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Implementing the U.S. National Nuclear Material Archive (NNMA) Program at LLNL

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Abstract

Lawrence Livermore National Laboratory (LLNL) is one of four U.S. national laboratories providing nuclear forensic analysis of materials for the U.S. National Nuclear Materials Archive (NNMA). Over the past year, despite restrictions imposed by the COVID-19 pandemic, LLNL completed its first analyses for the NNMA, while, at the same time, began developing the infrastructure and procedures to support increased analytical throughput in the coming years. In order to increase throughput, while still meeting the requirements from our other sponsors, we have been executing an aggressive plan to increase staffing, instrumentation, and facilities over the past year. The majority of candidate materials for NNMA analysis at LLNL are currently located at other sites. Consequently, our procedures must emphasize receiving only the amount of material required for analysis from the originating sites, and a robust process for receipt, analysis, and disposition. We are also addressing the need for an information management system for storing and interpreting results, as well as the quality assurance regimen necessary to provide full confidence in the analytical results. One of our key activities in 2020 was a comparison of full nuclear forensic analyses (FF) with a more restricted set of analyses, which we call "baseline characterization" (BC) analyses, with the goal of determining the cost-benefit tradeoff of reducing the number of analytes for some materials. We analyzed 4 different sets of materials for this comparison and performed 1 FF analysis and 2 BC analyses from each set.

Introduction

The National Nuclear Materials Archive (NNMA) program, operated by the National Nuclear Security Administration Office of Nuclear Forensics (NA-83), collects, characterizes and preserves nuclear material specimens to assess whether nuclear material found outside of regulatory control is consistent with materials that originate with the U.S. Department of Energy (DOE). Lawrence Livermore National Laboratory (LLNL) is one of four analytical laboratories within the U.S. national laboratory system that perform material analyses for the NNMA. The analytical capability within the NNMA is currently growing to accommodate a substantial analytical throughput that will be sustained for the lifetime of the NNMA – this requires that the analytical laboratories supporting the NNMA plan for and implement increases in staffing, equipment and laboratories. Here we present an overview of the work completed at LLNL over the past 18 months to establish a dedicated analytical capability to support the NNMA program.

Background and analytical capabilities

Lawrence Livermore National Laboratory currently provides operational analytical support for multiple U.S. Government organizations including the Department of Energy, the National Nuclear Security Administration, the Department of Homeland Security and the Department of State. This operational capability supports analyses for nuclear forensics, nuclear safeguards,

and other applications. To support these operational analytical needs, we have developed analytical protocols for a variety of bulk nuclear material sample matrices such as uranium and plutonium, as well as for trace level analyses of environmental samples. Our analytical capabilities fall into three broad categories: non-destructive analysis, destructive analysis, and spatially-resolved analysis. Non-destructive analysis methods include gamma spectrometry, physical mensuration, optical and scanning electron microscopy, and autoradiography. Destructive sample analysis includes elemental and isotopic analysis by alpha spectrometry as well as multiple mass spectrometry techniques such as quadrupole inductively-coupled plasma mass spectrometry (Q-ICP-MS), high-resolution (HR) single collector ICP-MS, multi-collector (MC) ICP-MS and light stable isotope MS. Spatially-resolved analysis includes secondary ion mass spectrometry and electron probe microanalysis.

Although the suite of analyses performed for the NNMA is similar to the analytical scope for a nuclear forensic investigation, the overall analytical throughput required for the NNMA represents a substantial increase over LLNL's typical analytical throughput. In addition, the analytical capability and expertise at LLNL has been developed to perform an extensive suite of analyses on a broad range of sample matrix types. Because of this large range in potential sample matrix types, we typically develop an individualized sample analysis plan and approach for each set of samples that we analyze, designed to address a specific set of nuclear forensic or other questions about the unknown material. This approach allows us to comprehensively evaluate unique or distinctive samples, but is not suitable for scaling up to meet the increased sample throughput required for the NNMA program. In order to meet the increased sample throughput required for NNMA, we have spent the past 18 months developing streamlined approaches for sample analysis and data reporting, and have developed and begun to implement plans to increase our overall analytical capacity through staffing hires and new instrument procurements. We achieved our first major analytical milestone in 2020 with the analysis of the first 12 samples for the NNMA, completed in the first nine months of the Covid-19 pandemic.

Analysis of the first samples for NNMA - under Covid-19 restrictions

Analyses for the NNMA fall into two categories: Full Forensics (FF) and Baseline Characterization (BC). Baseline characterization analyses utilize a limited suite of analytical approaches including gamma spectrometry, trace element analysis by single-collector ICP-MS, and uranium isotopic and assay analysis (for a bulk uranium sample type) performed by MC-ICP-MS. In addition to the analyses performed for BC analysis, FF analysis includes a comprehensive suite of analytical approaches including optical and electron microscopy, trace actinide analysis by isotope dilution mass spectrometry, radiochronometry analysis, alpha-spectrometry analysis of ^{232}U, light element concentration and stable isotope analysis, and spatially resolved isotopic, elemental, and phase analysis by NanoSIMS and electron probe (Figure 1). Full forensic analysis is typically considered the 'gold standard' for analysis of an unknown sample for a nuclear forensic investigation; however, it is also costly and time-consuming. In contrast, BC analyses are less expensive and can be performed more rapidly; however, BC analyses may not capture the range of sample attributes or signatures that are ultimately required to identify the origin or history of a sample.

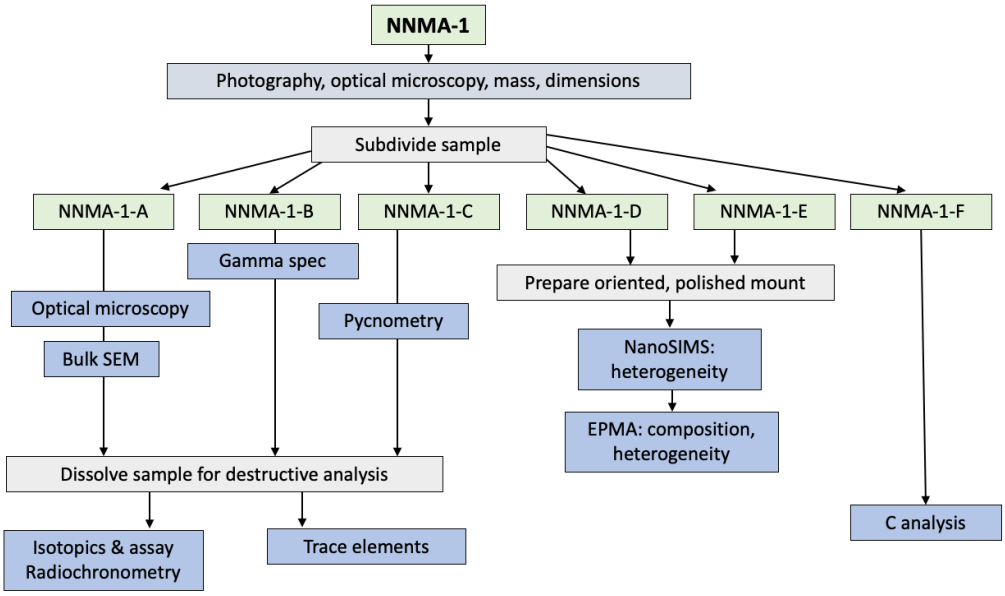

Figure 1. Schematic diagram showing typical approach for subsampling and 'full forensic' analysis of a sample for the NNMA. Green boxes represent a bulk sample or sample aliquots. Blue boxes represent analyses performed on the sample.

LLNL was scheduled to complete analysis of the first set of NNMA samples in 2020. We completed initial subdivision and gamma spectrometry analysis of the samples in February 2020, but laboratory-based analytical work came to a hard stop in mid-March 2020 when the Covid-19 pandemic halted most on-site work at LLNL. Reopening the laboratories following a several-month closure required a comprehensive evaluation of safety protocols, as well as plans to operate with reduced occupancy of the analytical laboratories. Furthermore, work planning needed to accommodate the availability of staff to come on-site to perform laboratory work, which was impacted by health and family care concerns. On-site analytical work to support NNMA restarted in late July 2020, under substantial Covid-related restrictions. A team of 26 people worked together to complete first set of 4 FF analyses for NNMA by the end of September 2020.

The sample set consisted of 4 samples of highly enriched uranium metal drill turnings, and the gamma spectra of the samples were consistent with this bulk composition. The samples appeared dark brown-gray with a coating of uranium oxide; 'pickling' of the samples in nitric acid prior to analysis removed the oxide coating and revealed shiny silver-gray surfaces. Optical and electron microscopy were used to image the entire samples and examine distinctive and contrasting textures on the opposing surfaces of the samples, as well as to characterize material adhering to the sample surfaces (Figure 2). Scanning electron microscopy and electron probe microanalysis showed that the samples are U metal with inclusions of uranium carbide and a lesser amount of uranium carbide nitride (Figure 3).

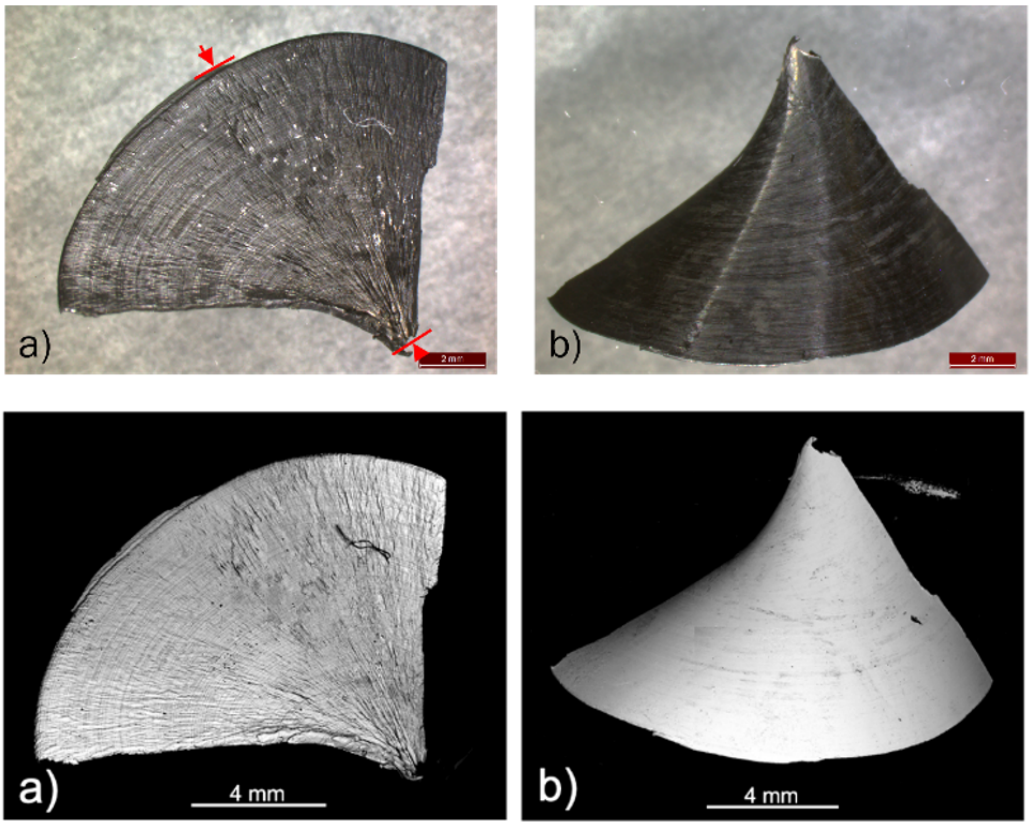

Figure 2. Optical micrographs (upper row) and backscattered electron images (lower row) of two surfaces of a NNMA sample composed of uranium metal.

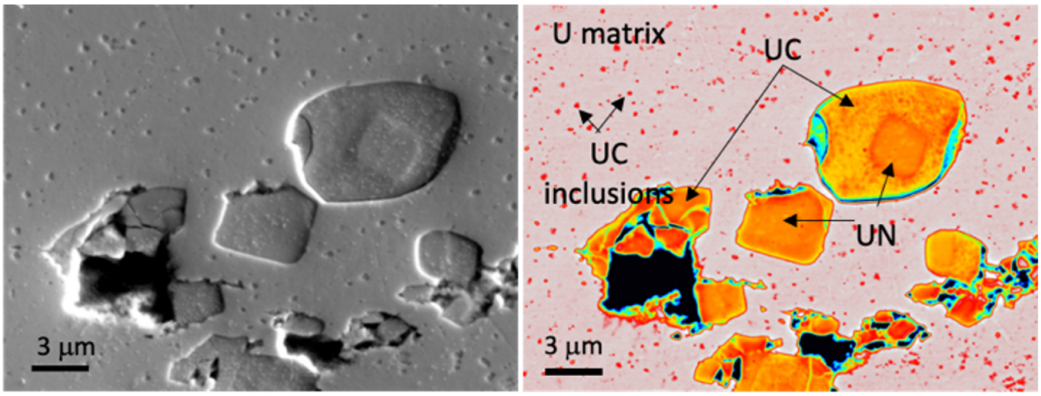

Figure 3. Secondary electron (left) and false-color backscattered electron (right) images show typical morphology of blocky and aggregate inclusions in uranium metal. Common inclusion compositions include uranium nitride and uranium carbide nitride.

Uranium isotopic analysis of triplicate sample dissolutions shows that the samples are isotopically homogeneous at the scale of the subsamples (about 250-400 mg), but that each of the four samples has a distinct isotopic composition (Figure 4). Nano-secondary ion mass spectrometry (nanoSIMS) analysis revealed that the samples have uniform U isotopic

compositions at the micron-scale (Figure 5). Trace element analysis showed that the samples contain about 250 to 350 μg/g metal impurities; some of these metals are distributed heterogeneously, as observed with NanoSIMS imaging (Figure 5). Radiochronometry analysis was performed using the ^{230}Th-^{234}U and ^{231}Pa-^{235}U radiochronometers. For each sample, the ^{230}Th-^{234}U model age is younger than the paired ^{231}Pa-^{235}U model age, and therefore the ^{230}Th-^{234}U model ages constrain the maximum age of sample formation. The ^{230}Th-^{234}U model ages range from 1963 to 1987, whereas the ^{231}Pa-^{235}U model ages define a narrower but older age range of 1957 to 1967 (Figure 6).

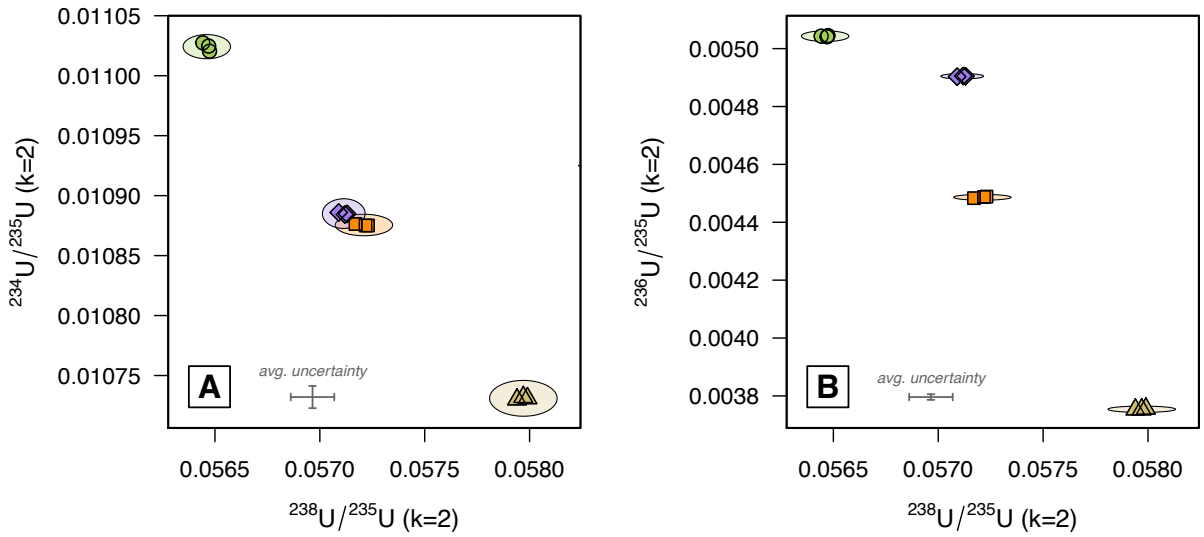

Figure 4. Uranium three-isotope diagrams of four different U metal samples; each sample is represented by symbols of a different color and shape. Individual symbols represent replicate dissolutions of each sample, and oblate fields represent the average value and uncertainty for each sample. The error bar symbol represents the average analytical uncertainty of a single measurement.

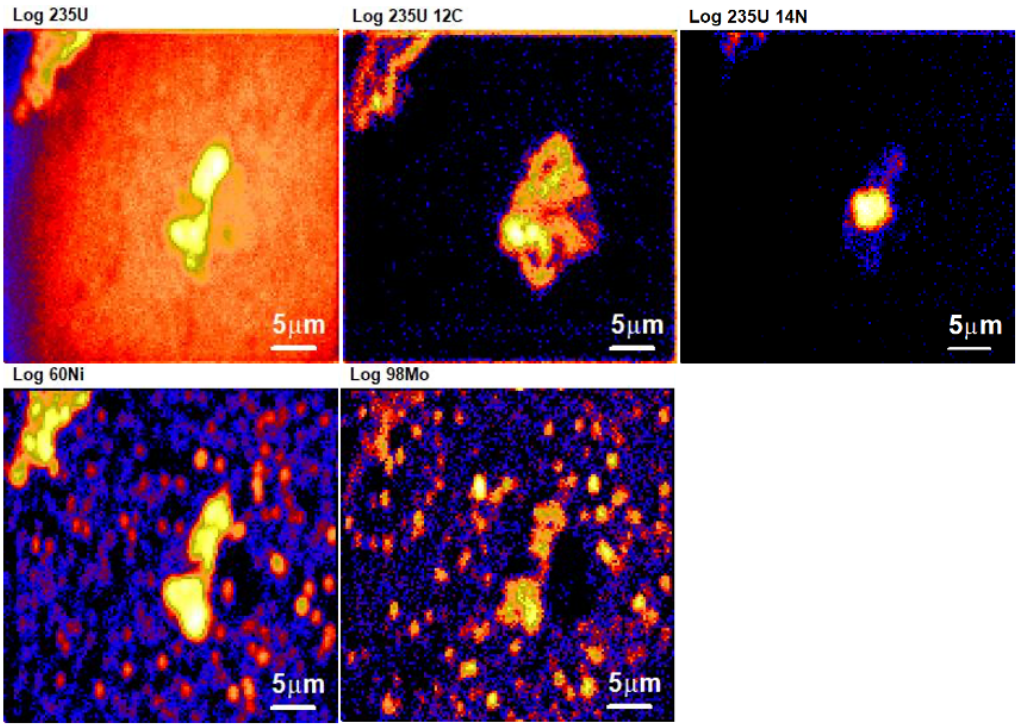

Figure 5. NanoSIMS images show U+, UC+, UN+ (top row, left to right) and Ni+ and Mo+ (bottom row, left to right).

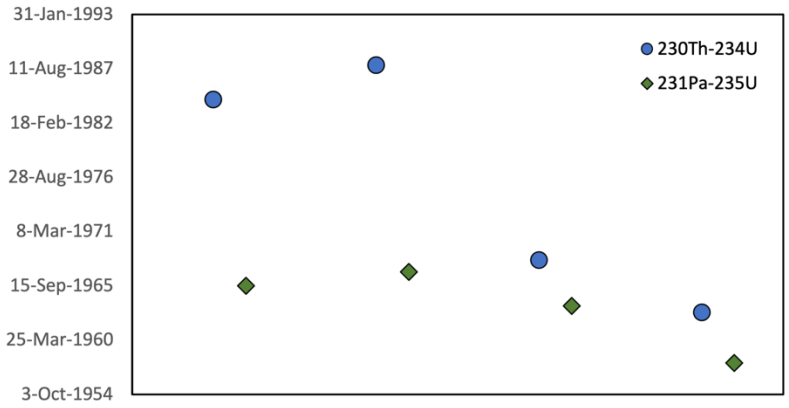

Figure 6. Radiochronometric model ages measured for four NNMA samples. For each sample, ^{230}Th-^{234}U and ^{231}Pa-^{235}U model ages are shown as pairs of circle and diamond symbols. Analytical uncertainties are smaller than the symbol size.

In addition to the four FF sample analyses described above, our work in 2020 included analysis of eight BC samples. Together, the 12 samples represented four material types, with one FF and two BC analyses performed for each material type. In part, the goal of these eight BC sample analyses was to evaluate whether it was possible to differentiate among the four material types using the less expensive and more rapid BC analysis approach. The four material types analyzed are all highly enriched uranium, with ^{238}U/^{235}U ratios that vary by slightly more than 10 times the analytical uncertainty of high-precision mass spectrometry. Variation among the minor isotope

ratios of $^{234}U/^{235}U$ or $^{236}U/^{235}U$ is not a signature that discriminates among the four material types (Figure 7).

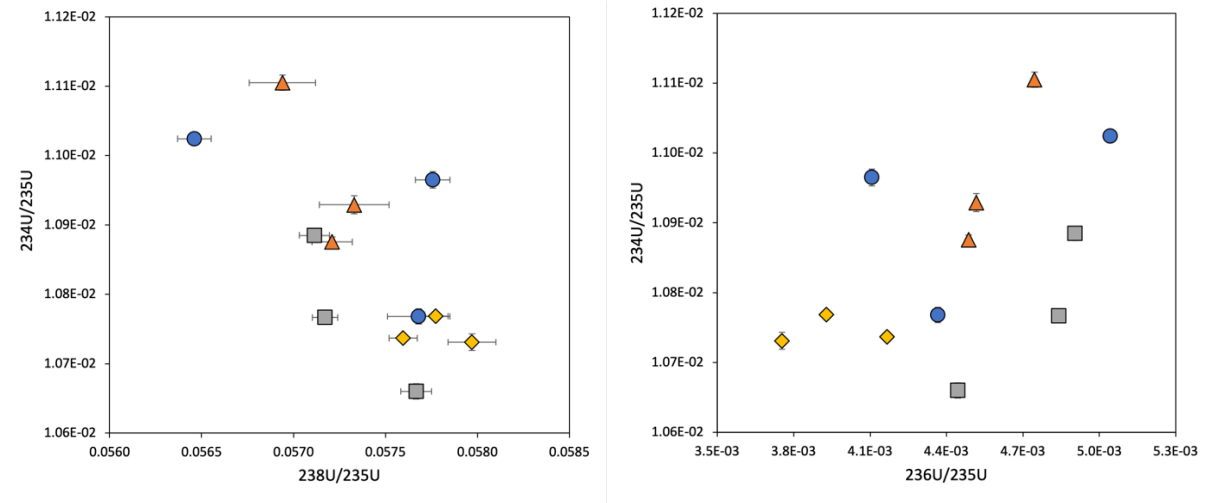

Figure 7. $^{238}U/^{235}U$ vs. $^{234}U/^{235}U$ (left) and $^{236}U/^{235}U$ vs. $^{234}U/^{235}U$ (right) variation among full forensics and baseline samples shows that U isotopic composition is not a discriminatory signature for these materials. Different material types are represented by different symbols; for each material type, one FF sample (average of three dissolutions) and two BC samples are shown.

Plans for growth and capacity increase

Given the longevity and extent of U.S. nuclear material production, the number of potential exemplars of nuclear material types within the NNMA could be exceedingly large. In order to ensure that the analytical component of the NNMA can be completed within a reasonable timeframe, e.g., 10 years, it was necessary to involve multiple national laboratories (Los Alamos National Laboratory, Oak Ridge National Laboratory, Pacific Northwest National Laboratory, and LLNL) in the NNMA analysis process, as well as for each laboratory to increase its analytical throughput significantly beyond the analytical capacity available at the start of the NNMA program. At LLNL, we are in the process of expanding our NNMA analytical throughput from 0 samples in FY19 to 50 samples/year from FY23 onward, while at the same time maintaining our analytical commitments to multiple other materials analysis programs. In order to achieve our projected sample throughput, we are increasing our analytical staff, our suite of analytical instrumentation, and our facilities to support both instrumentation and sample preparation (wet chemistry operations). We are also addressing logistics required for receiving large numbers of samples, analyzing them, and disposing of any residual material, all within the constraints posed by the on-site materials inventory at LLNL.

We are in the process of bringing seven new staff into our group to support NNMA analysis, including individuals with the following skillsets: project engineer, optical and electron microscopy, actinide isotopic analysis, trace elemental analysis. All of these new staff will have joined our team during the COVID-19 pandemic; this has presented unique challenges in orienting the new staff to LLNL and our laboratory operations, in training them in the NNMA analytical methods, and ensuring that their analytical work meets our exacting standards. In

addition, we have made special efforts to integrate these new hires into our overall analytical team. Whereas in the past, new staff would have rapidly gotten to know the larger group through regular and day-to-day in-person interactions, social distancing requirements have limited the ability for new hires to get to know others outside of their immediate work groups. As a result, we have sought approaches for developing a new integration process to compensate for the limitations on in-person interactions imposed by the Covid-19 pandemic.

Increased staffing levels for the NNMA project provides only part of the support needed for the increased analytical throughput. With increased staffing levels, we would quickly reach the capacity limits of our existing instrumentation. With dedicated sponsor funding for equipment and infrastructure, we are in the process of adding nine new pieces of equipment, as well as a new laboratory information management system (LIMS). We are adding capacity across the breadth of our instrument base, with procurement and installation of a new multi-collector inductively coupled mass spectrometry (MC-ICP-MS), a new high resolution ICP-MS (HR-ICP-MS), a new gas source stable element mass spectrometer, an additional bank of alpha spectrometers, two new planar gamma spectrometry systems, and a new environmental scanning electron microscope (SEM). In addition, in concert with our sponsor, we are developing a long-term equipment maintenance and recapitalization strategy to ensure that we have the ability to support NNMA with state-of-the-art analyses well into the future. Finally, we are currently procuring and developing a robust information management system for storing and interpreting results from all analytical techniques. In collaboration with our sponsor and the other NNMA laboratories, we are defining a quality assurance regimen that will provide full confidence in the analytical results.

At the time that we began analytical work for NNMA in late winter 2020, three of our wet chemistry laboratories were closed for renovation, as part of a long-term recapitalization strategy for LLNL's main radiological facility. So, to add to the challenges of ramping up an analytical capability in the midst of a pandemic, during the first 18 months of our NNMA work, we performed much of our sample preparation in borrowed laboratories, shared with multiple other programs. We have recently achieved beneficial occupancy of these newly renovated laboratories, and are in the process of returning to a more normal standing in our sample preparation efforts. At the same time, we are identifying creative approaches to utilizing other spaces in our building that can be used as instrument labs for the nine new pieces of equipment that will support the NNMA program.

The final component necessary to support a large-scale NNMA analytical capability is sample management. Our sponsor has set the goal of maintaining a 2-year queue of NNMA samples on site, to ensure that we maintain a steady stream of samples for analysis in the event that issues or delays arise in shipments of samples from the other sites within the DOE complex. We have maintained continuous coordination with our colleagues in materials inventory management at LLNL, ensuring that there is space in the overall site inventory to maintain this 2-year sample queue. We have also reevaluated and revised downward the total amount of each sample necessary to complete the required set of analyses. In the past, we would typically request more sample than the amount that was strictly needed for comprehensive analyses, to ensure that we have extra material to accommodate any unforeseen problems or opportunities during the

analysis process. However, with the large number of samples expected under this program, we could no longer afford that luxury and must limit our sample requests to the minimum amount needed – to minimize the amount of material transferred to LLNL and eventually analyzed or disposed as waste, but also to preserve sample for long-term storage in the archive. These material flows will continue to require our attention throughout the lifetime of the NNMA program.

Conclusions

The National Nuclear Materials Archive (NNMA) program collects, characterizes and preserves nuclear material specimens to assess whether nuclear material found outside of regulatory control is consistent with materials that originate with the U.S. Department of Energy (DOE). Lawrence Livermore National Laboratory (LLNL) is one of four analytical laboratories that perform material analyses for the NNMA. Over the past year, despite restrictions imposed by the COVID-19 pandemic, LLNL completed its first analyses for the NNMA, while, at the same time, began developing the infrastructure and procedures to support increased analytical throughput in the coming years. To that end, we have been executing an aggressive plan to increase staffing, instrumentation, and facilities.

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