JOINT SAMPLE ANALYSIS OF NUCLEAR FORENSIC MATERIALS PROVIDED BY KAZAKHSTAN

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ABSTRACT

Over the last few decades, nuclear forensics has become an essential tool in the fight against illicit trafficking of nuclear and radiological materials. Nuclear forensic analysis can provide information to law enforcement agencies regarding the composition, origin, process history and suspected use of the interdicted nuclear material. In the Republic of Kazakhstan, the Institute of Nuclear Physics (INP) is the primary nuclear forensics laboratory, responsible for the analysis of samples found outside of regulatory control in the country. The INP has been a long-standing partner of the U.S. Department of Energy, National Nuclear Security Administration's Office of Global Material Security (DOE/NNSA/GMS) and is an active member of international nuclear forensics community and the Nuclear Forensics International Technical Working Group (ITWG). As part of an on-going project coordinated through the International Science and Technology Center (ISTC) and GMS, INP has shared a set of five nuclear forensic samples with the Lawrence Livermore National Laboratory (LLNL) and Los Alamos National Laboratory (LANL) for joint, collaborative analysis. The sample set contains four uranium powders and one low enriched uranium fuel pellet. The joint analysis of this set of materials is being conducted using well-developed analytical plans. The measured material characteristics will populate an evolving nuclear forensics library. The participating laboratories (INP, LLNL and LANL) have employed similar and complementary techniques to learn more about these nuclear forensic materials and the methods used to study and catalog them. Through virtual and in-person meetings and quarterly reports, the participating laboratories have compared data and analysis methods on the Kazakhstan sample set, shared best practices on the implementation of a national nuclear forensic library and laid the groundwork for broader nuclear forensics activities in the region.

INTRODUCTION

Over the last few decades, the field of nuclear forensics has become an essential component in international efforts to combat illicit trafficking of nuclear and radiological materials. Nuclear forensics relates to the application of scientific methods and techniques to characterize the physical nature and chemical composition of an unknown nuclear material. This information

may allow for the age, origin, processing history, and suspected use of a sample to be identified, catalogued, and shared with law enforcement and related national agencies responsible for managing interdicted materials found outside of normal nuclear regulatory controls [1].

For a given material sample, the range of techniques that can be used in a nuclear forensics analysis is diverse, in some cases complex and may yield fairly distinctive characteristics associated with a given material sample. An analytical plan for a sample may encompass a sequence of non-destructive and destructive assessments to define its gross physical and chemical features, measure its radiation emissions, and identify its fundamental elemental and isotopic composition. Analyses may begin, for example, with simpler assessments such as visual inspection and characterization, optical microscopy, mass density and weight, and basic dosimetry, and may be followed by more complex analyses such as alpha and gamma spectrometry, scanning electron microscopy, energy dispersive X-ray analysis, and mass spectrometry [1].

Different laboratories may have differing technical capabilities and analytical expertise that may lead to different analytical approaches for a sample. They may have varying levels of experience in the area of nuclear forensics, specifically as it relates to defining defensible analyses and work-flows, maintaining custody of samples, and effectively interfacing with police and legal authorities in the overall effort. In an international arena, they may also be subject to different legal requirements and processes in effect in individual countries.

Below, we report on a series of ongoing nuclear forensics collaborations between the Institute of Nuclear Physics (INP) in Kazakhstan and the Lawrence Livermore National Laboratory (LLNL) and Los Alamos National Laboratory (LANL) in the Unites States. The INP is a leading nuclear forensics laboratory in the Republic of Kazakhstan responsible for the analysis of samples found outside of regulatory control in the country. Kazakhstan itself is the world's largest producer of mined uranium, accounting for almost 50% of annual world production and is the most economically dominant country in the Central Asia region. The INP has been a long-standing partner of the U.S. Department of Energy, National Nuclear Security Administration's Office of Global Material Security (DOE/NNSA/GMS) and is an active member of international nuclear forensics community and the Nuclear Forensics International Technical Working Group (ITWG) [2]. A portion of our interactions, coordinated through the International Science and Technology Center (ISTC) and GMS, involve joint, collaborative analyses of nuclear material samples exchanged between the US and Kazakhstan laboratories. Here, we report on ongoing work with a sample set provided to LLNL and LANL by INP.

ROLE OF A JOINT SAMPLE ANALYSIS

A collaborative, joint sample analysis between different laboratories can serve several different purposes. It allows the participating laboratories to employ similar and complementary techniques to learn more about these nuclear forensic materials and the methods and best work-flow practices used to handle, analyze, interpret, and catalog their characteristics. It provides opportunities for the participants to learn, practice, and demonstrate competence with new or existing analytical techniques. It also provides opportunities for a laboratory, or a network of laboratories, to demonstrate continued competence in performing specific types of analyses, as though a regular performance evaluation (quality assurance) program (PEP).

CURRENT ANALYTICAL EXERCISE

The current analytical exercise involves 5 samples provided to LLNL and LANL by INP. The current sample set contains four uranium powders and one low-enriched uranium fuel pellet of unknown origin and exact composition (Figures 1 and 3). The four powder samples are denoted by UL3, UL4, UL6, and UL7 and the pellet sample is denoted by PM7-2. Samples UL3, UL4, UL6 are comprised of approximately 4 g of a yellow-colored powder, sample UL7 represents approximately 4 g of black-colored powder, and sample PM7-2 is a 4.8 g, cylindrically-shaped pellet. INP retained additional portions of the same powders for their own analyses and a separate but similar pellet sample (PM7-1).

Figure 1: Four uranium powder samples (UL3, UL4, UL6, UL7) and one low-enriched uranium fuel pellet (PM7-2) being analyzed by LLNL and LANL in this exercise. The INP analyzed an equal portion of the same powder samples and a similar pellet (PM7-1).

The joint analysis of these materials is being conducted by INP and the US labs using well-developed analytical plans and standard operating procedures at each institution. The analytical plans represent the choice and sequence of analytical assessments that will be applied to individual samples (Table 1). These may differ among the labs because of differing or limited capabilities or among the samples because they require specific or unique approaches for characterization.

INP ANALYSIS SUMMARY

The INP conducted a number of nuclear forensic analyses on the powder samples and their fuel pellet specimen, as summarized in Table 1. These included a gross dosimetry assessment, optical microscopy, gamma and alpha spectrometry analyses, an optical-emission spectrometry (OES) analysis, and a scanning electron microscope and energy dispersive X-ray spectroscopy (SEM-EDS) study. Some of these efforts are briefly summarized below with along preliminary, leading results shown in Table 2 and Figure 2 (additional details will be forthcoming).

Analysis	LLNL/LANL	INP
Nondestructive Analyses		
Visual inspection, photography		
Weighing		
Optical microscopy		
Dosimetry	-	
Scanning Electron Microscopy (SEM-SEI)		-
Scanning Electron Microscopy (SEM-BSE)	-	-
Scanning Electron Microscopy/Energy Dispersive X-ray Analysis (SEM-EDS)		
Auger Electron Spectroscopy (AES)	-	-
Autoradiography	-	-
HPGe Gamma-Spectrometry (dry)		
Destructive Analyses		
HPGe Gamma-Spectrometry (solubilized)		
Alpha spectrometry	M	-
X-ray Fluorescence (EDXRF)	M	-
X-ray Fluorescence (WXRF)	M	-
X-ray Diffraction (XRD)		-
Davies-Gray Titration		-
Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)		-
Uranium isotopic composition by ICP-MS and/or TIMS		-
Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)		
Radiochronometry	-	-
HPGe gamma-spectrometry	-	-
Stable isotope mass spectrometry		
Neutron Activation Analysis (NAA)	-	-
HPGe (NAA col)	-	-
Other		
Cluster Analyses with Archived Sample Data	-	-

Table 1: Analytical plans adopted by INP and LLNL./LANL for the comparative analysis exercise involve both nondestructive and destructive analyses. M = maybe, depending on sample mass remaining or other intermediate results.

SEM-EDS: The structural characteristics and elemental composition of the samples were studied using a scanning electron microscope fitted with an energy dispersive X-ray spectroscopy (SEM-EDS) microanalysis system. This analysis was able to provide multiple microstructural images of each sample and semi-quantitative elemental assays of specific target points in each sample. The microstructural images were able to reveal fine textural details of each sample (see also Figures 2 and 3). Sample UL3 was described as a sub-spherical powder with a large number of agglomerations consisting of porous and spongy particles ranging in size from 3 to 100 μm. Sample UL4 is a powder consisting of porous and spongy sub-spherical particles ranging in size from 1 to 500 μm. The presence of angular rod-shaped particles was noted. Sample UL6 is a set of both spherical agglomerates and rod-shaped, needle-shaped (feather-shaped) particles from 1 to 100 μm. Sample UL7 is a sub-spherical needle-shaped (pin-shaped) particles that have fine grain coatings. Sizes are from sub-micron to several hundred microns. Sample PM7-1 is a pellet fragment whose grain size varies from 2 to 30 μm. A small number of small particles was observed on the sample surface. The elemental assays were dominated by uranium and oxygen in all samples (Table 2), with the exception of sample UL3, which had significant amounts of carbon and nitrogen. Other impurities were not noted in any of the analyses.
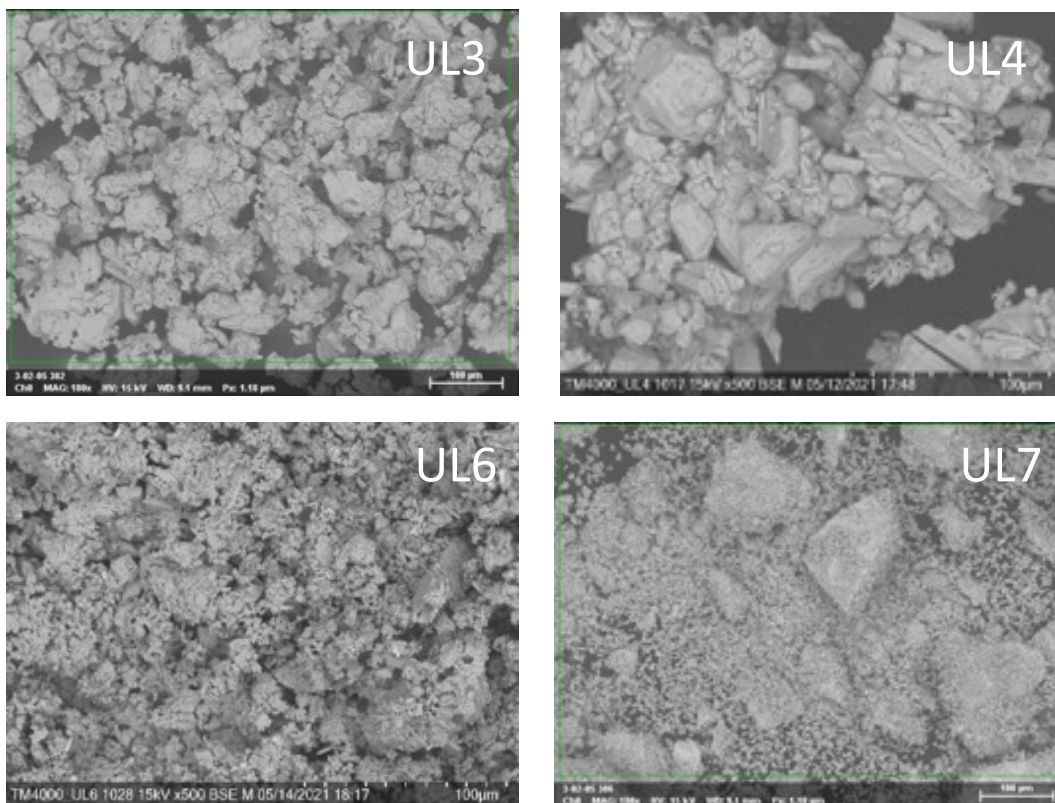
Figure 2: High magnification secondary electron (SEM) images of the four uranium powder samples (UL3, UL4, UL6, UL7) produced at INP.

Gamma Spectrometry: A nondestructive HPGe gamma spectrometry analysis was applied to the 4 powder samples to yield measurements of the specific activities of ^{235}U, ^{238}U, the $^{235}U/^{238}U$ activity ratio, and the overall content of uranium in the samples. Later, a solution-based (destructive) gamma spectrometry analysis was applied to solubilized versions of all samples, including a crushed portion of the pellet, to yield a set of analogous measurements. The specific activities of ^{235}U measured in these two approaches were in rough agreement (Table 2). However, the specific activity of ^{238}U was generally higher in the dry (nondestructive) analysis, which led to smaller $^{235}U/^{238}U$ ratios being identified in this approach. The uranium mass fractions identified in the samples were also significantly higher in the nondestructive results.

Alpha Spectrometry: Separately, an alpha spectrometry technique was applied to determine the volumetric activity of uranium isotopes (^{234}U, ^{235}U, ^{238}U) in each sample and measure the specific activity of uranium isotopes and their associated ratios ($^{234}U/^{238}U$, $^{235}U/^{238}U$). As above, the analyses were made on prepared liquid samples. These generally yielded comparable results to the Gamma measurements (Table 2), but ^{238}U data were somewhat larger and led to slightly smaller isotope ratios.

OES: The content of total uranium in the resulting solutions was determined by optical emission spectrometry (OES). Estimates of the total uranium mass fraction in each sample compared favorably with the solution-based gamma spectrometry results and were lower than the nondestructive gamma spectrometry results (Table 2).

Lab	Studies/ Samples	UL3	UL4	UL6	UL7	PM7-1	PM7-2
INP	**Scanning Electron Microscopy (SEM-EDS) Multipoint Samples**						
	Atomic concentration of U (%, std. error)	8.93 (2.79)	13.88 (3.74)	10.77 (1.71)	13.46 (1.84)	24.16 (4.13)	
	Atomic concentration of O (%, std. error)	59.79 (3.00)	86.12 (3.74)	89.23 (1.71)	59.49 (2.79)	75.84 (4.13)	
	Atomic concentration of C (%, std. error)	19.33 (6.53)	-	-	27.05 (1.07)	-	
	Atomic concentration of N (%, std. error)	11.95 (1.26)	-	-	-	-	
	Gamma Spectrometry (non-destructive)						
	Specific activity of ^{235}U (kBq/kg)	220 ± 9	260 ± 9	220 ± 8	340 ± 10	-	
	Specific activity of ^{238}U (kBq/kg)	9160 ± 25	9400 ± 27	8430 ± 25	101925 ± 30	-	
	Activity Ratio ^{235}U/^{238}U	0.024	0.028	0.026	0.003	-	
	Concentration of U in sample %	74.5	76.5	68.5	83.0	-	
	Gamma Spectrometry (after solubilization)						
	Specific activity of ^{235}U (kBq/kg)	200	220	200	320	3000	
	Specific activity of ^{238}U (kBq/kg)	6200	6630	6340	9780	13570	
	Activity Ratio ^{235}U/^{238}U	0.032	0.033	0.032	0.033	0.221	
	Concentration of U in sample (%)	50.5	54.0	51.5	78.0	83.0	
	Alpha Spectrometry						
	Specific activity of ^{234}U (MBq/kg)	6.2 ± 1.0	6.3 ± 1.0	6.5 ± 1.0	9.5 ± 1.0	68.5 ± 12.0	
	Specific activity of ^{235}U (MBq/kg)	0.2 ± 0.04	0.2 ± 0.04	0.2 ± 0.04	0.3 ± 0.06	3 ± 0.50	
	Specific activity of ^{238}U (MBq/kg)	9.0 ± 1.6	9.7 ± 1.8	10.0 ± 2.0	12.0 ± 2.2	13.0 ± 2.4	
	Activity Ratio ^{234}U/^{238}U	0.69	0.65	0.65	0.79	5.27	
	Activity Ratio ^{235}U/^{238}U	0.02	0.02	0.02	0.02	0.23	
	Total Uranium according to ICP-OES						
	U-total (%)	51.1 ± 2.3	55.4 ± 2.8	52.3 ± 2.4	80.8 ± 3.1	88.9 ± 3.4	
LLNL	**Scanning Electron Microscopy (SEM-EDS) Overscan**						
	Atomic concentration of U (%)	-	-	-	-		26.15
	Atomic concentration of O (%)	-	-	-	-		45.48
	Atomic concentration of C (%)	-	-	-	-		21.10
	Atomic concentration of Na (%)	-	-	-	-		2.73
	Atomic concentration of Al (%)	-	-	-	-		1.92
	Atomic concentration of Mg (%)	-	-	-	-		1.46
	Atomic concentration of Si (%)	-	-	-	-		1.16
	Gas Pycnometry						
	Average density (g/cm^3)	-	-	-	-		10.75 ± 0.015
	Gamma-Spectrometry using MGAU						
	Mass fraction ^{234}U/U-total	0.0034 ± 0008	0.0038 ± 0.0009	0.0026 ± 0.0004	0.0031 ± 0.0006		0.0300 ± 0.0015
	Mass fraction ^{235}U/U-total	0.5250 ± 0.0177	0.4857 ± 0.0195	0.4878 ± 0.0095	0.5122 ± 0.0112		3.2608 ± 0.0302
	Mass fraction ^{238}U/U-total	99.4716 ± 0.0179	99.5104 ± 0.0198	99.5096 ± 0.0096	99.4846 ± 0.0113		96.7092 ± 0.0306
	Activity Ratio ^{234}U/^{238}U	0.63	0.71	0.48	0.58		5.74
	Activity Ratio ^{235}U/^{238}U	0.03	0.03	0.03	0.03		0.22

Table 2: Preliminary results of analyses conducted by INP and LLNL on the four uranium powder samples (UL3, UL4, UL6, UL7) and the two uranium fuel pellets (PM7-1/PM7-2).

LLNL/LANL ANALYSIS SUMMARY

Both LLNL and LANL are in the beginning stages of their planned sample analyses listed in Table 1. LLNL has conducted preliminary sample investigations that include photographic documentation of the samples, microscopy and SEM-EDS analysis on the pellet (sample PM7-2), density and X-ray diffraction (XRD) analyses of the pellet, and a (nondestructive) Multi-Group Analysis for Uranium (MGAU) assessment on all samples to identify their uranium isotopic compositions.

Photographic Documentation: Detailed photographs of the 5 samples received at LLNL are shown in Figure 3. These can be compared with the INP descriptions summarized above.

Figure 3: Close-up images of the four uranium powder samples (UL3, UL4, UL6, UL7) and fuel pellet sample (PM7-2) received at LLNL.

Optical Microscopy of Sample PM7-2: The pellet sample PM7-2 is described as dull gray in appearance and exhibited a few areas of losses, most notably near each edge. Physical and visible morphological features on the sample were documented using an optical microscope at different magnifications and a three-dimensional optical scanner (Figure 4). Notably, the lateral/curved sides of the pellet showed a rougher surface than the flat/circular surfaces, possibly from differences in machining of the two surfaces.

SEM-EDS Analysis: Microstructural characteristics and elemental composition of sample PM7-2 were studied using an SEM-EDS analysis system. Micromorphological features, defects and impurities, as well as semi-quantitative chemical compositions, were identified at several surficial locations (Figure 5). Localized elemental analysis via an EDS overscan confirmed the major amounts of uranium in all spectra (> 80 wt%), with minor amounts of oxygen and carbon (Figure 6). This is similar to the INP EDS analysis of Sample PM7-1 in terms of the U and O point-wise detections, but also identifies trace amounts of C, Na, Al, Mg, and Si. These are most likely surface contaminants from shipping handling and will be confirmed in upcoming analyses. The results in Figure 6 have been converted to atomic concentrations for comparison with the INP data in Table 2.

Density Measurements: A gas pycnometer was used to determine the volume of the entire pellet and calculate its density. The instrument uses helium gas, sample and reference chamber volumes, and standard stainless-steel spheres to calibrate the system. Stainless steel reference spheres of a known combined volume (2.1450 cm^3) were used as a verification check on the day of analysis. The average density was calculated to be 10.75 ± 0.015 g/cm^3. This value is slightly less than the known density of UO_2 of 10.97 g/cm^3.

XRD Analysis: An X-ray diffraction (XRD) analysis was performed in the pellet sample. Phases were identified by comparison of observed peaks to those in the International Centre for

Diffraction Data (ICDD PDF-4+ 2023) powder diffraction databases. A single crystalline phase matching ICCD references for UO2 and UO2.25, both cubic forms of the oxide was identified (Figure 7).
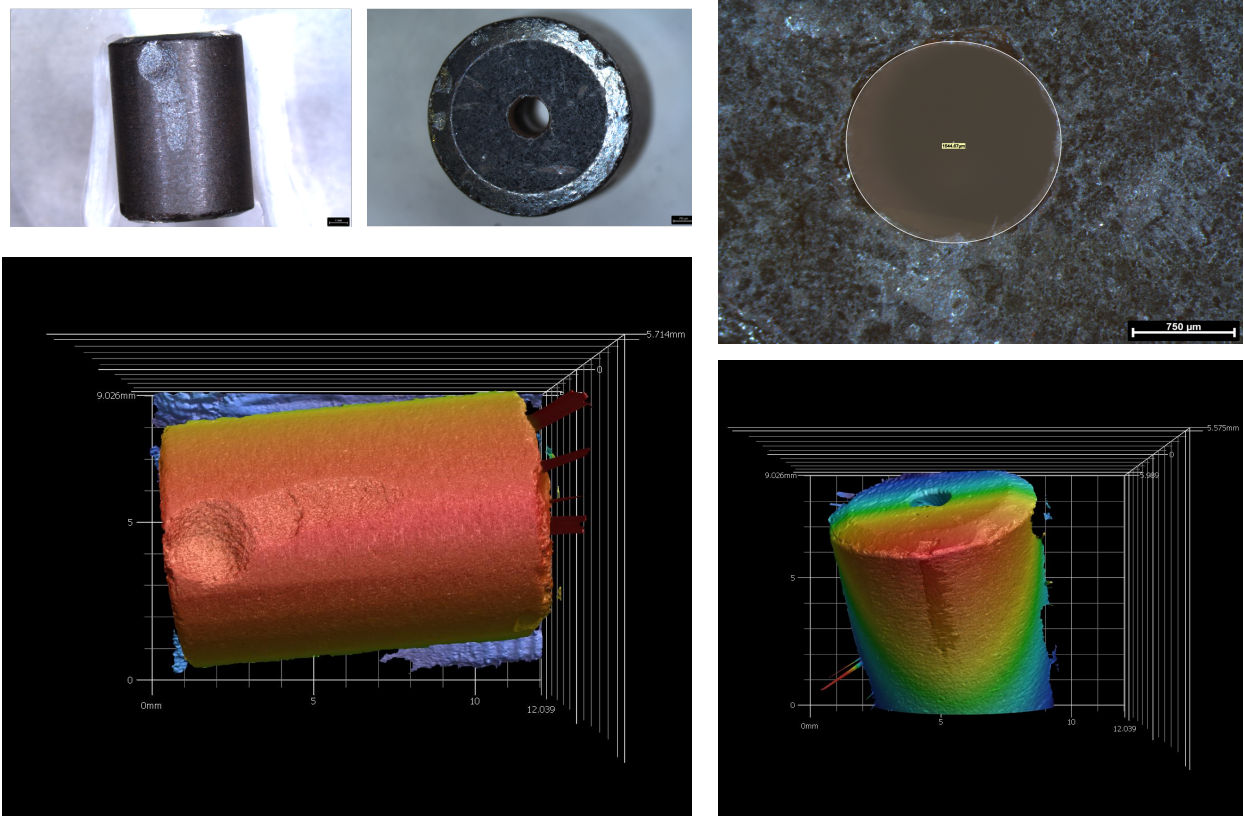

Figure 4: Representative images of the fuel pellet sample (PM7-2) received at LLNL using optical microscopy (top) and a three-dimensional optical scanner (bottom). Note the defect area in the leftmost scanned image.
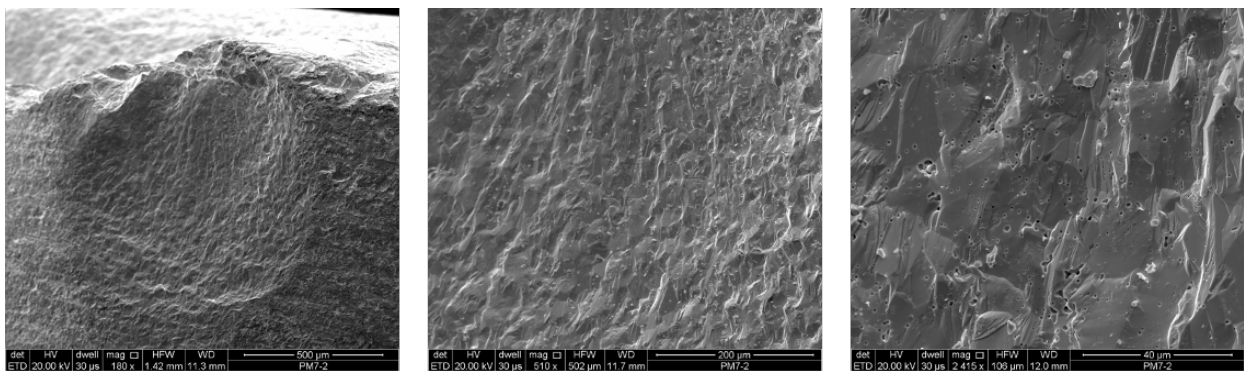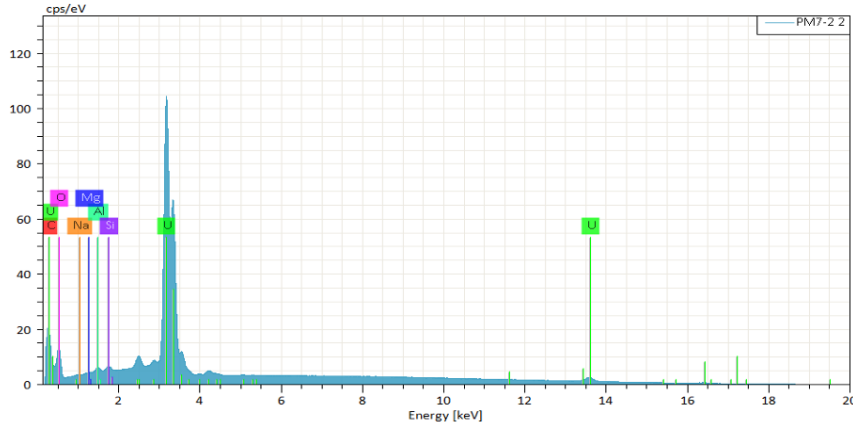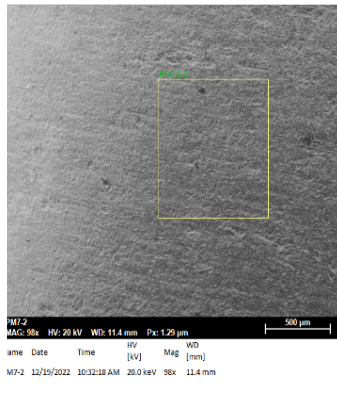

Figure 5: Secondary electron images of a defect area on the pellet (shown in Figures 3 and 4)

Spectrum	C	O	Na	Mg	Al	Si	U
PM7-2 2	3.43	9.85	0.85	0.48	0.70	0.44	84.26

Figure 6: Overscan EDS spectrum from the lateral side of PM7-2 showing a typical bulk composition in weight % that is seen throughout the sample. Weight % results from this analysis were converted to atomic fractions in Table 2.
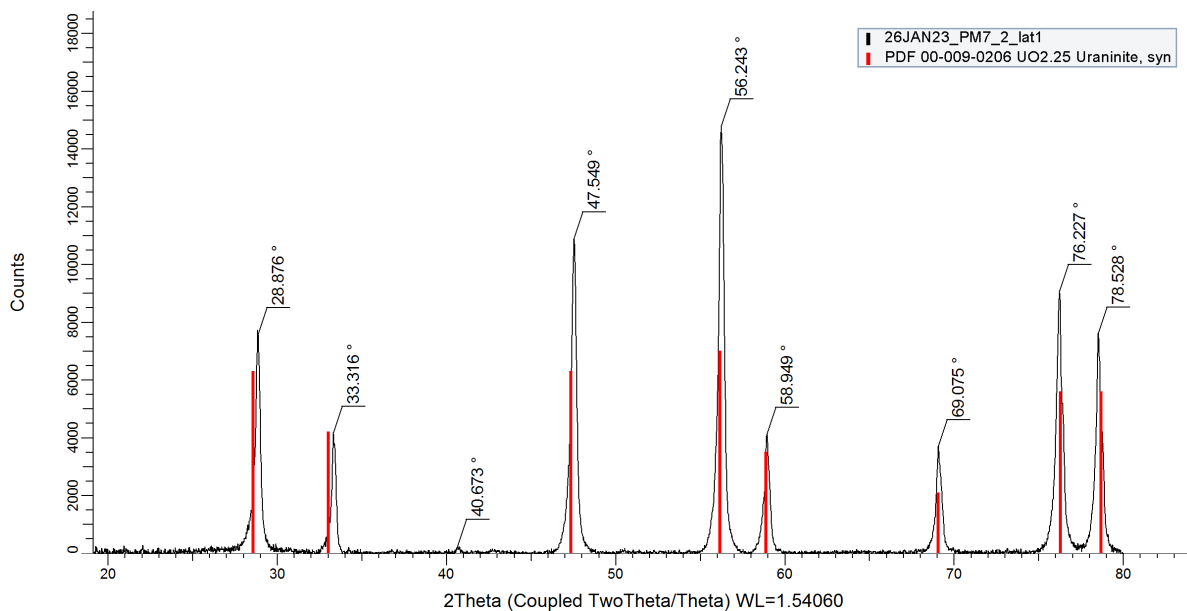

Figure 7: X-ray diffraction pattern the and lateral/curved surface of the PM7-2 pellet sample, with $UO_{2.25}$ pattern overlaid.

MGAU Assessment: The samples were counted with a planar HPGe detector, and a Multi Group Analysis for Uranium (MGAU) screening assessment was performed to estimate uranium isotopic composition in all samples using Canberra MGAU software (v4.2). The observed mass fractions of ^{234}U, ^{235}U, and ^{238}U in the powder samples are somewhat different than their natural abundance counterparts (< 0.01, 0.7, and 99.3, respectively), but should be regarded as approximate until additional analyses are available. For comparison purposes, activity ratios for

^{235}U/^{238}U were calculated from the mean mass fraction results. For the powder samples, they are in fair agreement with values reported by the INP gamma spectrometry analysis based upon solubilized samples (Table 2). These results will be supplemented in the future with a more comprehensive assessment of the full spectrum for U isotopes and their progeny.

NEXT STEPS

LLNL and LANL are anticipating the completion of additional sample analyses in the near future to assess uranium concentrations, isotope ratios, and major and trace element concentrations in the 5 samples. These will employ using methods of HPGe gamma-spectrometry, Davies-Gray Titration, and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), and perhaps additional SEM-EDS and XRD analyses.

Following the completion of the major analyses, the laboratories plan to confer and discuss the technical results, their accuracy, precision, reliability, and repeatability, and the forensics related conclusions that may be drawn from the results, both individually and collectively. For example, INP has reached several conclusions already regarding the purity and chemical composition of the samples (e.g., uranyl nitrates with or without micro-impurities, uranium oxides with micro-impurities, nuclear fuel materials). Importantly, the presence of multiple complementary analyses should be seen as a way to seek confirmatory conclusions or suggest additional interpretations or analyses should be made.

Fundamentally, the collected sets of analytical results and subsequent interpretations, once complete, should be subject to validation and verification efforts and certified with respect to the laboratory procedures used, duplicate analysis specifications, and related quality assurance requirements. Additionally, the analyses and results become candidates for inclusion in Nuclear Forensics Library(ies) and for comparison with existing data in such libraries [3]. Ultimately, such comparisons may shed additional light on the provenance and interpretation of newly acquired samples. The INP and sister institutes in Kazakhstan are actively in the process of developing and expanding such libraries for these types of national applications.

REFERENCES

[1] IAEA Implementing Guide, Nuclear Forensics in Support of Investigations, IAEA Nuclear Security Series No. 2-G (Rev. 1), STI/PUB/1687 978-92-0-102115-1

[2] Nuclear Forensics International Technical Working Group (ITWG) Guidelines, http:/www.nf-itwg.org/index.html#nav-guidelines

[3] IAEA Non-serial Publication, Development of a National Nuclear Forensics Library: A System for the Identification of Nuclear or Other Radioactive Material out of Regulatory Control, AEA-TDL-009 978-92-0-108218-3, www.iaea.org

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