023.34 GHz, respectively). These lasers are combined using a fiber optic combiner, and then directed through the atomic vapor plume to selectively probe the ^{238}U and ^{235}U absorption lines. A third 683 nm diode laser is locked to the same ^{238}U transition and used a wavelength reference in an offset locking scheme to lock the 683 nm probe laser wavelength to the ^{235}U isotope transition.

After transiting the plume, the probe beams are then separated using a diffraction grating and directed to two compact photodetectors that measure the transmitted laser powers. Comparison of the laser power immediately prior to the ablation pulse, with the power at the time of maximum atomic column density (15 to 20 µs after the ablation pulse) yields an absorbance signal that is directly proportional to the atom concentration of each isotope. The measured absorbance signals are processed to provide the ^{235}U/^{238}U ratio determinations each time the ablation laser fires.

The sample substrate is mounted to a miniature XY translation system that raster scans the sample surface at the focal point of the focused ablation laser beam. The nominal ablation laser spot size is 40-µm diameter, and the scan parameters are 80-µm step increments at 25 measurements/sec. For these settings, LAARS assay of a 12.7 mm diameter DA sample consists of approximately 20,000 discrete ^{235}U/^{238}U ratio measurements, which takes 17 minutes to complete.

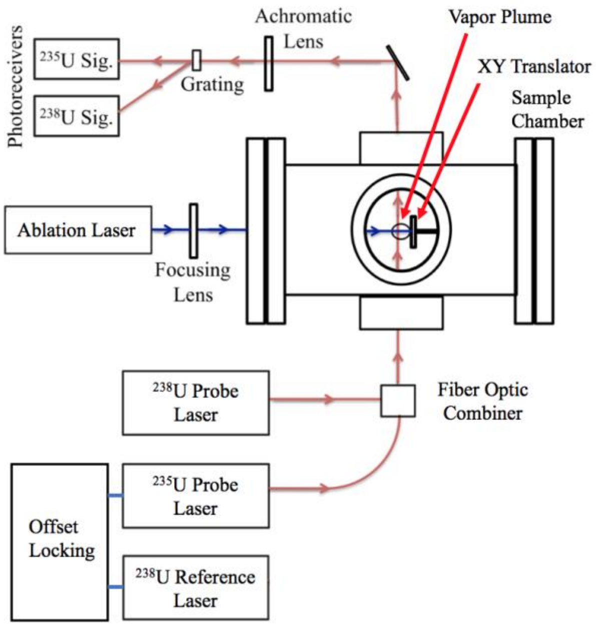

Figure 1. Simplified LAARS schematic, illustrating the laser paths and major components.

A LAARS prototype laboratory instrument was developed as part of the project's technology advancement plan. The instrument consists of subsystem modules for the diode laser system, detection, and power distribution. These subsystems are integrated into 482.6 mm (19 inch) rack enclosures that mount in a standard 27U instrument cabinet. The sample chamber and optical interface, ablation laser, and detection module are currently mounted on an optical table. A vacuum pumping station, argon gas cylinder, and mass flow controller are used to control the sample chamber pressure and gas balance. Additional engineering is planned to integrate and miniaturize these components into the instrument cabinet, so that will be feasible to ship the LAARS instrument for future on-site evaluation. The current LAARS prototype specifications are provided in Tables 1 and 2. A Windows desktop computer is used to operate the LAARS instrument software, which was developed using National Instrument's LabVIEW. The instrument control and signal collection hardware are based on a National Instrument's USB data acquisition system.

TABLE 1. LAARS Size and Weight Specifications

Component	Dimensions	Weight (kg)
Instrument Cabinet with Modules	60 cm (W) × 140 cm (H) × 96 cm (D)	100
Sample Chamber	25 cm (W) × 46 cm (H) × 76 cm (L)	30
Vacuum Pumping Station	25 cm (W) × 29 cm (H) × 43 cm (L)	28
Detector Module	46 cm (W) × 13 cm (H) × 96 cm (L)	3
Ablation Laser		
Head	13 cm (W) × 10.5 cm (H) × 17 cm (L)	3
Controller	65 cm (W) × 45 cm (H) × 22 cm (L)	4

TABLE 2. LAARS Operation Specifications

Parameter	Specification
DA Sample Format	Solid uranium on 12.7 mm diameter substrate
Operating Environment	Nominally ±2°C temperature and minimal vibration
Power	110 VAC, 20 A (220VAC, 10A) Single phase
Warming Up Time	30 minutes
Sample Assay Time	30 minutes
Typical Assay Precision	<1% relative precision

3.0 Single-Use Destructive Assay Samples for LAARS

Under a parallel project, PNNL developed a UF_6 DA sampler concept called the Single-Use Destructive Assay (SUDA) sampler, as shown in Figure 2. The SUDA sampler is designed to collect UF_6 samples in a geometry that could be directly analyzed by LAARS without requiring any sample preparation [Barrett, et. al., 2014]. SUDA sample assays can also be directly determined by LA-ICP-MS or by mass spectrometry, following a simple sample preparation method. Briefly summarizing here, the SUDA sampler uses a small sample substrate (i.e., silicon wafer) coated with a zeolite nanocrystalline thin film. Zeolite-based adsorbent films provide efficient UF_6 collection without requiring liquid nitrogen condensation. The adsorbent film can be conveniently designed to capture a specific quantity of uranium mass (µg to mg) by controlling the zeolite film thickness, pore size, volume, and water content. During the DA sampling, the UF_6 is converted to the more chemical stable and less toxic UO_2F_2, by hydrolysis with the prescribed water content in the zeolite film. The solid UO_2F_2 particles are then confined within the zeolite matrix and the hydrogen fluoride (HF) by-product is subsequently neutralized by the alumina/silicate composition of the internal channels, forming chemically stable compounds, AlF_3 or SiF_4.

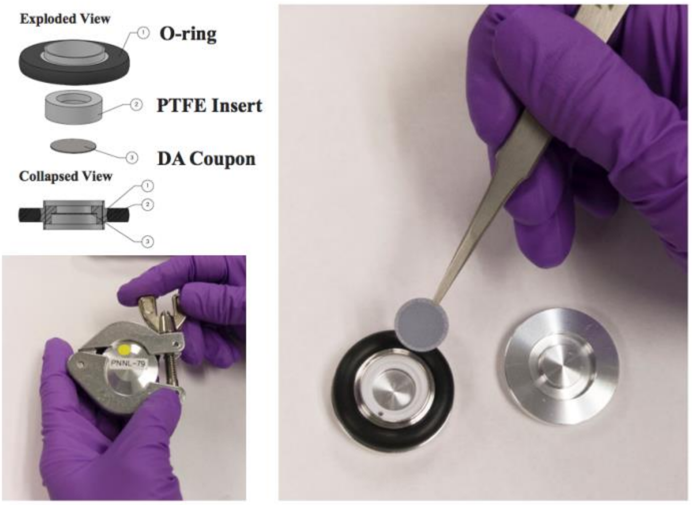

Figure 2. The PNNL-developed Single-Use Destructive Assay (SUDA) sampler.

To prepare the sorbent film, a colloidal solution of the synthesized zeolite (hydrated sodium aluminosilicate) is used to carefully spray-coat zeolite material onto a 12.7 mm diameter silicon wafer (previously rinsed with acetone, methanol, and isopropyl alcohol). The outer diameter of the wafer is masked during the coating process, as shown in Figure 3, to provide an uncoated surface for handling with tweezers. The resulting sorbent film is about 0.5 µm thick. The zeolite-coated wafer is then calcined in a furnace for 48 hours at 450 °C. After calcination, the wafer is weighed to determine the total zeolite mass on the wafer. The target zeolite mass is typically 100 to 200 µg. This zeolite mass which will capture between 140 to 280 µg total uranium mass, which is ideal for LAARS assay.

Figure 3. A silicon wafer coated with the zeolite sorbent thin film.

The as-prepared wafers are then transferred to a SUDA sampler for natural UF_6 exposure using a sampling tap located in PNNL's Radiochemical Processing Laboratory. The SUDA sample was exposed to ~10.7 KPa UF_6 vapor for about two minutes, and then transported to the LAARS laboratory for direct analysis.

4.0 LAARS Assay Measurement

The LAARS assay result is determined by collecting time-resolved absorbance waveforms for ^{235}U and ^{238}U isotopes, after each ablation laser shot. Prior LAARS studies using metal uranium foil samples (an ideal LAARS sample geometry) provided near-optimum conditions that produced high-assay precision. These assays exhibited absorbance waveforms with long lifetimes (> 150 µs) and similar shapes between both isotopes. The combined ^{235}U and ^{238}U absorbance measurement values were typically clustered near 1000 milli-absorbance. Excellent measurement signal-to-noise ratio (SNR) is achieved at this absorbance level, which corresponds to 10% transmission of the ^{238}U probe laser beam through the vapor plume. Additionally, the shot-to-shot measurement results were similar across the entire sample surface, which is expected for a homogeneous, uniformly distributed uranium sample. These observations provide the metrics needed to judge the potential LAARS assay performance for any given sample geometry.

The LAARS measurement results for the SUDA UF_6 DA sample is shown in Figure 4. The absorbance waveform timescale was typically 150 to 200 µsec (Figure 4A), which is reflective of the isotope's ground state lifetimes that the probe lasers are monitoring. The ^{235}U absorbance (^{235}A) is significantly lower than the ^{238}U absorbance (^{238}A), simply due to the smaller ^{235}U atom population in the uranium vapor plume. During the LAARS measurement, the DA sample surface is raster-scanned, point-by-point, to produce about 10,000 of absorbance measurements for each isotope. The raster-scan spatial map for this sample is shown in Figure 4B. The spatial map color bar is scaled to combined absorbance of the two isotopes. This LAARS assay of a UF_6 SUDA sample reveals the desired long absorbance lifetimes and uniform combined absorbance in the region containing the zeolite sorbent film (Figure 4B, yellow area). Weak combined absorbance is seen at the substrate edge, in the region without the zeolite sorbent film. This is due to minor UF_6 surface condensation or mask bleed-through during the zeolite film coating process.

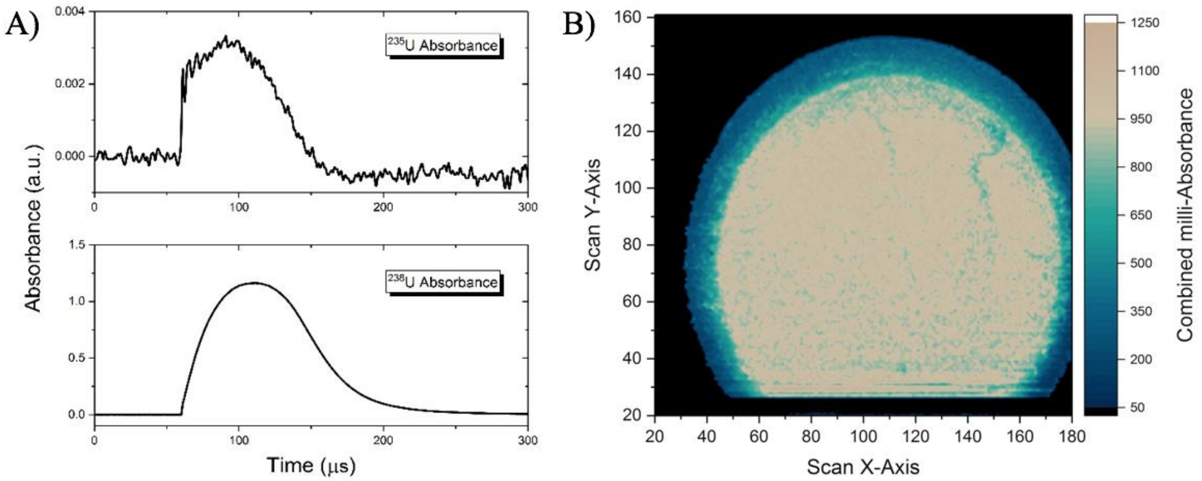

Figure 4. (A) Typical LAARS absorbance waveforms for ^{235}U and ^{238}U. (B) LAARS spatial map showing uniform combined absorbance in the yellow region where the substrate has the zeolite thin film coating.

The absorbance waveforms are processed by the LAARS filtering algorithms, which are very effective at removing anomalous data, such as non-resonant absorbance by particles in the probe laser beam path or waveform asymmetry produced by undesirable quenching effects. Figure 5 shows the LAARS assay distribution for the natural UF_6 DA sample shown in Figure 4B. The $^{235}U/^{238}U$ atom ratio is determined from each absorbance measurement by:

$$^{235}U/^{238}U\ \% = 100\% \times (^{235}A/^{238}A) / ((T_F) + (^{235}A/^{238}A)) \qquad (1)$$

The constant, T_F, is the ratio of each isotope's absorption cross section. This LAARS assay reveals a distribution that is narrow, elliptical, free from fliers, and clustered around the optimum 1000 milli-absorbance level. The distribution population includes 1663 assay estimates, with a $^{235}U/^{238}U$ ratio mean of 0.725±0.025% (1-sigma) that compares well to the known value of NU source used in PNNL's UF_6 sampling tap.

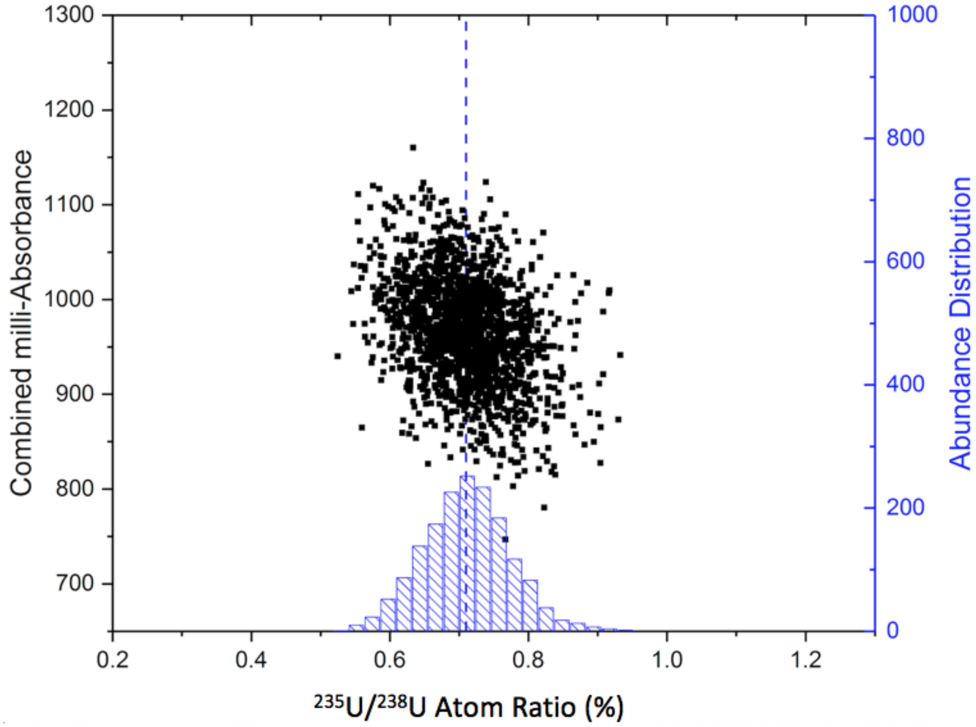

Figure 5. Processed LAARS combined absorbance distribution versus calculated $^{235}U/^{238}U$ ratio for a UF_6 DA sample collected by the SUDA sampler.

5.0 LAARS Assay Replicate Studies

Two replicate studies were conducted to assess the current LAARS assay relative precision, with respect to the IAEA’s International Target Values (ITV for natural and LEU DA by mass spectrometry. A replicate study refers to a statistically random sampling process used to determine repeatability, reproducibility, or relative precision, which then can be used to estimate future sampling outcomes. This approach is applied to estimate the LAARS sample-to-sample assay relative precision. The replicate experimental design incorporates random DA sample selection, assay by LAARS, and assigning that assay result as one of the replicate values. This process is repeated for all samples in the replicate study. In this context, a replicate measurement in not the same as repeated measurements of the same sample, which does not provide information relevant to the ITV measurement uncertainty. All DA samples were collected by the SUDA sampler using the preparation and exposure methods described in Section 3. The NU samples were collected using PNNL UF_6 sampling tap and the LEU samples were collected at the UF_6 Test Loop laboratory at Oak Ridge National Laboratory (ORNL).

5.1 Natural Uranium Replicate Study Results

In preparation for the NU replicate study, 12 SUDA samples were prepared and exposed to natural UF_6. The known $^{235}U/^{238}U$ atom ratio (i.e., 0.7255 ±0.00004%) of the natural UF_6 source was determined by assaying two SUDA samples using a high resolution multi-collector inductively coupled plasma-mass spectrometer at PNNL. Seven SUDA samples were selected for LAARS assay and the remaining three were used for initial instrument alignment and screening.

During each day of the replicate studies, the LAARS instrument was powered on and the probe laser frequencies were locked to their respective uranium isotope transitions. Individual SUDA samples were loaded into the LAARS sample chamber, and then removed after the assay measurement was completed. At the end of the day, the LAARS instrument was powered off. The raw absorbance data for each LAARS replicate measurement is stored as it was acquired by the LAARS instrument control and data acquisition software. After all assays were completed, the replicate data was analyzed using custom post-processing software. All software was developed by PNNL using National Instrument’s LabVIEW. The post-processing application imports the raw absorbance data and allows the user to select a region of interest (ROI) on the combined absorbance spatial map, as shown by the red horizontal and green vertical cursors in Figure 6. The same region of interest was used for all replicates.

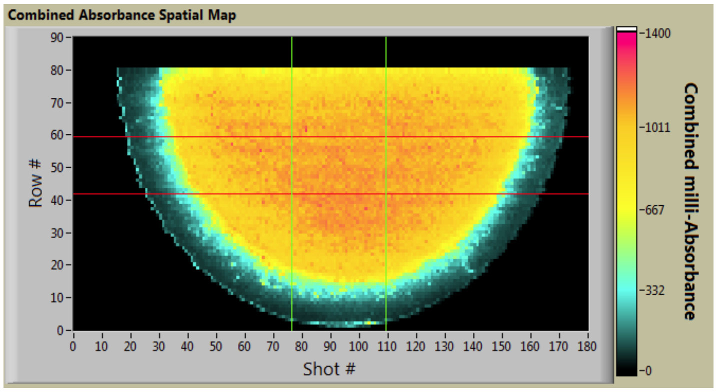

Figure 6. The region of interest is selected using the red horizontal and green vertical cursors.

A series of PNNL-developed filtering algorithms are applied to the ROI data to remove spurious data, and then the ^{235}U/^{238}U atom ratio for each data point remaining in the distribution is determined using equation #1. A windowed, area under the (absorbance) curve is used as the isotope absorbance values, ^{235}A and ^{238}A, in equation #1. The filtered LAARS ^{235}U/^{238}U ratio distribution is plotted vs. combined milli-absorbance, as shown in Figure 7. Spurious outliners can be manually discriminated (after verifying that the ^{235}U absorbance waveform is anomalous) using the vertical yellow cursors. The distribution population mean enrichment and standard deviation are then determined for the remaining data bracketed by these cursors. These values are used as the LAARS assay result.

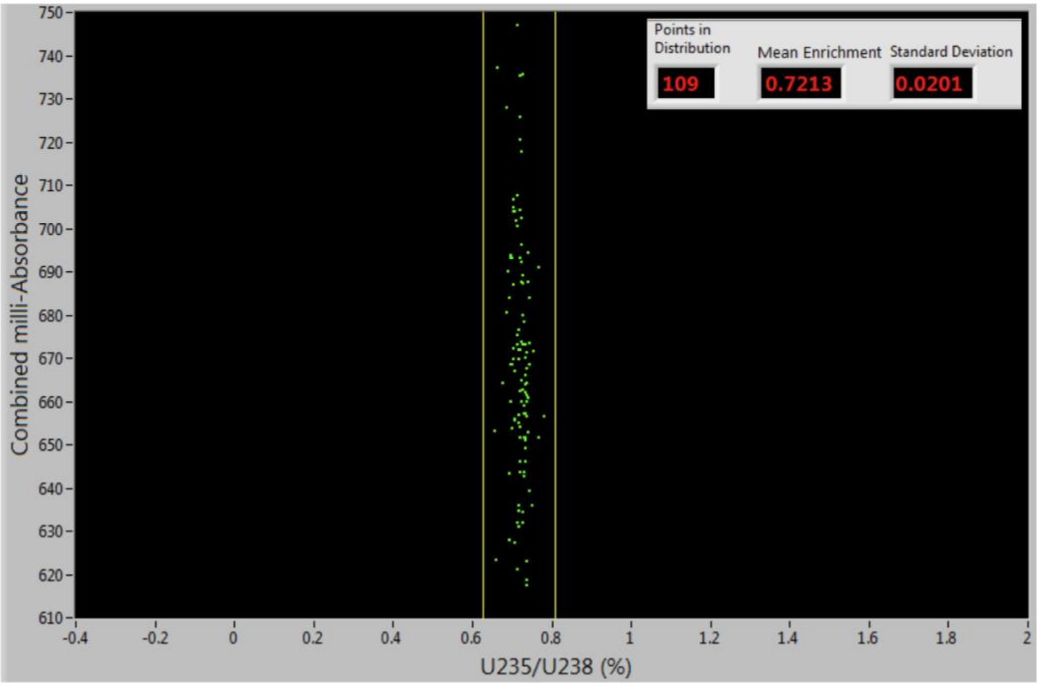

Figure 7. The filtered LAARS ^{235}U/^{238}U ratio distribution. The yellow vertical cursors are used to manually discriminate spurious outliers.

The second sample in the replicate matrix was arbitrarily selected to roughly calibrate the LAARS assay. This procedure consisted of adjusting the transition factor variable (in the post-processing application) until the assay mean and the known source values were about the same. This transition factor value (i.e., $T_f = 0.33$) remained fixed for all other NU replicate assays. This calibration method was sufficient for our purposes, because replicate study only focused on assay precision, rather than the total LAARS measurement uncertainty. Measurement uncertainty assessment would require a rigorous calibration; however, a certified uranium standard was not readily available at the time this study was conducted.

The replicate study was conducted over a 14-day period. Each LAARS replicate assay produced between about 100 to 350 assay estimates. The distribution mean was determined and reported as the single-point assay value. The standard error was then determined using the distribution standard deviation and population. The assay mean for each replicate is shown by the blue dot. The error bars represent the standard error of the assay estimate. The standard error is used, rather than the standard deviation, because each estimate in the assay distribution represents an uncorrelated sampling (by LAARS) of the mean assay value. In this case, the standard error is more informative with respect to the replicate trends.

The replicate study results are summarized in Figure 8. The mean of all replicates is shown by the solid red line, and for reference, the red dash lines provide the ±0.28% ITV thresholds for that mean. Only two assays exceeded the ITV with respect to the replicate study mean. The replicate $^{235}U/^{238}U$ mean and standard deviation for this study is 0.7213±0.0025% and the LAARS relative precision for NU SUDA samples is 0.35%. This precision is almost a factor of 2 better than prior LAARS replicate studies that used DA samples prepared from dried uranyl acetate solutions and only 1.2X greater than the ITV for NU DA measurements.

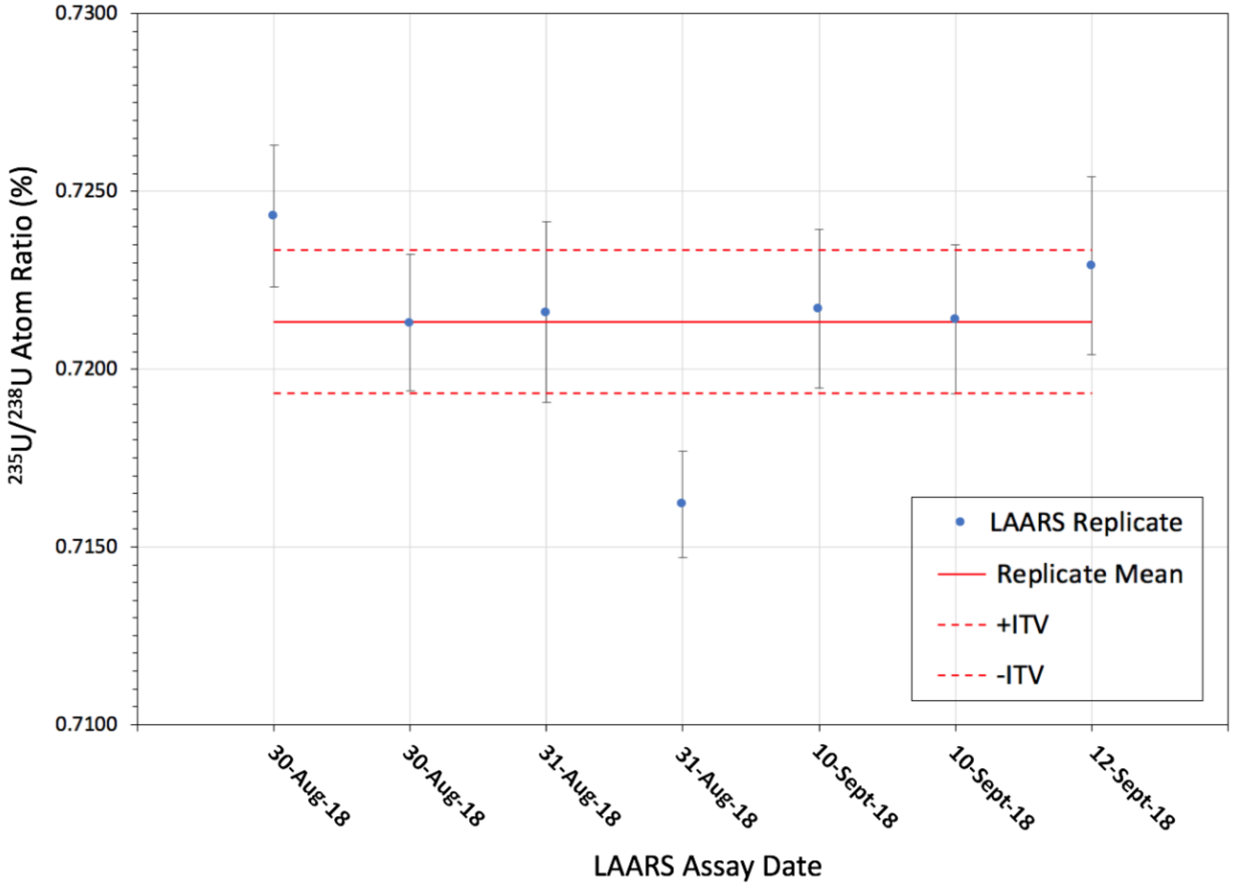

Figure 8. The LAARS natural uranium replicate study results.

5.2 LEU Replicate Study Results

The LEU replicate study was conducted using the same methods described in NU replicate study (Section 5.1). However, in this study both the LAARS short-term and long-term assay repeatability was evaluated. The short-term repeatability was estimated by sequentially assaying two different areas of the same SUDA sample. These assays were taken about 1 hour apart without removing the sample from the LAARS sample chamber. While the method did not provide two definitive replicates, it did provide useful information about the short-term measurement reproducibility. SUDA samplers were used to collect DA samples at ORNL from a LEUF$_6$ sampling tap in February 2018. The samples were shipped to PNNL and stored until assayed by LAARS in September 2018. The ^{235}U/^{238}U atom ratio for the sampling tap source was determined independently at ORNL by mass spectrometry, and that value (i.e., 4.9038±0.0018% 2-sigma) was used as the known value.

The individual LAARS assays produced significantly better measurement results, compared to the NU samples assayed in the first replicate study. The combined absorbance typically increased from 800 to 1200 milli-absorbance, as well as a significant increase in the ^{235}U peak absorbance, as shown in Figure 9. The increased ^{235}U absorbance (and corresponding LAARS measurement SNR), due to the larger ^{235}U atom concentration in the probed LEU vapor plume, improves the fidelity of the ^{235}A value used in determining the isotope atom ratio. Interestingly, the atom concentration increased by < 7X, while the peak absorbance increased by > 10X. This suggests LAARS assay performance for NU samples may be limited by the low SNR of the ^{235}U absorbance measurements. This could be resolved by increasing the uranium mass loading on the SUDA sample, which would increase the ^{235}U atom concentration in the vapor plume. An alternate ^{238}U transition, with lower absorption cross section, would need to be selected to prevent saturation of the ^{238}U absorbance measurement. This approach would also better balance the SNRs of each isotope absorbance measurement. This would lead to greater common-mode noise reduction realized by the ratio calculation used in Equation 1. The current calculation relies on a low SNR numerator and a high SNR divisor, which is less than ideal.

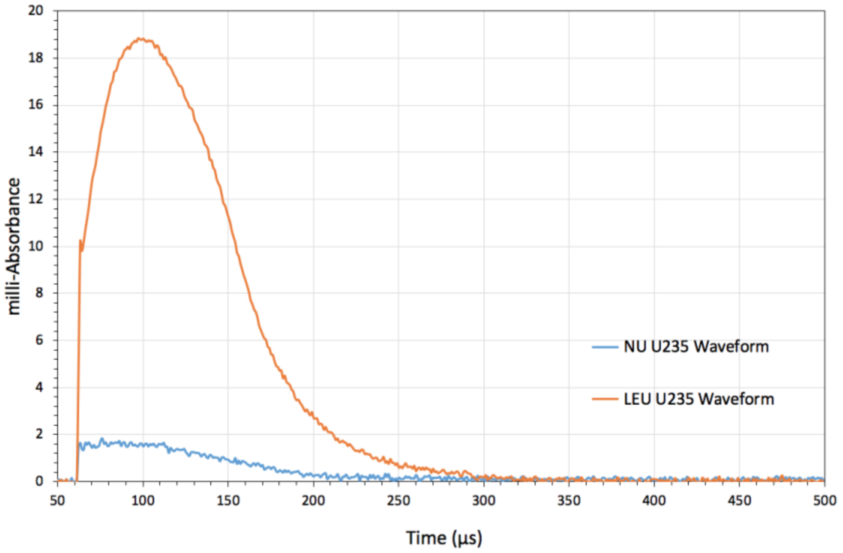

Figure 9. Comparison between the NU and LEU ^{235}U absorbance waveforms.

The replicate study included 8 LEU SUDA samples that were assayed by LAARS over a three-day period. Each SUDA sample was loaded into the LAARS sample measurement chamber, and half of the surface area was analyzed to determine single replicate assay value. After completion of the first assay, the second half was assayed by LAARS without removing the sample from the measurement chamber. The measurement provided a second replicate assay of the same sample, taken about 1 hour apart. This approach was intended to evaluate the LAARS short-term measurement repeatability. The other 6 SUDA samples were assayed using the same steps. The fourth sample in the replicate matrix was arbitrarily selected to roughly calibrate the LAARS assay, as was done in the NU replicate study.

The assay data was processed using the approach discussed in Section 5.1. Most replicate assay distributions had standard deviation values of < 0.023% 1-sigma and populations that ranged from 221 to 763. Three of the 16 LAARS replicates (Sample #3, 1st half, and Sample #6, both halves) had assay distribution shapes and standard deviations that differed significantly from the remaining 13 assays, suggesting some issue occurred during the assay measurement. In addition, the assay values had ~2% relative biases, with respect to the replicate mean, that skewed the replicate study relative precision. These three replicates were excluded from the replicate study for these reasons. Further investigation will be needed to ascertain the mechanisms responsible for the anomalous assays.

The LAARS LEU replicate study results are summarized in Figure 10. Assay of the same sample (i.e., short-term repeatability) are shown with the same color marked border. Only the second half assay of Sample #3 is shown. The error bars represent the standard deviation (1-sigma) of each replicate assay distribution, rather than standard error as used in the NU replicate. The standard deviations were similar to the values observed in the NU replicate study. Consequentially, the standard error for each LEU replicate assay is about 7X smaller (scaling with the ratio of the two assay values). In this case, error bars based on standard error would diminish the statistical information presented in Figure 9. The replicate study mean and standard deviation was determined to be 4.918±0.0276%, resulting in a LAARS relative precision of ±0.56% for LEU samples collected by the SUDA sampler. This precision only 3.7X greater than the ITV for LEU DA measurements. It is also similar to best performance seen in prior LAARS replicate studies that used DA samples prepared from dried uranyl acetate solutions. The replicate mean bias, with respect to the known value was found to be only +0.045%. The slightly better relative precision seen in NU replicate study is surprising, considering the significantly better SNR observed in the LEU ^{235}U absorbance measurements. The short term repeatability for the first 4 assays is < 0.15% relative, which is excellent. The relative repeatability ranges between 0.4% to 0.73% for the other sample comparisons, which is similar to the 3-day replicate study relative precision.

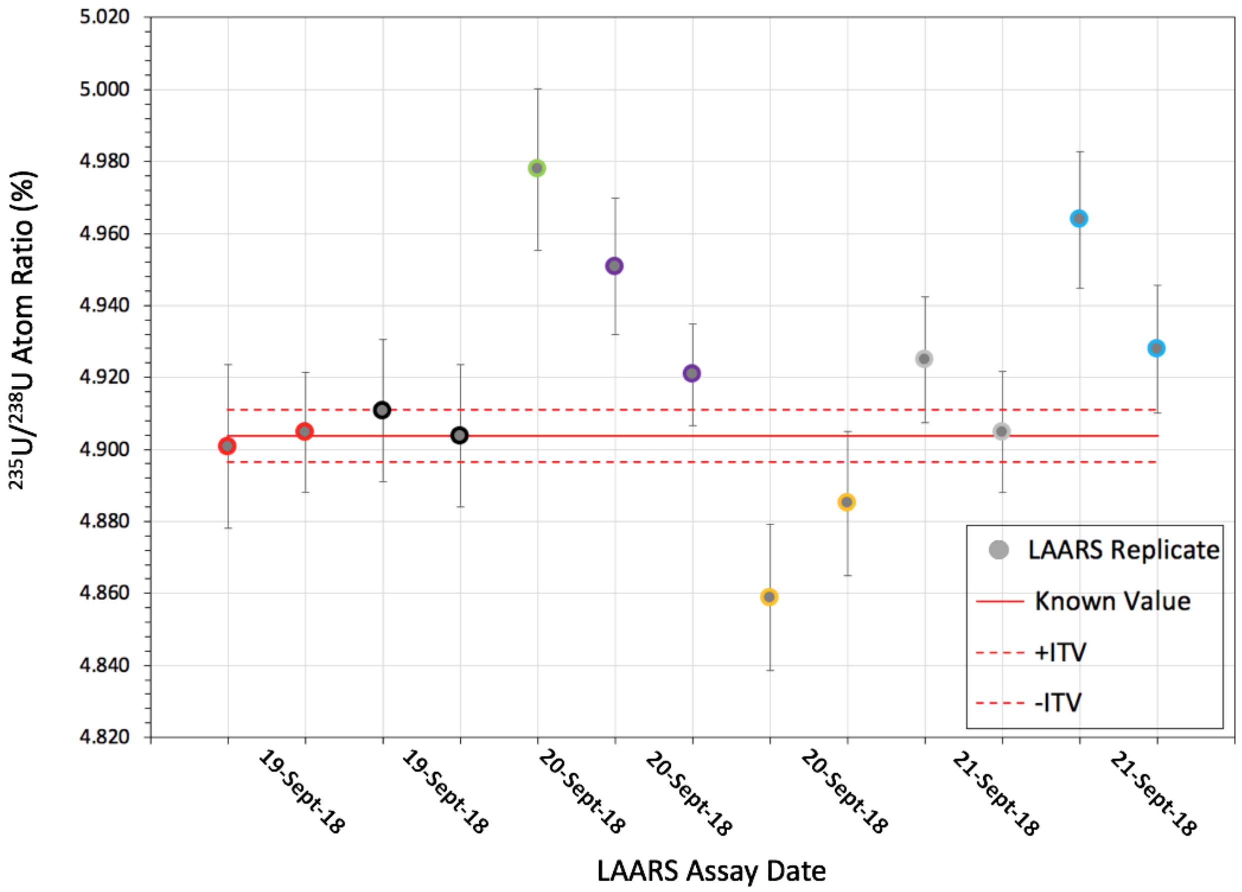

Figure 10. The LAARS LEU replicate study results.

6.0 Summary

The IAEA has successful deployed and tested laser-based technologies for a variety of safeguards applications. The continued advancement of laser technology will continue to fuel future IAEA adoption of new and novel laser-based safeguards tools. PNNL is currently developing one such tool, called LAARS, for quantitative measurements of uranium DA samples. LAARS uses tunable diode lasers to simultaneously measure atomic ^{235}U and ^{238}U absorption in an ablation plume created by a pulsed laser. The LAARS method is targeted for either on-site or laboratory-based DA, in support of uranium enrichment plant safeguards.

The recent SUDA sampler technology advancement and UF_6 field sampling demonstrations compelled PNNL to evaluate the LAARS assay performance with this new DA sample geometry. Two replicate studies were conducted to assess the current LAARS assay relative precision, with respect to the IAEA’s ITV for mass spectrometry assay measurement uncertainty for NU and LEU DA samples. All DA replicate samples were collected by the SUDA sampler to evaluate the combination of these two safeguards technologies for on-site DA applications. The NU samples were collected using PNNL UF_6 sampling tap and the LEU samples were collected at the UF_6 Test Loop laboratory at ORNL.

These first assessments of the SUDA sample assays by LAARS were very encouraging. The $^{235}U/^{238}U$ atom ratio mean and standard deviation for the NU replicate study was 0.7213±0.0025% and the LAARS relative precision for NU SUDA samples was 0.35%. This precision is almost a factor of 2 better than prior LAARS replicate studies that used DA samples prepared from dried uranyl acetate solutions, and only 1.2X greater than the ITV for NU DA measurements. The LEU replicate mean and standard deviation was 4.918±0.0276%, resulting in a LAARS relative precision of ±0.56% for LEU sample DA. This precision only 3.7X greater than the ITV goal, and is similar to best performance seen in prior LAARS replicate studies that used dried uranyl acetate solutions. The slightly better relative precision seen in NU replicate study is surprising, considering the significantly better signal levels observed in the LEU ^{235}U absorbance measurements. This result suggests that future assay precision improvements are possible through further optimization of the LAARS and SUDA sampler technology combination.

7.0 References

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