Actinides and Rare Earths
Room 123 - Session AC+MI-ThA
Forensics, Disposal and Pu

Moderators: Itzhak Halevy, Ben Gurion Uni. Be'er Sheva, **Alison Pugmire**, LANL, **Paul Roussel**, AWE

2:15pm **AC+MI-ThA-1 A New Approach for Nuclear Forensics Investigations of Uranium Dioxide : Application of Laboratory Based Photoelectron Spectroscopy with Hard and Soft X-ray Sources***, **Stuart Dunn**, P. Roussel,* AWE, UK*; A. Wood, B. Spencer, R. Harrison,* University of Manchester, UK*; P. Kaye, M. Higginson,* AWE, UK*; W. Flavell,* University of Manchester, UK **INVITED**

Nuclear Forensic investigations rely on the analysis of the chemical and physical properties to determine the provenance of nuclear materials, found out of regulatory control. X-ray photoelectron spectroscopy (XPS) has been shown to be a powerful tool in supporting material assessment by analysis of the top few nanometres of the surface. With the onset of laboratory based hard x-ray photoelectron spectroscopy (HAXPES) instrumentation, this provides the opportunity to probe deeper into the bulk. Furthermore, HAXPES spectra of high Z elements will have multiple core level peaks occurring over a range of different depths and analysis of these can offer a unique non-destructive depth profile. The work presented in this study demonstrates the utility of a combined XPS and HAXPES analysis to isolate forensic signatures on the surface and into the bulk of uranium dioxide. Survey quantification shows the changing stoichiometry, utilising a 9.25 KeV excitation range of HAXPES, from different average depths within the sample matrix. Peak fitting of high-resolution spectra allows identification of oxidation states as well inspection of secondary features, which provide insight into the material characteristics. Combined with XPS analysis, this shows different chemical and elemental states at the surface into the bulk sample, highlighting the usefulness of this approach. QUASES-Tougaard analysis was performed to determine the in-depth distribution of atoms, developing a consistent model to describe the surface overlayer, correlated to the chemical and stoichiometric differences over the excitation range. Finally, the MNN X-ray excited Auger electron spectra are acquired from uranium dioxides for the first time for use in the application of a Wagner or chemical state plot. This study is the first in a series of analysis campaigns on uranium bearing materials.

2:45pm **AC+MI-ThA-3 Making Use of X-ray Emission Signatures in the Scanning Electron Microscope to understand f-Element Speciation and Phase***, **Mark Croce**,* Los Alamos National Laboratory **INVITED**

While X-ray absorption spectroscopy is exquisitely sensitive to signatures of chemical speciation and phase, what if similar information could be obtained from the scanning electron microscope? Scanning electron microscopes have become more than imaging tools – they are accessible microanalysis platforms with nanoscale spatial resolution and are compatible with a wide variety of samples including those not suitable for X-ray absorption spectroscopy. Although the physics relating the chemical and physical state of an atom to X-ray emission is more complex than for X-ray absorption, there are still distinct signatures present in the X-ray emission spectra. The twofold challenge is to measure them and interpret them. Recent development in low-temperature microcalorimeter spectrometers has made it possible to simultaneously achieve the energy resolution and detection efficiency needed to observe this fine structure in X-ray emission resulting from the interaction of the microscope's electron beam with a sample. In parallel, extending molecular and atomic theory to interpret X-ray emission spectra is beginning to allow use of this capability as a research tool to determine chemical speciation and phase for f-elements including cerium, uranium, and plutonium even in non-ideal samples. We present progress towards developing what we call "Hyperspectral X-ray Imaging" using a large-array microcalorimeter X-ray spectrometer with <10 eV FWHM energy resolution at 3 keV coupled to a commercial scanning electron microscope, recent results on lanthanide and actinide samples, and future applications of the method to support f-element science. LA-UR-24-21795

3:15pm **AC+MI-ThA-5 Automated Particle Analysis of Actinide-Bearing Nuclear Wastes***, **Edgar Buck**,* Pacific Northwest National Laboratory

Automated particle analysis (APA) is performed on the Scanning Electron Microscope/X-Ray Energy Dispersive Spectroscopy (SEM-EDS) and enables the characterization of morphology and composition of particles. This method allows hundreds to thousands of particles to be examined and reduces operator bias. We have applied APA methods to radioactive Hanford tank waste materials containing rare earth elements, uranium, and plutonium. The challenge for APA with highly heterogeneous materials is the variability in particle size. An important component of the APA is the preparation of the samples for analysis and the segmentation routines used to locate particles of interest. Biased results can be generated during the deposition of particles with larger particles tending to fall out more quickly than smaller particles, and therefore can become concentrated at the center of the sample stub, where the material is directly pipetted. It is important to be aware of the factors controlling the deposition of the particles and analyze the entire SEM stub to obtain representative data. Image segmentation routines have to be calibrated to prevent missing particles and for obtaining accurate morphological data. In this presentation, we will describe the efforts to characterize and classify the actinide-rich wastes.

3:30pm **AC+MI-ThA-6 Development of X-Ray Spectromicroscopy Techniques for Nuclear Safeguards and Nuclear Forensics***, **David Shuh**, A. Ditter, N. Cicchetti, O. Gunther,* LBNL*; J. Brackbill,* UC Berkeley/LBNL*; R. Lim, A. Baker, S. Donald, B. Chung,* LLNL*; R. Coles,* BNL*; A. Duffin, J. Ward, M. Miller,* PNNL

The on-going development of improved characterization methods and signatures is crucial to ensure that nuclear safeguards and forensics activities remain effective. For these purposes, the development of X-ray techniques is particularly useful because of their elemental specificity and non-destructive nature that could enable a first-in capability. Tunable synchrotron radiation X-ray approaches provide a means to extend the scope of safeguards and forensics investigations in elemental, chemical, and structural analysis which can be done in imaging modes that in some cases, reaches to the nanoscale. The ability to use tunable, focused X-ray beams makes synchrotron radiation sources a potentially disruptive tool for addition into the array of characterization techniques currently employed, particularly for the investigation of particles or areas of interest in smaller specimens possessing bulk-like characteristics. However, the use of synchrotron radiation methods also presents some unique challenges for the implementation of safeguards and forensic efforts at the synchrotron radiation facility sites (ALS, APS, NSLS-2, and SSRL). Synchrotron radiation-based safeguards and forensics studies over the past several years conducted at nearly all of the U.S. Dept. of Energy synchrotron radiation user facilities throughout the X-ray spectrum have furthered this case, as well as clearly identifying areas that require improvement. At the same time, there have been significant performance improvements in fixed-energy laboratory-based X-ray instrumentation suitable for contemporary, spatially-resolved safeguards and forensics (primarily XRF) studies. Additionally, there have been continued efforts and strides made towards the realization of true laboratory-based X-ray light sources that could provide competitive X-ray flux and tunability, albeit in the future, that might provide the best combination of performance and characteristics necessary for safeguards and forensics characterization activities. A current assessment of the relative strengths and drawbacks of the respective X-ray approaches, as well as a performance comparison will be presented, leading into an overall the future outlook in terms of safeguards and forensics.

3:45pm **AC+MI-ThA-7 Site-Specific and Spatially Resolved Morphological and Chemical Analysis of Plutonium and Uranium Materials***, **Brandon Chung**, A. Baker, S. Donald, T. Li, R. Lim, U. Mehta, D. Rosas, D. Servando-Williams, N. Cicchetti,* Lawrence Livermore National Laboratory*; A. Ditter, O. Gunther, D. Shuh,* Lawrence Berkeley National Laboratory

Nuclear forensics requires accurate identification of distinguishing material characteristics to delineate the material's origin-to-interdiction information. Morphological and chemical variation in nuclear materials over large scales of observation can provide valuable information that can assist interpretation of the material's varying provenance, process, and pathways. We will describe our efforts to strengthen operational and scientific methodologies to employ the focused ion beam-scanning electron microscopy (FIB-SEM) on uranium (U) and plutonium (Pu) materials for internal morphological analysis including site-specific 3D microscopy and spatially resolved characterizations of material features using transmission electron microscopy (TEM) and X-ray synchrotron spectromicroscopy. Both U and Pu materials show variations in the internal chemical composition and morphology from their production processes and storage environments. This information is of potential use in discriminating material signals to identify the origin and history of interdicted nuclear materials.

4:00pm **AC+MI-ThA-8 An Entropic Approach to Estimating Orbital Occupancies in Plutonium*, Miles Beaux,*** Los Alamos National Laboratory

Janoschek, et al. described the ground state of plutonium (Pu) as being "governed by valence fluctuations, that is, a quantum mechanical superposition of localized and itinerant electronic configurations." [*Science Advances*, 1, 6 (2015)]. By representing this ground state generally as

$$[\mathrm{Rn}]7s^{2+\gamma s,Pu}5f^{6+\gamma f,Pu}6d^{0+\gamma d,Pu}7p^{0+\gamma p,Pu}$$

where $\gamma_{s,Pu}$,$\gamma_{f,Pu}$, $\gamma_{d,Pu}$, and $\gamma_{p,Pu}$ represent potentially non-integer deviations from the integer occupancies of their respective orbitals, a combinatorial approach can be applied to the allowable permutations of quantum electronic configurations as a means of describing the electron degrees of freedom. This approach enables a classical statistical mechanics methodology to be applied to the discrete quantum states for conceptualizing and investigating the multiconfigurational ground state of Pu. Specifically, an over-approximation (with Hund's rule relaxed) and an under-approximation (with Hund's rule enforced) of electronic structure entropy has been established for varying ranges of potentially near energy degenerate occupancy configurations for plutonium. This bracketing of electronic structure entropy is compared with the known molar entropy of Pu to narrow down the set of possible localized and itinerant electronic configurations that can reasonably contribute to the quantum mechanical superposition of Pu's multiconfigurational ground state, as well as to estimate the non-integer orbital occupancies of its 7*s*-, 5*f*-, 6*d*- and 7*p*-orbitals.

LA-UR-24-22282

4:15pm **AC+MI-ThA-9 The Problem with the Second Derivative Method in EELS**, JG Tobin,*** University of Wisconsin-Oshkosh

The second derivative mode of peak analysis in electron energy loss spectroscopy (EELS) in a Transmission Electron Microscope (TEM) has been quantitatively evaluated in terms of the accuracy of the method.*This includes a demonstration of the importance of the second derivative peak width, the second order dependency of the accuracy upon that peak width and effect of high frequency noise in the spectra.It was found that, while EELS does converge to an X-ray Absorption Spectroscopy (XAS)-like limit (electron dipole transition) at high energies, there are significant issues with the 2nd Derivative Model.

1. There is no fixed relationship between non-derivative peak intensities and 2nd derivative peak intensities.Changing peak-shapes changes the ratio.
2. Assuming that peak-shapes remain constant, which may not be justified, there is a second order dependence of the ratio upon the peak width of the 2nd Derivative peak.
3. The second order dependence upon the peak width manifests itself in two very distinct ways: with random errors and systematic errors.
    1. The random error from high frequency noise places a limit on the number of significant digits in the BR result.
    2. The systematic error has shown up in the BR predictions and 5f population estimates (n) for the localized systems Pu, PO_2 and UO_2.

The 2nd Derivative Mode in EELS should be used with great caution in quantitative BR analyses of 5f populations.

*J. G. Tobin, "A quantitative evaluation of the 2nd derivative mode in electron energy loss spectroscopy," J. Electron Spectroscopy Rel. Phen. 268, 147387 (2023), https://doi.org/10.1016/j.elspec.2023.147387

Author Index

Bold page numbers indicate presenter