# Development of Nuclear Forensics using Synchrotron Radiation-Based Analysis at the National Synchrotron Light Source-II

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## ABSTRACT

To identify illicit nuclear materials, and undeclared pathways associated with their production, we must be able to determine their origin even in situations where the evidence of their presence consists only of sub-micron dust or particle debris. The Brookhaven National Laboratory's Nonproliferation and National Security Department, in collaboration with the National Synchrotron Light Source II, has investigated how synchrotron-based capabilities can support actinide analysis of nuclear samples, such as those that might be collected during safeguards inspections. Our primary focus has been to provide automated, high-throughput, and non-destructive x-ray fluorescence microscopic analysis of environmental samples with a higher spatial resolution and sensitivity than would be achievable solely with current laboratory-based techniques. This paper describes work that has been performed by a multi-laboratory team for the National Nuclear Security Administration's Office of Defense Nuclear Nonproliferation and discusses additional ways that synchrotrons can be employed for nonproliferation and arms control.

**Keywords:** X-ray Spectroscopy, Submicron Resolution X-ray Spectroscopy, Tender X-ray Spectroscopy, NSLS-II, Brookhaven National Laboratory, Nuclear Verification, Arms Control

## 1. INTRODUCTION

State-of-the-art, high brightness synchrotron facilities such as the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory (BNL) are capable of generating x-ray beams that can be focused to probe sub-micron sized areas to characterize their chemical and structural properties non-destructively. [1] To accommodate current demands and prepare for future needs of treaty verification agencies, we use the extraordinary capabilities of NSLS-II to provide full spectrum x-ray fluorescence (XRF) data that are analyzed to determine the elemental composition, from which the source and processing history of sampled nuclear materials may be deduced.* This type of analysis for actinide particles in environmental samples (the group of radioactive elements with atomic number, Z, 89-103 in the periodic table) potentially plays an important role in detecting undeclared nuclear materials, and clandestine activities that could lead to the production of nuclear weapons.

To evaluate the effectiveness of using synchrotron-based microprobe techniques for nuclear forensics, we used prepared actinide, non-actinide, and mixed environmental samples. The results of our studies show that synchrotron-based x-ray microscopy provides substantially greater throughput speed, spatial resolution, and sensitivity than traditional laboratory-based techniques, while preserving the samples for subsequent analysis and/or retention.

## 2. NON-DESTRUCTIVE ANALYSIS OF ENVIRONMENTAL SAMPLES

Synchrotron-based microprobe techniques have been widely adopted by material and environmental science to generate spatially resolved sample composition information. NSLS-II beamlines provide multiple capabilities for studying the chemical properties of nuclear substances. Table 1 lists the beamlines that specialize in x-ray microscopy and were evaluated using test samples containing known actinide particulates.

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*In the interest of brevity we have limited our discussion to only a few examples of the extraordinary capabilities of the NSLS-II. The studies we describe here are only a small sample of the value that NSLS-II can provide to nuclear forensics research.

We used a sample of tyuyamunite provided by PNNL to demonstrate the synchrotron's ability to differentiate uranium-containing minerals with different minor elements. The x-ray beams at NSLS-II are non-destructive to most materials. Additionally, they offer unprecedented spatial resolution and sensitivity that are far superior to traditional methods. Figure 1 illustrates the difference between using a synchrotron-based microprobe technique versus a more traditional scanning electron microscope (SEM) energy dispersive spectrometer (EDS) method. Both the XFM and EDS systems successfully scanned and analyzed the 2 μm tyuyamunite particle $(Ca(UO_2)_2V_2O_8)$. However, the XFM results had substantially better sensitivity to the actinide elements, as well as other minor elements in the sample that EDS was not able to detect. The minor elements, here lead and iron, are some of the clues that make it possible to reconstruct the history of the original, much larger, sample. For example, we may investigate whether there are tools made of a combination of lead and iron that are used in the machining process of tyuyamunite, and if so, in what geographic locations those tools are commonly used. Another investigative path may be to see if iron and lead are commonly found in any areas where tyuyamunite is mined.

In addition to enhanced sensitivity and spatial resolution, synchrotron-based microprobe techniques are substantially faster than traditional laboratory techniques. Using standard, laboratory-based microprobes with their associated manual analysis techniques, a single nuclear sample like the one shown in Figure 2 can take between three to six months to fully scan and characterize. Using the synchrotron-based microprobe techniques that we evaluated at NSLS-II, we can perform the same sample analysis in a matter of hours.

These more efficient and effective methods, as described in greater detail in Sec. 2.1, allow us to measure and analyze a much greater number of samples, and therefore, allow us to create larger bases of evidence from which to investigate the history of nuclear materials.

Table 1. The three NSLS-II beamlines with differing capabilities used to evaluate the feasibility of synchrotron-based microprobe techniques for analysis of nuclear materials with both actinide and non-actinide particles.

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| **Submicron Resolution X-ray Spectroscopy Beamline (SRX)** | The SRX beamline scan particles at a resolution of 1 μm in a few minutes, with detection limits below 10 ppm for elements from titanium to uranium (Z of 22-92). |
| **Tender X-ray Spectroscopy Beamline (TES)** | The TES beamline can be used to identify various important elements such as: phosphorous, sulfur, chlorine, potassium, calcium, titanium, cadmium, tin, uranium, and many more. |
| **X-ray Fluorescence Microprobe Beamline (XFM)** | The XFM beamline can quantify elements in heterogeneous materials. It also offers a polychromatic mode ideal for rapid 2-D and 3-D x-ray fluorescence imaging and tomography. |

## 2.1 Key results from actinide analysis at multiple NSLS-II beamlines

To evaluate the nuclear verification capabilities of the NSLS-II beamlines listed in Table 1, we used test samples prepared in advance by Pacific Northwest National Laboratory (PNNL); these samples contained uranium minerals, thorium oxide, and a mixture of non-actinide materials, ranging in size from 0.5 μm to several microns. The particles in the sample were measured and analyzed using, in part, the newly developed Synchrotron Network Automation Program in Python (SnapPy) software which automates the workflow that formerly took multiple experts and beamline scientists to achieve. [2] Using SnapPy at beamlines like XFM allows us to take preliminary scans to examine larger areas and rapidly determine what particles, in a particle-rich sample, are of most interest to us. Figure 2 shows an example of a high-speed scan taken at the NSLS-II XFM beamline of a sample's full surface area. We use raster scans such as these to gather preliminary information about a sample and identify other beamline resources to be used on targeted areas for further, higher-resolution scans.
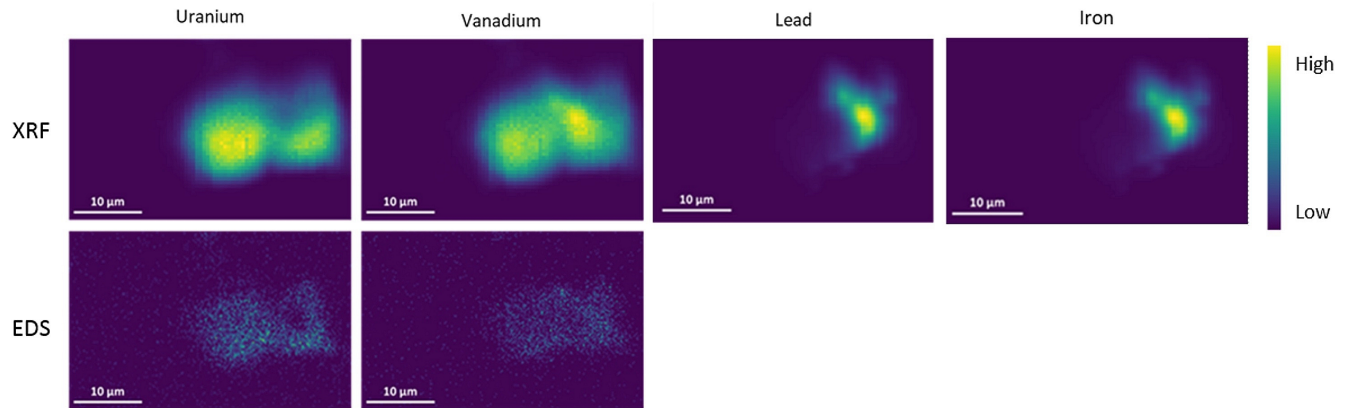
Figure 1. High resolution XRF maps (upper row) taken at NSLS-II XRF beamline, and corresponding maps taken using a traditional energy dispersive spectrometer (EDS) method (lower row) of a tyuyamunite particle. The XRF maps are not only able to detect the additional presence of lead and iron, but show that they are co-located, which EDS would not be able to detect.

With further scans of these areas of interest we obtain sub-micron resolution information about their chemical composition, which can be used to point to the origin of the nuclear (or non-nuclear) materials. Figure 3 shows a high-resolution, sub-micron scan of an actinide sample. Here, the uranium particles are always co-located with thorium particles, however, there are also scattered particles of isolated thorium. Other analysis methods, such as fission track analysis, would not be able to distinguish between isolated thorium particles from ones co-located with uranium. The presence and arrangement of minor components in a sample provide fingerprints that we use to determine key variables that could discriminate the age, production process and source of a nuclear material sample.
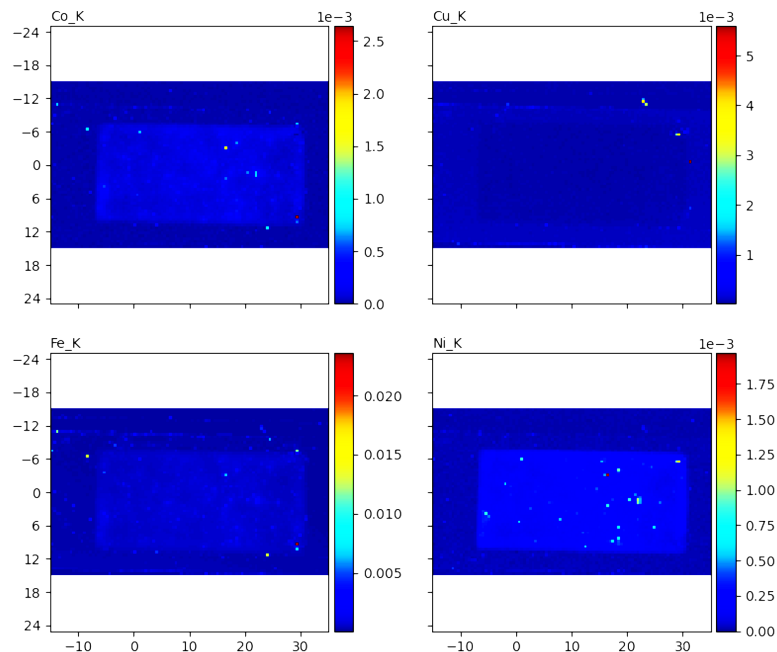


Figure 2. A full surface scan of non-actinide particles in collodion taken at the NSLS-II XFM beamline showing the cobalt, copper, iron and nickel content, all of which are consistent with the expected composition of maraging steel. Higher speed raster scans help identify areas of interest for targeting for further, higher-resolution scans.
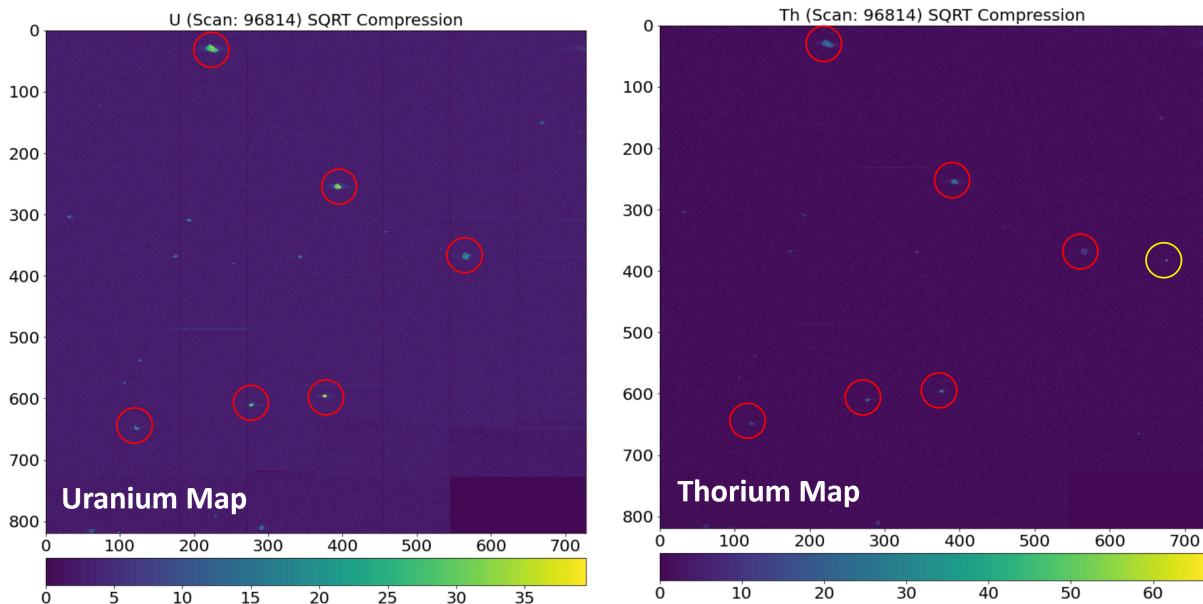
Figure 3. Uranium and thorium XRF maps from a wide-area scan taken at the NSLS-II SRX beamline and x-ray florescence processed by PyXRF [3] and SnapPy [2] software. The maps are presented using a square-root signal suppression algorithm to enhance the visibility of lower concentration particles. All uranium particles contain thorium (circled in red), but there was also a single thorium-only particle (circled in yellow). Other methods, such as fission track analysis, would not be able to distinguish the combined uranium and thorium particles from the isolated thorium particles.

## 3. FUTURE DEVELOPMENT

Nuclear fuel cycle facilities produce evidence of their activities, such as enrichment, fuel fabrication and reprocessing. Much like conventional crime scene investigation, treaty verification regimes rely on technology to assist in the collection and analysis of that evidence. The results of our evaluation of synchrotron-based microprobes for nuclear forensics studies shows that these synchrotron-based XRF facilities employ fast, non-destructive techniques that provide detailed and spatially resolved information about the chemical composition of particulate matter while preserving the sample for additional analyses at other beamlines or using other techniques. Follow-on analyses at other synchrotron beamlines would require precise and reliable methods of indexing particle locations allowing the ability to track individual particles through a series of analyses. A promising method developed at PNNL for a specific sample mounting system is currently under evaluation [1], but alternative methods should not be ruled out. An obvious non-synchrotron-based, destructive analysis method would be mass spectrometry for the identification of actinide isotopes.

The successful use of beamlines at NSLS-II, at the Advanced Light Source (Lawrence Berkeley National Laboratory) and at SLAC National Accelerator Laboratory suggests another approach for the future, namely development and eventual construction of a beamline system dedicated to forensic analysis of samples collected for nuclear forensic purposes. Ideally a single beamline would have the flexibility to provide the energy range to identify elements from fluorine to the actinides (atomic numbers 9 to 96), but this is unlikely due to detector system and crystal monochromator requirements. Similar considerations apply when addressing the need to conduct wide-area, low-resolution scans for triage purposes, e.g., to verify the presence of actinides quickly, followed by high-resolution scans to gain further evidence of the extent and composition details of numerous elements down to sub-micron scales which can be very time-consuming. The construction of dedicated beamlines makes it possible to address several issues noted in our studies to date: handling radioactive samples, ensuring continuity of knowledge of the samples, managing sensitivities associated with the samples or the data produced (potentially including classified data), and finally expanding access to beamtime. At present NSLS-II is an ideal candidate because it has room for at least 20 more beamlines and is equipped with a storage ring that provides

a record-setting x-ray source in terms of brightness. The potential for the nuclear nonproliferation community to utilize the current capabilities at Department of Energy (DOE) synchrotron light sources would only result in greater effectiveness and efficiency in addressing forensic science needs.

Easier access to synchrotron methods could help verification agencies prioritize samples and avoid expensive isotopic analysis of samples that contain no material of interest. Current international safeguards protocols for environmental sample analysis involve lengthy and expensive processes and tools. The samples are prioritized based on sample origin and current safeguards concerns. There is currently no approved protocol for screening samples to identify those that contain material of interest before destructive analysis is performed. As a result, many blank or otherwise irrelevant samples are analyzed. Moreover, current protocols call for samples to be divided with one half being sent to an analytical laboratory for analysis and the other half being archived for later analysis. This procedure assumes that material is uniformly distributed on the cotton swipe, which is unlikely to be the case and could result in the inability to confirm results through secondary tests. Synchrotron triage of an environmental sample can non-destructively identify those samples that contain particles of interest and enable the IAEA or other treaty verification organization to prioritize the samples based on actual content. There is no chance of cross contamination during this process because the sample can remain enclosed in the plastic bag in which it was placed during collection. Once prioritized, samples can be sent for analysis or returned to storage.

Another area of development which would improve sample throughput is the use of multi-pixilated detectors like the Maia detector. Use of this detector, which contains 348 individual detectors on a 5 cm$^2$ frame, was reported in a study at NSLS-II of a 10-by-10 cm$^2$ environmental cotton swipe that contained dust and uranium oxide. [4] The XRF scan with the Maia was completed in 3.5 hours, which is a fraction of the data collection time associated with the single-element detector normally used at that beamline. The detector is not readily available, and only one was fabricated. Although detector development may be outside the scope of this paper's main topic, it is an area where developments could impact beam access and use.

Finally, we will continue to improve workflow concepts including the continued development of our automated scanning and analysis capabilities with SnapPy. An important goal of this research would be to provide a more complete understanding of what synchrotrons can provide to National Nuclear Security Administration (NNSA) end-users, as well as to develop methods and fundamental theory to better connect chemical and microstructural observations of nuclear materials to their age, material processing, and locations of origin. As these nuclear verification projects continue, we will gain even more experience with synchrotron methods and desirable high-throughput/routine capabilities that can be automated for forensic science applications. NSLS II is also uniquely constructed such that the beamlines can be taken outside of the facility into a separate satellite building. This allows experiments to be isolated from the rest of the building effectively containing the samples for safety reasons or for a separate secure environment. This is a unique capability of the facility and very useful when a remote end location is needed for conducting an experiment in a safe and secure area.

The investments into the methods and instrumentation needed for advancing synchrotron-based nuclear verification will work in concert with outreach that we will conduct with the DOE Office of Basic Energy Sciences - which is responsible for the operation of national synchrotron facilities - and with the synchrotron laboratories themselves to articulate national security research and development needs to help pave a path for stakeholders to create policies that encourage synchrotron-based facilities to support national security objectives. The growth and organization of such a nuclear nonproliferation synchrotron user community could allow users to provide guidance to the NNSA, articulate research support needs to the light source laboratories, and provide resources and training to better support end-users.

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