NUCL 1

Deciphering a nuclear threat -- Nuclear forensic advances and pressing needs

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Nuclear forensics is the technical field of interpreting signatures and other clues in or about potential nuclear threats, such as nuclear materials that have slipped outside of regulatory control, nuclear devices that could produce nuclear yield, and other classes of radiological threats such as Radiological Dispoersal Devices and Radiological Exposure Devices. Technical information developed in nuclear forensics investigations is fused with other intelligence or law enforcement investigation results to ulitimately rule in or rule out potential perpetrators. Progress has been made in advancing the scientific capabilities needed to interpret the clues in nuclear/radiological materials and related evidence, but much work remains to be done. Recent advances in nuclear forensics are reviewed, and the open needs for research are discussed.

NUCL 2

Morphology and chemical speciation of nuclear materials for forensic science

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For many years, much actinide research has focused on characterization of nuclear materials for development of more efficient fuels, as well as understanding transport and fate of actinides in the environment. To better understand morphologic and chemical signatures of uranium oxide process materials and how this information might provide insight into sample provenance for forensic analyses, we conducted studies to explore the use of powder X-ray diffraction and X-ray absorption spectroscopy along with Scanning electron microscopy. Temporal changes in chemical speciation as a function of controlled temperature and relative humidity may yield additional information indicative of storage history. Here, we present studies to characterize morphology and chemical speciation of a variety of actinide oxide materials for forensic analyses. LA-UR-16-21662

NUCL 3

Preparation and characterization of glass analogs for post-detonation debris material

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Following a nuclear detonation, radiochemists and post-detonation debris diagnosticians are tasked with performing high-quality analyses of fallout debris samples and accurate device interpretation. Debris formed following a nuclear detonation commonly consists of a heterogeneous glassy matrix containing uranium, plutonium, neptunium, americium, and fission/activation products. Homogeneous and well-characterized reference materials are critical for accurate post-detonation debris analysis. Such reference materials can include aged nuclear explosion debris from the Nevada Test Site (e.g., Trinitite) as well as "fresh" doped-glass material. Recent work has highlighted the often heterogeneous nature of historical debris, which presents a problem from the aspects of safeguards accountancy and verification as well as micro-scale characterization (i.e., microbeam analysis). In this regard, the work presented here will focus on creation of homogeneous, "fresh" doped-glassy standards containing uranium, plutonium, surrogate fission products (e.g., Sr, Cs, Pm, Sm, Eu), and urban material (e.g., Fe and Ca from construction material, stainless steel, aluminosilicate phases as a surrogate for dirt). Traditional and sol-gel approaches to glass synthesis were used with the goal of creating a final material that is homogeneous on a mesoscopic scale (i.e., hundreds to thousands of nm).

NUCL 4

Evaluation of ammonium bifluoride dissolution of refractory minerals for nuclear forensic analysis

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Development of rapid and field deployable chemical dissolution methods could lead to rapid radiochemical analysis near the site of a debris field following a nuclear detonation. Recently, fusion with ammonium bifluoride (NH_4HF_2) has been demonstrated to dissolve the mineral trinitite without requiring direct use of hydrofluoric acid. Instead, the solid NH_4HF_2 salt decomposes forming HF vapor when heated past 125 ^{o}C. An evaluation of the NH_4HF_2 dissolution process on a variety of geologic certified reference materials with varying refractory mineral content will be presented. Experiments were conducted using both ICP-MS data collection and in-situ radiotracers produced in the reference materials using neutron activation. Focus on elements important in the fission yield as well as volatile elements, which could be lost during the fusion process, are of particular interest. We will describe the effect of varying the time of fusion on the elemental recovery. The rate of silicon loss during the NH_4HF_2 fusion on samples of silicate powder and geological standard reference materials will also be reported.

NUCL 5

Neutron imaging studies of *in situ* growth of neutron and gamma detector materials

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The studies described here are aimed at addressing the critical need to develop dependable crystal growth techniques of solid-state materials used as radiation detectors for both national security and medical applications. We present our activities using pulsed neutron, radiographic imaging and simultaneous diffraction techniques to examine the synthesis of both CZT and CLYC with the goal of identifying the conditions that favor the production of defect free materials. The probable outcome of these studies would be to identify: (1) the thermodynamic and convective conditions that exist at the furnace wall, within the melt and at the crystal melt interface, (2) the nature and creation of solute segregation, voids, and crystal dislocation networks (3) the variations in crystal stoichiometry and (4) the formation of multi-crystalline domains.
Using a pulsed neutron beam and time of flight detection methods we exploit the penetrating power and wavelength dependence of neutron absorption (of Cd and Li) to perform measurements during crystal growth (i.e. with the materials inside the furnaces in the liquid state and at the liquid solid interface). Furthermore, solid boules can be examined (*nondestructively and without cutting or segmenting)* either inside the furnace or free standing. The objective of these studies include: the validation/improvement of the modeling studies of CLYC and CZT growth behavior, the development of new/improved furnace design and the identification of optimum growth techniques that enable the production of large boules of defect free, single crystalline materials in a timely and cost effective manner. We provide our preliminary results that include the experiential setup at LANSCE and sample neutron radiographic and synchrotron based IR images of CZT flat solid plates. Furthermore, we include MCNP calculations of optimum incident energy and sample isotopic compositions to enhance the contrast of various elemental components of the materials.

NUCL 6

Trace element and isotopic signatures of uranium ore concentrates: Forensic applications

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Four samples of uranium ore concentrate (UOC) originating from a sandstone-hosted roll-front ore body in the Powder River Basin uranium province (Wyoming, USA) have been analyzed for trace element and isotopic composition. Trace element concentrations were determined using both laser ablation (LA) and solution mode (SM) high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) analytical techniques on both a ThermoScientific Element 2 and Nu Instruments Attom. Variations in sample introduction (LA vs. SM) technique and instrumental (Element 2 vs. Attom) method does not affect the obtained chondrite-normalized rare earth element (CN-REE) patterns. Measured CN-REE patterns correlate strongly with data collected from primary uraninite (UO_{2+x}) originating from the same locality as UOCs. Isotopic measurements were made on a Nu Instruments Nu Plasma II multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS). This study shows that despite processes related to in-situ mining, UOCs retain a characteristic REE signature which can be used for source attribution.

NUCL 7

Online trace-level quantification of uranium in environmental water

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Nuclear nonproliferation efforts and treaty verification require portable, robust radiation detectors capable of detecting trace-levels of radionuclides in environmental matrices. A recent development in environmental sensing is a portable, flow cell detector that utilizes extractive scintillating resin. Extractive scintillating resin serves the dual purpose of (1) concentrating the radionuclide of interest and (2) serving as a radiation transducer. Previous resins were produced by physically absorbing organic extractants and fluors in a polymer matrix, which resulted in unstable resins as the active components leach from the polymer over time.

This contribution describes our work to synthesize a new class of extractive scintillating resin in which the fluor and the ligand are bound covalently within the polymer matrix. Two approaches have been taken to synthesize these resins: (1) synthesis of a 4-vinylbenzyl chloride containing polymer followed by solid-phase synthesis techniques to add the uranium-selective ligand and (2) one-pot polymerization utilizing a polymerizable fluor and ligand. In the first approach, suspension polymerization was used to prepare resin beads comprising 4-vinyltoluene; divinylbenzene; the fluor, 2-(1-napthyl)-4-vinyl-5-phenyloxazole; and the solid phase reactant, 4-vinylbenzyl chloride then the resin was functionalized with methylphosphonic acid. In the second approach, resins were prepared by suspension polymerization comprising 4-vinyltoluene; divinylbenzene; 2-(1-napthyl)-4-vinyl-5-phenyloxazole; and the ligand, ethyleneglycol methacrylate phosphate. Resins were characterized by Fourier-transform infrared spectroscopy to support functionalization. Fluorescence properties were studied with

spectrofluorometry to measure emission wavelength and intensity. The detection efficiency of the resins in near neutral pH water was evaluated by sequentially loading uranium onto a resin-packed column followed by standard scintillation counting of the column. Resins synthesized by the first approach detected uranium-233 with an efficiency of 40% in pH 4, distilled water. The flow cell efficiency of the resins was evaluated in an online, flow-cell detector. Resins synthesized by the first approach showed 20% flow cell efficiency in pH 4, simulated ground water. Results from this research are laying the groundwork for the development of portable radiation sensors capable of online monitoring of waterborne alpha-emitting radionuclides.

NUCL 8

Chemical and isotopic characterization of North America uraninite samples: forensic applications

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Uranium ores can be found in a wide variety of geological settings, including high temperature magmatic, metamorphic and low-temperature sedimentary deposits. UO2, the most essential raw material for fuel preparation, incorporates variable quantities of trace elements during crystallization, thus its chemical signature will reflect the environment of formation. In this work micro-X-ray fluorescence, electron microprobe, and laser ablation- inductively coupled plasma mass spectrometry (LA-ICPMS) analyses were carried out on individual uraninite grains from various localities in North America; these include uraninite samples from the “Rod Ewing Mineral Collection” and were retrieved from deposits in North Carolina, New Hampshire, Colorado, Utah, Wyoming, Arizona, and New Mexico. Samples are representative of nine different geologic environments including pegmatites, hydrothermal systems, synmetamorphic, collapsed breccia pipes, meta-sedimentary, petrified wood and sedimentary (tabular and roll front) deposit types.

The goal in relation to nuclear forensics was to obtain detailed chemical (major, minor, and trace elements) and isotopic (e.g., Sr) characterization of uraninite samples with regards to establishing characteristic chemical and isotopic signatures for uraninite formed in similar geological environments. Of particular interest is the rare earth element (REE) composition of uranium oxide due their low sensitivity to redox changes and their ionic radii are close to that of uranium, allowing for easy substitution for uranium. Chondrite normalized rare earth elements (REEs) plots display significant differences, reflecting the different nature of the geologic deposit type amongst samples. The 87Sr/86Sr ratios of the investigated material vary over a wide range spanning between 0.7096 and 0.7680 and may help distinguish samples of different origins. Samples originated from low temperature deposits display the lowest 87Sr/86Sr

ratios (0.7096- 0.7193), whereas those samples formed within meta-sedimentary and collapsed breccia pipes show the highest ratios (0.7526- 0.7680).
Results indicate that 87Sr/86Sr ratios used in combination with chondrite normalized REE patterns may be a helpful tool in gathering unique information on the provenance of uraninite type material.

NUCL 9

Rapid uranium isotopic analysis using ultrafiltration and alpha spectroscopy

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Clandestine activities involving the separation or manipulation of special nuclear material (SNM) for the purpose of developing a weapon of mass destruction is likely to result in the contamination of environmental waters. The capability to conduct isotopic analyses for waterborne SNM would be a powerful nuclear forensics tool. Despite widespread interest, there currently is no fieldable measurement system available for low-level isotopic identification of waterborne uranium.

This contribution describes our efforts to develop a high throughput analytical technique for waterborne isotopic analysis. Alpha spectroscopy substrates were prepared by two methods: (1) physical deposition of a uranium-selective, water-soluble polymer film on ultrafiltration membranes and (2) grafting uranium-selective ligands from the surface of ultrafiltration membranes. Uranium was loaded onto the substrates by filtering uranium-contaminated water through the ultrafiltration membranes. The uranium-selective, water-soluble polymer was prepared by the copolymerization of 2-hydroxylethyl methacrylate and 2-ethylene glycol methacrylate phosphate. The ligand-grafted membrane was prepared by the UV-polymerization of 2-ethylene glycol methacrylate phosphate with N,N-methylene bisacrylimide. Membranes were characterized by Fourier-transform infrared spectroscopy before and after modification to support the deposition or grafting of the polymer on the membrane surface. The capacity for uranium, 1.9 mmol U/ g, was determined from equilibrium binding experiments.
The effect of membrane preparation method and membrane pore size on peak resolution in the alpha spectrum was investigated for pure uranium containing solutions at pH = 6. To mimic more realistic conditions, the selectivity of the membrane was tested using uranium-233 in simulated groundwater. Both uranium-coated membranes prepared from distilled water and groundwater showed resolutions of 40-60 keV in the alpha spectrum and detection efficiencies of 12% for uranium-233. The membranes showed both high resolution and fast preparation time. The permeability of the polymer-coated, ultrafiltration membranes (MWCO 100 kDa) was determined to be 1190 LMH/bar which means 5 L of contaminated groundwater can be processed per hour at 414 kPa through a 45 mm ultrafiltration cell. The results of this research are laying the

foundation for the development of a novel rapid, field portable method for isotopic identification of waterborne SNM.

NUCL 10

New natural uraninite reference material for nuclear forensic analysis

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The accurate and precise measurement and validation of chemical and isotopic signatures in nuclear materials for forensic analysis is highly dependent on the use of high quality standard reference materials. There is presently a lack of suitable, matrix-matched, and well-characterized U-bearing standard materials for nuclear forensic analysis. Uraninite (UO_2) is an ideal natural standard material because it is the primary mineral used to manufacture uranium ore concentrate (UOC) that is employed for the nuclear fuel cycle and weapons grade fuel. However, establishing a natural standard material poses a challenge because these materials are typically inhomogeneous in large amounts. For example, the widely used Mistamisk uraninite from Québec (Canada) exhibits significant chemical heterogeneity at the 10s to 100s of microns scale.

In this study, uraninite from Utah (USA) has been characterized for its major, minor, and trace element abundances using a variety of micro-analytical techniques. The chemical signatures of the uraninite were investigated at the macro (cm)-scale with micro-X-ray fluorescence mapping, and at high-spatial resolution (10s of micron-scale) using electron microprobe (EMP) and laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses. Based on EMP analyses, the uraninite is characterized by fairly homogeneous and average contents of 90.37±0.58 wt% for UO_2 and 2.67±0.13 wt% for CaO. Due to its homogenous distribution, CaO wt% abundances were used as the internal standard when conducting LA-ICP-MS analysis in order to calculate trace element abundances and monitor for instrumental drift. Trace elements present in notable abundances (100s to 1000s ppm) include V, Y, Zr, Ba, Sr, and Pb; concentrations for the latter two elements display a negative correlation. Th abundances are extremely low (<1 ppm). Chondrite-normalized rare earth element (REE) abundances show depletion in the light REEs, particularly for lanthanum, with the remaining REEs defining a flat pattern at levels just slightly above 1000 times chondrite. Overall, results obtained thus far indicate fairly homogeneous major and trace element compositions at both the centimeter and micron scales. For comparison, additional material will be processed for bulk sample solution mode-ICP-MS analysis. Future work will also include Pb, Sr, and U isotopic characterization of the uraninite using both solution- and laser ablation-multicollector (MC)-ICP-MS techniques.

NUCL 11

Divalent cation incorporation into actinide oxides

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Unique microstructural signatures in actinide oxides can elucidate the origin and process history, indicating the processing temperatures and chemical impurities. Divalent cation incorporation into uranium dioxide (UO_2) is key for predicting impurity (e.g., Ca^{2+}) controls on microstructural features in stored actinide oxides. The mechanism of cation incorporation into solid phases can elucidate the thermodynamic stability and kinetic feasibility of the doped systems. In this study, quantum-mechanical calculations are used to evaluate the charge-balanced mechanisms of divalent cation ($M^{2+} = Ca^{2+}$ and Mg^{2+}) incorporation into 2×2×2 AcO_2 supercells (UO_2 and PuO_2). The Hubbard U formalism as implemented in VASP was used to properly treat the bonding characteristics of the uranium and plutonium 5*f* electrons. The direct substitution of a divalent cation (M^{2+}) into an actinide (Ac^{4+}) vacancy results in a charge imbalance. Three charge-balancing mechanisms were evaluated in this work – 1) the substitution of a divalent cation for an actinide and an oxygen ($M^{2+} \rightarrow Ac^{4+}+O^{2-}$); 2) the substitution of two divalent cations for an actinide ($2M^{2+} \rightarrow Ac^{4+}$) ; 3) the substitution of a divalent cation and an oxidized actinide for two actinides (*e.g.*, $M^{2+} + Ac^{6+} \rightarrow 2Ac^{4+}$). For case 1, M^{2+} is substituted in the Ac^{4+} vacancy, in the O^{2-} vacancy, and at a bisector between the U^{4+} and O^{2-} vacancies. All initial positions converged to M^{2+} substitution in the Ac^{4+} vacancy, resulting in a favorable incorporation energy for Ca^{2+} in UO_2 ($\triangle E_{incorp} = -0.64$ eV). For case 2, two M^{2+} are substituted on the faces of the cube formed by the oxygen coordinating the Ac^{4+} vacancy, and results in a highly unfavorable incorporation energy (*e.g.*, $\triangle E_{incorp} = 5.22$ eV for Ca^{2+} in UO_2). For case 3, the initial M^{2+} is substituted in the Ac^{4+} vacancy, and the charge balancing U^{6+} is positioned at various distances from the M^{2+}. The oxidation of Ac with incorporation of M^{2+} was the most favorable incorporation mechanism (*e.g.*, $\triangle E_{incorp} = -3.30$ eV for Ca^{2+} in UO_2). Interestingly, charge density analysis shows the presence of U^{5+}, rather than U^{6+} in the optimized structures. Further calculations were performed to consider oxidation of two Ac^{4+} to Ac^{5+} upon M^{2+} incorporation, resulting in lower incorporation energies (*e.g.*, $\triangle E_{incorp} = -3.44$ eV for Ca^{2+} in UO_2). Thus far, atomic scale calculations indicate that divalent cation incorporation likely leads to oxidation of the actinide species near the impurity.

NUCL 12

Morphological effects of variable calcination conditions for the thermal decomposition of uranyl peroxide

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Traditional signatures in nuclear forensics, such as uranium parent–daughter isotope ratios, can provide critical information as to the origin and age of the source materials, but they provide no means by which to trace the provenance or process history of the material. In this application, the morphological and microstructural properties of uranium oxides are being investigated using a variety of characterization techniques as a signature for identification of provenance and process history of uranium materials. The utility of the morphology and microstructure for assessing process history cannot be realized without a fundamental understanding of how the morphology changes during different synthetic routes and how the material ages over time in controlled temperature and humidity environments. Results will be presented discussing the synthesis of high purity UO_3 and the synthetic factors (i.e. starting material, temperature, pressure, time) that influence the resulting morphology. The surface morphology of the samples was characterized using high resolution scanning electron microscopy and the resulting images were statistically compared using the Morphological Analysis for Material Attribution (MAMA) software developed at Los Alamos National Laboratory.

NUCL 13

Using Sr resin with mixed acid matrices

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Most current radioanalytical protocols have been developed for the analysis of air, water, soil and bioassay samples. While these protocols build the foundation of operational environmental monitoring, they are not necessarily suitable for the analysis of samples that will be encountered in the aftermath of a nuclear incident. In such a situation, it will be important to determine the amount of ^{90}Sr and other isotopes of interest present in the affected area to ensure the appropriate response. Due to the likelihood of such an event occurring in an urban or metropolitan area, it is crucial to have procedures that can be used to rapidly and accurately separate and determine radioactive materials from matrices found in these environments. Of particular interest for emergency response and nuclear forensics are methods that can be applied to the analysis of concrete, steel, and glass.

Chromatographic resins have been used for radioanalytical separations for several years now, and are the basis for most common techniques used to isolate radiostrontium in a rapid fashion. The only published methods for strontium selective resin (Sr Resin) use exclusively nitric acid as the aqueous phase for the separation. Unfortunately, steel and other urban materials are often dissolved in other acids, commonly including hydrochloric and/or hydrofluoric acids, which require conversion to a purely nitric acid system for further analysis based on the currently available methods. Previous work has shown no significant reduction in strontium retention in 3 M HNO_3 with up to 0.5 M HCl in the system. This work takes a more in-depth look at mixed acid systems. The results indicate that while there is a significant drop at lower ionic

strengths, even solutions containing significant concentrations of other mineral acids can be effective mobile phases at high ionic strength.

NUCL 14

Improving rapid separations for nuclear forensics through computational techniques

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Accurate structural and thermochemical descriptions of lanthanide- and actinide-containing compounds is essential to accelerate separations in nuclear forensics. Performance and predictive capabilities of computational approaches including density functional theory (DFT) and the correlation consistent Composite Approach tailored to lanthanides and actinides (*f*-ccCA) will be discussed. Structural analysis and thermochemical predictions including coordination preferences, electron population analysis, binding Gibbs free energies, enthalpies, and entropies, and their effects on extraction selectivity will be presented.

NUCL 15

Development of a chemical system for rutherfordium using TEHA and TEHP

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Studies of the chemical properties of the heaviest elements have always been difficult due to the short half-lives and low cross sections involved. To solve this problem, atom-at-a-time methods are necessary to determine the properties of short-lived isotopes. Extremely fast kinetics for the chemical reactions studied (on the same order as the nuclide's half-life) are required, and the system should have potential for automation. [1] One potential technique, extraction chromatography, offers a way of investigating rutherfordium's properties, without the solvent waste generated in liquid-liquid extractions. A rapid method involving the use of a ligand with high intragroup selectivity is necessary to discover more about element 104. Studies with the homologs of rutherfordium, zirconium and hafnium, can be performed using liquid-liquid extractions as well as extraction chromatography. From literature reviews, tertiary amines and phosphates show promise in extracting group 4 elements. In particular, tris(2-ethylhexyl)amine (TEHA) and tris(2-ethylhexyl)phosphate(TEHP) can be used to selectively extract zirconium and hafnium from a chloride matrix. [2] Results of a study investigating the solvent extraction and the use of extraction chromatography resin of Zr

and Hf from various mineral acids by these two ligands will be presented. The development of an extraction system for rutherfordium based on these extractants can help to further elucidate its properties.

NUCL 16

Rare earth element sorption to UO_2

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Rare earth elements (REEs) are natural trace elements capable of providing significant insight into geologic aging processes and are a powerful tool in discriminating geologic deposit type. The robust tracer properties of the REE are of interest to the nuclear forensic community, specifically in understanding the environmental aging processes of uranium bearing minerals. Furthermore, studying the diffusion of trace elements into and out of solid-phase nuclear materials in contact with water under different aging scenarios may lead to the identification of definitive aging signatures.

Batch-sorption experiments were designed to test the partitioning of twelve REEs between the aqueous and solid phases of a UO_2 suspension as a function of time and pH. The concentrations of lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), and ytterbium (Yb) in the aqueous phase was monitored using inductively coupled plasma mass spectrometry (ICP-MS).

The fraction of REE associated with UO_2 increased with increasing pH and equilibrium was established within 24 hours. All REEs displayed a similar sorption curve with the noted exception of Sm, Nd, and Yb, which exhibited preferential sorption at a low pH. This trend does not align with the lanthanide contraction, as Sm and Nd are light REEs.

Future work includes dissolving UO_2 that has not been exposed to solutions containing REEs in order to determine the original REE signature and using this signature as a comparison for UO_2 that has been exposed to solutions containing REE. In addition, the mechanism(s) of REE interactions with UO_2 will be probed with advanced spectroscopic and microscopic techniques.

NUCL 17

Modern measurements of uranium decay rates

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Radioisotopic dating techniques are highly valuable tools for understanding the history of physical and chemical processes in materials related to planetary sciences and nuclear forensics. It has been widely recognized that accurate and precise decay constants (λ) are critical to radioisotopic dating, particularly the calibration benchmarks λ_{235U} and λ_{238U}. Alpha counting experiments in 1971 measured λ_{235U} and λ_{238U} with ~0.1% precision, but have never been independently validated at comparable precision and the metrological traceability of these experiments is sub-optimal. New direct measurements of $\lambda_{238U,}$ $\lambda_{234Th,}$ $\lambda_{235U,}$ and λ_{234U} are underway, using independent approaches for each nuclide. Our approach to λ_{238U} measurement is to measure ingrowth of ^{234}Th in chemically purified, isotopically enriched ^{238}U solutions, by quantitatively separating the Th and allowing complete decay to ^{234}U. All of the measurements are done using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), aiming at 0.05% precision (95% confidence level). We expect that, combined with improved measurements of λ_{234Th}, this approach will result in values for λ_{238U} with < 0.1% uncertainty. The current status and optimization of the chemical separation employed will be discussed. λ_{234Th} is being evaluated using direct decay measurements with a Si surface barrier charged particle detector in coincidence with a high-purity Ge (HPGe) gamma detector. For the measurement of λ_{235U} and λ_{234U}, isotopically enriched samples are chemically purified and analyzed for U concentration and isotopic composition by MC-ICP-MS. Counting sources with a known quantity of U are prepared by electrodeposition and the α-activity will be measured in the coincidence counting apparatus, which allows reduced uncertainty in counting efficiency. An overarching goal of the project is to ensure the quality of results including metrological traceability in order to facilitate implementation across diverse disciplines.

NUCL 18

Determination of Am-241 in weapons grade plutonium for chronometry applications

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We will report on our efforts to develop a method for the determination of Am-241 in weapons grade plutonium for chronometry applications. The in-growth of Am-241 from Pu-241 is a well regarded nuclear forensic chronometer for duration since last chemical separation. Nuclear forensic sponsors are typically interested in results from two or more independent analytical methods that show statistical agreement, e.g. 95%

confidence interval overlap, based on JCGM GUM based uncertainties. They are also interested in results with a low relative uncertainty to more tightly constrain the time frame for the last chemical separation. Isotope Dilution Mass Spectrometry (IDMS) is a well-regarded technique for measurement of Am-241 for this purpose given its achievable uncertainty, e.g. <1% (k=2). Our focus has been an alternative method using a combination of spectrometry techniques that can approach the same level of precision as IDMS but in an independent manner.

NUCL 19

Structural characterization of hydrolyzed of the uranium tetrafluoride solids

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Technical nuclear forensics may include the characterization of nuclear materials produced from various uranium chemical conversion processes, such as oxides, fluorides, diuranates, and others. When these species are stored for long durations, environmental factors may induce chemical transformations within a sample with change in the temperature or humidity, or both. Uranium tetrafluoride (UF_4) is an intermediate in both the processing of uranium ore, and the production of nuclear fuel. Published research focused on the uranium fluorine system, UF_4 chemical changes induced by the environment are rare, in part due to its assumed chemical inertness. Additionally what published results on hydrolysis of UF_4 are available are often contradictory. J. Dobratz *et al* reported UF_4 almost completely decomposes in water at room temperature within 24 hours. Whereas A. Roberts *et al* reported that boiling water for 72 hours had no noticeable effect on UF_4 solids. It has been proposed, and which previous work supports, that at elevated temperatures,UF_4 will hydrolyze and oxidize to uranyl fluoride (UO_2F_2), but characterization of these reactions has not been clarified for typical environmental regimes.

Anhydrous UF_4 material is commercially available and can be manipulated by systematically changing the temperature and humidity such that both Raman spectroscopy and powder X-Ray Diffraction measurements can be made in-situ. Our efforts have focused on 1) determining the progeny of UF_4 hydrolysis using elevated temperatures and relative humidities to expedite hydrolysis and determine final speciation, and 2) methodical control of temperature and relative humidity are used to identify intermediates and establish approximate kinetics for both temperature and humidity variances. Known UF_4 Raman bands (130.7, 168.4, 296.9, and 360.8 cm^{-1}), anhydrous UO_2F_2 bands (180, 442, and 915 cm^{-1}), and hydrated UO_2F_2 bands (174 and 867 cm^{-1}) are used to compare and contrast changes in time, temperature, and humidity.[4] Results from this effort will validate/disprove the above decomposition pathway while providing a timeline for hydrolysis.

NUCL 20

Understanding the surface chemistry of PuO_2

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Pu metal is unique is in its bulk and surface properties due to highly-correlated 5f electrons. It is believed that the native oxide which develops on metals is highly disordered and it is largely the role of these electrons which stabilizes these structures and dictates the surface chemistry. The growth and formation of these oxides, and the subsequent chemistry and the thermo-physical properties these oxides possess, is of particular interest to the nuclear fuels industry. The use of plutonium in Mixed Oxide (MOX) fuels makes understanding the fundamental chemistry ever important, particularly with regards to their use in next generation reactors. High purity oxides and oxide grown on metal surfaces were studied using a variety of techniques, e.g. EXAFS, reflectometry, and ellipsometry, to determine the impact of sample morphology and preparation on chemical and physical properties. The local structure and its impact on the material’s optical properties will be discussed.

NUCL 21

Determining speciation of U and Pu in spent nuclear fuel via electrospray ionization mass spectrometry

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Used nuclear fuel (SNF) contains almost one-third of the periodic table. A selective separation of the long-lived actinides (An) from the fission products of intermediate life-time (^{90}Sr, ^{137}Cs, ^{99}Tc, and ^{131}I), and the relatively shorter lived lanthanides (Ln) reduces both the amount and radiotoxicity of the waste. Nonetheless, a fundamental understanding of the thermodynamic properties of complex formation and speciation in solvent extraction systems is needed for the development of advanced spent nuclear fuel reprocessing systems. In this work, methods have been developed using electrospray ionization – mass spectrometry (ESI-MS) to characterize the speciation of U and Pu with tributyl phosphate (TBP) and dibutyl phosphate (DBP) as would be found in the PUREX process. The polarity of the ionization source was altered to observe both positive and negative gas phase ions. U and Pu complexed to TBP resulted in complexes that could be observed as positive ions, but no negative ion species were observed. In contract, U and Pu complexed to DBP could be observed as both positive and negative ions. Using the relative abundance of ions observed in the gas phase, apparent stability constants were calculated to enable comparison of the gas phase

species to known solution species. The protocols developed in these studies help determine fundamental actinide complexation chemistry in solvent extraction systems, and demonstrate the potential of ESI-MS for process control monitoring in spent nuclear fuel reprocessing facilities.

NUCL 22

Thorium incorporation in phosphates matrices: the case of the rhabdophane and xenotime

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The management and the conditioning of radwaste represents a major challenge in the nuclear industry. Therefore a variety of host matrices have been studied, including several phosphate based ceramics. They represent promising candidates for the conditioning of actinides (III, IV) owing to their facile way of preparation and their high chemical durability.

The incorporation of actinides in these phases has been extensively studied, in particular by solid-state methods, but requires a grinding step and could lead to the formation of heterogeneous compounds. For such reasons, the synthesis of target compounds in aqueous solution were developed to obtain pure phases with a better homogeneity.

In this study, a particular attention was paid to the insertion of thorium (Th^{4+}) into original solid solutions of $Er_{-x}Th_x(PO_4)_{1-x}(SiO_4)_x$ which were obtained in application of the method developed during the synthesis of the coffinite ($USiO_4$). Therefore, hydrothermal conditions were used (250 °C, 7 days) and the analysis of the PXRD data showed the formation of single phases. The structure crystallizes in the zircon-type structure ($I4_1/amd$ group, tetragonal system) as observed for the end-members $ThSiO_4$ and $ErPO_4$.. The Rietveld refinement of these data confirmed the formation of a complete solid solution in agreement with the Vegard's law. A thorough analysis was also carried out by Raman spectroscopy and EXAFS at the Er and Th edges and showed an exciting structural evolution.

NUCL 23

Correlation between surface morphology and crystallographic orientation in polycrystalline UO_2

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The surface features and corresponding thermodynamic characteristics of UO_2 play an important role in the evolution of fission gas bubbles and the propagation of micro-fractures in the fuel pellets used in commercial nuclear reactors. Therefore, a better understanding of the surface behavior of UO_2 helps improve the credibility of fuel performance models. Here coordinated experimental efforts to quantitatively correlate crystallographic orientation and surface faceting features in UO_2 are reported upon. A sintered polycrystalline UO_2 sample was thermally etched to induce the formation of surface faceting features. Synchrotron Laue microdiffraction was used to obtain a precise crystallographic orientation map for the surface grains. Scanning electron microscopy (SEM) was utilized to collect the detailed information on the surface morphology of the sample. The surface faceting features were found to be highly dependent on the crystallographic orientation. In most cases, Triple-plane structures containing one {100} plane and two {111} planes were found to dominate the surface of UO_2. The surface morphology is also influenced by the local fluctuation of hydroxidation. Additionally, the orientation-morphology relationship established in this study revealed a practical alternative method of determining crystallographic orientation solely based on the surface features captured by SEM images.

NUCL 24

Structure and spectra of uranyl fluoride hydrates

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Uranyl fluoride (UO_2F_2)is an important byproduct of the nuclear fuel cycle, resulting from the hydrolysis of uranium hexafluoride with water. Due to its status as a waste product, its physical characteristics have not received significant attention from a basic chemistry point of view. However, UO_2F_2 is also an ideal model system for studying actinide chemistry. In particular, UO_2F_2 is a closed-shell system with significant crystal symmetry (*R-3m* symmetry), which may be amenable to density functional theory approaches.

Several reports indicate the presence of crystal hydrates, nominally of the formula $UO_2F_2+(H_2O)_x$, but these structures have not been identified or solved. Using neutron diffraction, we show at least three values of x are possible and characterize the dynamics of the associated water molecules via quasielastic neutron scattering. The confirmation and understanding of crystal hydrates of uranyl fluoride is an important step to building a fate and transport model as we are faced with the environmental consequences of UO_2F_2 production.

To complement these studies, we use inelastic neutron scattering and density functional theory calculations to measure and calculate the vibrational frequencies of the most common form of uranyl fluoride, the partially hydrated $UO_2F_2+0.4(H_2O)$ crystal. Several low-frequency vibrational modes of water are observable that can be potentially identified spectroscopically, opening a pathway towards the applied goal of identifying environmental UF_6 leakage in real-time.

NUCL 25 – Withdrawn.

NUCL 26

Characterization of irradiated metallic fuels using synchrotron radiation and electron microscopy

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Metallic nuclear fuels are candidates for both high performance research and test reactors, as well as for transmutation-based reactors. These metallic fuels exhibit a variety of advantageous characteristics including ease of fabrication, high thermal conductivity, high fuel density, and high melting point. During the operation of these fuels, the microstructures are altered due to the extreme environments that these fuels are subjected to (e.g. neutron damage, generation of fission products, high temperatures, etc.). This talk will discuss recent research that has been carried out with both synchrotron radiation and electron microscopy to characterize the resultant radiation damage with a specific emphasis on phase formation/alteration, atomic coordination, and chemistry within the fuels and the interaction region at the fuel-cladding interface.

NUCL 27

Oxalate complexation with Hf(IV) and its applications to the PUREX process

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The understanding of the chemistry of interfering fission products during the reprocessing of spent nuclear fuel (SNF) is crucial for developing advanced reprocessing schemes. One of such interfering fission products is Zr, which co-extracts with U(IV) and Pu(IV). In solvent extraction based systems, such as the Plutonium Uranium Recovery by Extraction (PUREX) process, the addition of specific complexing holdback agents in the aqueous phase can prevent the co-extraction of these fission products (e.g. Zr) with the targeted elements (e.g. U and Pu, in the case of PUREX). This work presents the experimental determination of thermodynamic data for the complexation of oxalate (a potential holdback ligand) with tracer concentrations of $^{175+181}$Hf(IV) (an analog for Zr(IV) chemistry), using a solvent extraction technique

with a 1 M $HClO_4$ aqueous solution. Stability constants for 1:0:1 and 1:0:2 Hf(IV)-oxalate complexes and associated Δ_rG, Δ_rH, and Δ_rS were determined from solvent extraction data and van't Hoff analyses. The measured Hf(IV)-oxalate stability constants at 25 ± 1°C, log β_{101} = 10.10 ± 0.05 and log β_{102} = 18.96 ± 0.04, and additional literature thermodynamic data were used to model U(VI) and Pu(IV) extraction by tri-*n*-butyl phosphate (TBP) in the presence of Hf(IV) and oxalate. This research was funded by the U.S. Department of Energy Nuclear Energy University Program (NEUP) through grant DE-NE0000674.

NUCL 28

Synthesis and characterization of $Ln_{1-2x}Ca_xTh_xPO_4.nH_2O$ rhabdophane-type precursors to monazite

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Monazite, *i.e.* $LnPO_4$ (Ln = La-Gd), has been widely studied as a potential matrix for nuclear waste management. Among several properties of interest, its very high resistance to aqueous alteration as well as to radiation damages was particularly pointed out. Also, the original nine-fold coordination of the cation in the monoclinic monazite-type structure (space group $P2_1/n$) allows the crystal lattice to accept numerous substitutions. This property was used to prepare tetravalent actinides-bearing compounds, leading to the so-called cheralite-family, *i.e.* $Ln_{1-2x}Ca_xAn^{IV}{}_xPO_4$. Unfortunately, if dozens ways of preparation (dry, wet, hydrothermal methods) are available in the literature for monazites, only solid-state chemistry routes were up to now mentioned for the synthesis of cheralites.
In this work we present an alternative way based on wet chemistry method to prepare thorium-based cheralites, based on the initial precipitation of $Ln_{1-2x}Ca_xTh_xPO_4.nH_2O$ precursors with the rhabdophane type structure (monoclinic, C2 space group). Several series of samples were prepared considering various lanthanides cations and different weight loadings in thorium. Further XRD characterization then allowed to precise the stability range of such precursor in terms of chemical composition. Complete physico-chemical analysis was also completed through spectroscopic analyses, SEM observations, and thermogravimetric analyses.

NUCL 29

Oak Ridge National Laboratory: Unique isotope research & development

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Oak Ridge National Laboratory (ORNL) has a long history in the production of heavy elements and more recently in the discovery of super heavy elements (SHEs). Although

ORNL originated as part of the Manhattan Project, developing processes and techniques for the production, separation, and purification of ^{239}Pu in 1944, its name has been synonymous with a wide range of isotopes. Research and development of new isotope production and purification techniques is enhanced by ORNL's unique facilities—the Radiochemical Engineering Development Center and the High Flux Isotope Reactor. Research into novel methods for the transmutation of curium to heavier actinides and development of thin actinide targets for SHE discovery is at the forefront of ORNL's Isotope Program.

NUCL 30

Applications of absorption spectroscopy and chemometrics for plutonium monitoring in nuclear materials processing facilities

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Electronic absorption spectroscopy is a powerful method for determining solution-phase Pu concentrations that is insensitive to isotopic distribution and provides complementary information to the results of radiological methods. We will discuss the development of new in-line and off-line absorbance methods for process control, accountability, and criticality protection measurements in support of nuclear processing missions. In-line methods simultaneously measure multiple Pu oxidation states across a wide range of nitric acid concentrations. Off-line methods rely on quantitative conversion of the Pu to a single oxidation state. While absorbance spectroscopy has long been used for these purposes, our work extends the capability of the method in several ways. Rigorous, real-time wavelength and intensity calibrations to natural and/or NIST-traceable standards minimize inter-instrument variability. Chemometric models can be developed in a central laboratory and directly ported to field or lab line instruments without the development of a transfer matrix. In-line methods use several classification criteria to assign spectra to a subregion of the overall range of process conditions. Localized partial least-squares (PLS) models require fewer components than global models. The resulting set of localized models is more robust and covers a wider concentration range while adding only a small amount of computational overhead. For off-line methods, a classic (ISO 9463) approach is based on quantitative oxidation to Pu^{6+} while using Beer's Law to interpret the 830 nm peak. However, control or independent measurement of temperature and acidity is required to reduce variability. PLS ameliorates these issues and addresses chemical interferences. We will also discuss instrument requirements for measurement of the sharp Pu^{6+} peak with current diode array spectrophotometers.

NUCL 31

Synchrotron radiation studies of advanced nuclear energy materials

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Advanced nuclear energy systems are envisioned to operate at high temperatures, high burn-up, harsh neutron irradiation, and corrosive environments. New materials and nuclear fuels with improved performance, safety and reliability are needed for the increasingly demanding operating conditions. The fundamental challenge in developing new materials with improved irradiation, temperature, and corrosion resistance is to understand and control chemical and physical phenomena in complex systems over multiple time and length scales. Solving these scientific and technical challenges will require an integrated approach of all available computational and experimental capabilities. Historically, the application synchrotron radiation characterization techniques have revolutionized the materials science of semiconductors, superconductors, proteins, and drug design. These synchrotron radiation techniques, however, have not been made readily available to the nuclear material scientific user community. There are many reasons that these modern tools have not been well utilized by the nuclear community. Over the last decade, many of the barriers to the study radioactive materials and synchrotrons have been overcome. The use of synchrotron radiation techniques represents an important opportunity that needs to be fully exploited for nuclear materials research and development. This talk will focus on the application of synchrotron techniques to measure the electronic structure and the nano- and meso-scale geometric structure of materials of interest to the nuclear community. The methods that have been used to handle radioactive materials safely at synchrotron radiation facilities will also be discussed.

NUCL 32

Models for large scale nuclear collective motion --Fission and superheavy element synthesis

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As experimentalists, we make tests of pre- and post-dictions to establish the validity of models of large-scale nuclear collective motion and the uncertainties in these models. Our studies of fission focus on the total kinetic energy (TKE) release and its variance for the fast neutron induced fission of ^{232}Th, ^{233,235}U and ^{239}Pu. The TKE release shows a modest decrease with increasing neutron energy but the instrument-corrected variances are constant. The TKE can be correlated with the Brosa modes (increasing symmetric fission) but the variances are puzzling. ^{232}Th(n,f) appears to behave differently than the other systems.
In attempting to clarify models of SHE synthesis, we have tested and extended models of multi-nucleon transfer reactions to make n-rich heavy nuclei. There is good agreement between measurements of near or below target yields with the shell-sensitive models of Zagrebaev and Greiner (for ^{136}Xe + ^{208}Pb) and an underestimate of the yields of trans-target nuclei. The fission corrected GRAZING model is only useful for predicting the yields of small (few nucleon) transfer reactions.
In our experiments on the factors influencing SHE synthesis, we have experimentally characterized the trends in P_{CN} and the importance of Kramers corrections to fission-neutron competition in hot fusion reactions.

NUCL 33

PHITS Monte Carlo simulations for ^{225}Ac production with 78-192 MeV protons incident on ^{232}Th targets compared with experimental effective cross sections

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High energy proton spallation reactions on natural thorium metal targets have been utilized to produce multi mCi quantities of ^{225}Ac. Theoretical cross sections for Ac and Th isotopes as well as for a select number of the fission products produced in these reactions were generated by the Monte Carlo radiation transport code PHITS to

simulate the experimental data obtained from sixteen irradiations of Th metal targets with 25-210 μA proton beams ranging in energies from 78 to 192 MeV. Irradiations were conducted at Brookhaven National Laboratory (BNL) and Los Alamos National Laboratory (LANL), while target dissolution and processing was carried out at Oak Ridge National Laboratory (ORNL). At ORNL, a series of ion exchange columns was employed to isolate Ac from dissolved Th, Pa, Ra, and numerous fission products. PHITS simulated cross sections for the production of ^{225}Ac range from 7.8 to 28.2 mb in the incident proton energy range of 78 to 192 MeV. The experimental cumulative cross sections for ^{225}Ac are less than the simulated values by approximately a factor of two and vary from 3.6 to 16.7 mb over the same energy range. Based on these data, production of curie quantities of ^{225}Ac is possible by irradiating ~80 grams of ^{232}Th target (5.0 g cm^{-2}) for 10 days at either BNL or LANL proton irradiation facilities.

NUCL 34

Random probability analysis of recent ^{48}Ca + ^{251}Cf experiments

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The extent of the region of enhanced stability near Z=114 and N=184 is not completely known. To attempt to produce the heaviest isotopes of element 118, new experiments were performed using ^{48}Ca projectiles and a ^{251}Cf (mixed isotope) target at the Dubna Gas Filled Recoil Separator (DGFRS) located in the Flerov Laboratory of Nuclear Reactions in Dubna. Progress on the production of ^{294}118 and heavier isotopes of element 118, cross-section measurements, and nuclear decay properties will be discussed. The main discussion of this talk will focus on the analysis of the probability that observed decay chains are due to random events occurring in the detectors or electronics rather than correlated decay chains, using the LLNL-developed method of Monte Carlo Random Probability analysis. This probability will be discussed for recent ^{48}Ca + ^{239,240}Pu experiments in addition to the element 118 experiment and will be compared with other techniques for estimating such probabilities in super heavy element production reactions in which few decay chains are observed.

NUCL 35

IsoChain: A user-friendly, two-group nuclear transmutation and decay code

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Nuclear transmutation calculations are fundamentally important in many fields, such as the production of radionuclides. Analytical solutions for the differential equations governing nuclide transmutation and decay become unwieldy as the number of nuclides in a problem increases. Sophisticated codes, such as ORIGEN-S, that can perform such analyses have been developed, but they can require a substantial amount of time for the user to become proficient and/or set up even a simple problem. To provide a more user-friendly application, a FORTRAN code called LAURA was developed, and later it was rewritten in Java. The Java version of LAURA is called IsoChain, and the Java language was selected for a number of reasons including good numerical capabilities as Java implements 64-bit floating point numbers independent of platform. Thus, IsoChain will run without recompiling, on Linux, Apple OS X, and MS Windows. Java has a mature and extensive library for implementing graphical user interfaces and is a modern object-oriented language that assists and enforces good programming practices. A default library is provided, incorporating decay parameters and infinitely dilute cross neutron sections for many nuclides. For a specific problem, user can create libraries by modifying cross section data, half-lives, adding nuclides not included in the default library, or can create totally new libraries containing for example 14 MeV cross sections for calculations involving fusion neutrons. The user interface, for setting up calculations and adding to or modifying library data, is through a chart of the nuclides created by IsoChain. A full demonstration of IsoChain will be presented and the program will be available from RSICC at rsicc.ornl.gov.

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NUCL 36

Radiation transport modeling to support nuclear forensics measurements

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Nuclear forensics measurements have traditionally been made using some form of mass spectrometry on a chemically separated liquid sample. While mass spectrometry does provide accurate results, performing radiation detection measurements can provide additional useful data. Effective incorporation of these measurement techniques to characterize alpha particle, beta particle, and gamma-ray emissions requires simulation of these processes and subsequent radiation transport through a system using Monte Carlo modeling methods. Models such as these are intended to aid in the design process of a new instrument to perform radiological characterization of samples separated by gas chromatography for nuclear forensics.

NUCL 37

Comparison of experimental and computation thermodynamic parameters in lanthanide materials

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In the event of a nuclear detonation, the need for rapid analysis capabilities will be paramount. In response to this need, a number of groups have begun to develop gas phase separation capabilities in an effort to bypass the current liquid separations. To develop methods for gas phase separations, it is required that the thermodynamic values for entropy and enthalpy are well known such that retention times for the species of interest can be predicted. The described project highlights a two-fold approach where the values for entropy and enthalpy of adsorption/desorption can be indirectly determined using thermogravimetric analysis. The second thrust utilizes current computational techniques which provide structural and thermochemical descriptions whereby the values for entropy and enthalpy of adsorption can be estimated without experimental measurements. This work represents an important merger between the computational f-element efforts and applied gas phase separations. This work will highlight how current computational techniques and other theoretical efforts contribute to better understanding of experimental parameters, which will serve to improve the response time in the unlikely event of a nuclear detonation.

NUCL 38

Award Address (Glenn T. Seaborg Award for Nuclear Chemistry sponsored by the ACS Division of Nuclear Chemistry and Technology). 60 years in radiochemistry: Major highlights

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Over the course of sixty years in radiochemistry, I have been involved in many different aspects of the subject. Most notable are four different programs which have had a far-reaching influence on nuclear and radiochemistry applications. The four programs are: the first analysis of the lunar surface, new extraction chromatographic resins for transuranic nuclides (TRU) and strontium analysis, coupled columns, and a new ^{99}Mo/^{99m}Tc separation chemistry. In each case, the four programs involved a rather simple radiochemical separation, but ultimately had far-reaching consequences.

NUCL 39

Use of low pressure chromatography with an automated generator system for generating radioisotopes for nuclear medicine

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Presentation will discuss use of various resins available in conjunction with an automated low pressure chromatographic system to generate daughter radioisotopes from their parent. Various resins available from Eichrom Technologies will be discussed and how those resins can be deployed on an automated separation system. Such a system, known as RadioGenix, developed by NorthStar Medical Technologies, LLC will be discussed. The value of these separations and the automated generator system in nuclear medicine applications will be highlighted.

NUCL 40

20+ Years with Phil Horwitz: a lot of work and a lot of fun

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The author shares with Phil Horwitz ~100 publications in international journals, books and conference proceedings plus 12 patents, the result of over 20 years scientific association (and friendship).
He will present highlights of the work performed in close association with Phil (from CMPO solvent extraction chemistry to liquid membranes, new extraction chromatographic and ion exchange materials, bifunctional organophosphorus extractants), together with memories and anecdotes highlighting Phil's eccentricity and unique personality.

NUCL 41

From surveyor alpha source to Eichrom: Phil Horwitz's contributions to f-element separations

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During more than fifty years of active engagement in f-element chemistry and separation science, Phil Horwitz has had an enormous influence on both the practical applications and fundamental science of lanthanide and actinide separations. His introduction to f-element solution chemistry came at the University of Illinois in the laboratory of lanthanide chemistry pioneer Therald Moeller. After a brief stint at Dow Chemical, Phil joined the exciting and energetic world of actinide separation science in

the Chemistry Division at Argonne National Lab, working alongside organophosphorus extractant (most notably HDEHP) developer Don Peppard. As the separations group leader Phil led the development of the TRUEX process (based on CMPO extractants), Thermally Unstable Complexants (TUCS, decomposable diphosphonate chelating agents), Diphonix resin (immobilized diphosphonate complexants in a resin phase), and the CSEX and SREX (crown ether based extractant systems) processes, among many other innovations in separation science, mainly motivated by developing large scale applications. His research activities represent a focused combination of sound fundamental chemistry and application development. Ultimately, his interest returned to extraction chromatographic materials, which actually began with the preparation of a ^{242}Cm ionization source for NASA's lunar Surveyor mission. This shift led to the creation of Eichrom Industries, where Phil has continued to innovate for nearly two decades. Of course, Phil does not work 24 hours a day, 7 days a week; in his spare time he has developed a strict exercise and diet regimen, has rid his neighborhood of four legged "intruders" (with several interesting tales to tell as a result), has formalized some "Commandments of Solvent Extraction", and has relieved the tension of the workaday world by being a semi-dedicated fan of the Chicago Cubs (though how that fandom relives tension is a mystery to this Chicago White Sox fan). In this presentation selected highlights of Phil's many contributions to actinide and lanthanide separation science and technology will be discussed.

NUCL 42

From radiochemistry to ionic liquids and beyond: Lessons from Phil on separations and life

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This talk explores how I learned radiochemistry while on sabbatical in the Group of Phil Horwitz at Argonne National Laboratory and how this propelled our work into the field of ionic liquids. From our initial focus on technetium separations using aqueous biphasic systems (ABS) and Aqueous Biphasic Extraction Chromatography (ABEC) through our entry into the field of ionic liquids (ILs), radiochemistry has allowed us to rapidly and efficiently characterize multiple systems and provide key chemical insight to guide our work. However, my lessons went beyond radiochemistry and into 'Phil's Rules of Separations,' 'marketing wins over superior technology,' and other key insights crossing the boundaries of fundamental research and practical application. This presentation will provide a personal journey of my intersection with Phil's World and how it affected my research trajectory.

NUCL 43

Search for Ac-225

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Actinium-225 and its daughter Bi-213 have tremendous potential as nuclides for therapeutic nuclear medicine applications. However, the development of treatments using these nuclides is hampered by the limited supply of Ac-225 and its parent Th-229. Th-229 and Ac-225 are primarily legacies of U-233 produced in the United States Thermal Breeder Reactor Program. While existing U-233 stocks represent a potentially very significant quantity of Th-229 and Ac-225, access to most of the fissile U-233 material has been restricted or outright denied. The authors will present a history of their contributions in support of the identification and utilization of potential sources of Th-229/Ac-225, from discontinued programs to isolate Th-229 from U-233 stocks and Ac-225 from metric tonnes of aged Th-232/U-233/Th-229 LWBR Fuel to on-going programs to produce Ac-225 from high energy proton spallation of Th-232.

NUCL 44

Spectral adjustment techniques for fast neutron energy distribution

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The characterization of the energy distribution of a neutron fluence is difficult in experiments with constrained geometry or DC neutron signal where techniques such as time of flight cannot be used to resolve the distribution. The measurement of neutron fluences in reactors, which often present similar challenges, has been accomplished using radioactivation foils as an indirect probe. Spectral adjustment codes use statistical methods to adjust apriori predictions of the fluence, such as MCNP, using quantified radioactive residuals produced in these foils. We have applied a modification of this established neutron fluence characterization technique to experimentally characterize the neutron fluence in the critical assemblies at the National Criticality Experiments Research Center (NCERC) and the spallation neutron flux at the Isotope Production Facility (IPF) at Los Alamos National Laboratory (LANL). Results of the adjustment procedure and future diections for the work will be presented.

NUCL 45

Full-core simulations of the MURR core during steady state operations to accurately predict irradiation parameters for isotope production

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As the demand for neutron-based medical isotope production increases, it is important to be able to accurately model the production under varying irradiation conditions.

Assessment of the irradiation parameters necessary for viable production of many medical radioisotopes can be very challenging. To address these challenges, high-fidelity full-core models to optimize the irradiation parameters for a set of isotopes produced in the University of Missouri Research Reactor's (MURR) central flux-trap and reflector have been developed. The set of isotopes includes Mo-99, I-131, Lu-177, Ir-192, and Sm-153. The simulations consist of a networking suite of codes and databases including MCNP, ORIGEN, MONTEBURNS, an in-house developed critical rod-height search routine, and fuel megawatt-day, control-rod and beryllium reflector burn-up selection databases, respectively, to accurately model target irradiations during routine full-power operation for a given core configuration. The uncertainties between the model predictions and the measured activities for these isotopes are found to be well within 5%.

NUCL 46

Role of simulation in the design and commissioning of FIONA: a new mass analyzer for superheavy elements

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Over the last decade, six new superheavy elements (Z = 112 - 118) and over fifty new transactinide isotopes ($Z \geq 104$) have been synthesized in compound nuclear fusion reactions using ^{48}Ca on actinide targets. These transactinides are short-lived, with their resulting decay chains ending in spontaneous fission before reaching a known mass region. At the Lawrence Berkeley National Laboratory, we use the 88"-cyclotron to produce heavy ion beams and the Berkeley Gas-Filled Separator (BGS) to synthesize and separate the resulting SHE from transfer reactions products and unreacted beam. Unfortunately, the BGS's high beam suppression comes at the cost of mass resolution and detection is limited by high background due to its close proximity to the target and beamstop. Ongoing upgrades to the BGS, including a beam thermalization scheme, will allow us to couple a dedicated vacuum mass analyzer to the BGS. Known as FIONA (Fast Identification Of Nuclide *A*), the analyzer is a novel mass separator based on an unbalanced Wien velocity filter. It has been designed for 100% transmission with an expected mass resolution of 2000 $A/\Delta A$. In addition to knowing the mass of a single SHE ion, these upgrades greatly increase sensitivity by moving detection to a lower background area, helping our ongoing investigations of the nuclear structure and decay properties of SHE. I present the role of ion optic simulations, specifically using SIMION, in the design and commissioning the FIONA test setup and the future directions of the project.

NUCL 47

Modeling microchannel plate detectors for improved performance

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Microchannel plate (MCP) detectors are extremely useful detectors of electrons, ions, and photons due to their high gain and nanosecond time response. Implementation of a resistive anode, helical delay line anode, cross-strip anode, or more recently induced signal plane has made MCP detectors position sensitive. A position sensitive MCP can also be coupled with a photocathode to provide a compact, position sensitive MCP photomultiplier (MCP-PMT). Both MCPs and MCP-PMTs can be used in the wide variety of applications from imaging of radioactive beams to neutron radiography. In all these applications, in addition to its fast time response, the position resolution of the detector is of critical importance. Position resolution not only impacts the ability to resolve features in imaging an object but it also limits the ability to distinguish two spatially separated particles, simultaneously incident on the detector. Using simulations the various factors that influence the position resolution attainable with MCP detectors will be explored. The intrinsic position resolution obtained for a single incident electron in laboratory measurements will be compared with the simulation results. In some applications, in addition to the intrinsic resolution the transport of the electron from a secondary emission foil to the front surface of the MCP limits the measured position resolution. We will explore with simulation the position resolution associated with different detector configurations and compare the simulation results with laboratory measurements.

NUCL 48

Challenges in chemical separation of ^{225}Ac produced via proton irradiation of ^{232}Th target

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Both ^{225}Ac, as an in vivo ^{225}Ac/^{213}Bi generator, and ^{213}Bi have been used successfully in targeted alpha therapy (TAT) preclinical and clinical research. This project describes an initiative to enhance production of ^{225}Ac to meet the growing demand by investigating the use of high energy proton spallation reactions on natural thorium metal targets. Simultaneous production of rather large quantities of fission products in the target is the main complexity associated with the direct production of ^{225}Ac via proton spallation of the ^{232}Th target. To this end, we have developed a chemical procedure composed of classical ion exchange and extraction chromatography to separate microgram amounts

of actinium from ~13 g of thorium target and fission products. We have tested Eichrom TEVA, LN, and BDGA resins for separation of ^{225}Ac from ^{140}La and other lanthanides. Among the fission products, ^{140}La with a half-life of 41 h is the main concern because its chemistry resembles that of Ac with a similar ionic radius (coordination number = 6) and a 3^+ ionization charge. While TEVA did not provide any separation, LN resin provided some non-optimal separation, and good separation was obtained in BDGA.

NUCL 49

Investigations using LN, LN2, and LN3 resins for separation of actinium and lanthanum

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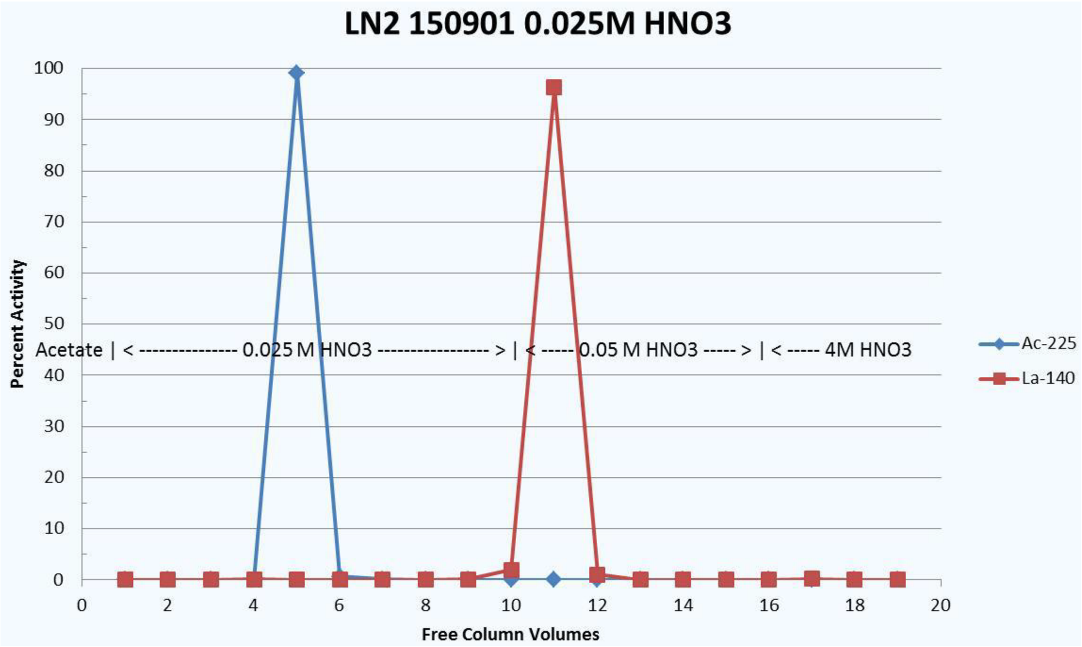
The separation of elements with similar chemical properties often presents purification challenges, especially when one seeks the level of purity required for medical applications. One such situation involves the separation of lanthanum from actinium. These two elements exhibit very similar chemistry, such as ionic radius (6 coordination) and ionization charge (3^+), making separation difficult. An evaluation of the performance of a series of extraction chromatographic resins, LN, LN2, and LN3 (all available through Eichrom Inc.) was conducted for the separation of carrier-free ^{140}La from ^{225}Ac. LN resin is based on the ligand bis-di-ethyl-hexyl phosphoric acid (HDEHP), LN2 is based on phosphonic acid, and LN3 is based on phosphinic acid. While LN and LN3 resins gave varying degrees of separation, the number of column volumes between the eluted elements was not adequate to ensure complete separation. LN2 did provide better separation with the use of low acid concentration for elution (Fig. 1). Elution profiles will be presented.

Fig. 1: Actinium/lanthanum separation on an LN2 column. Loading in sodium acetate/acetic acid buffer and washing with 0.025 *M* HNO_3.



NUCL 50

Extraction chromatography aids medical isotope production

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In conventional ion-exchange chromatography separation is achieved based on the charge of the ionic species. It is a technique of the first choice for the purification of medical isotopes. However, it often lacks selectivity and therefore requires substantial number of theoretical plates, longer columns, and slow flow rates to achieve desired purification levels. In production of short lived isotopes the time necessary for post irradiation target processing is critical to minimize losses of the isotope to the radioactive decay. Hence, it is highly desirable to develop fast and efficient separation scheme without compromising chemical yield and radionuclidic purity of the isotope of interest. While in some cases solvent extraction can complement conventional chromatography this approach is complicated by potential contamination of the final product with organic solvents.

Extraction chromatography combines the power of solvent extraction with convenience and elegance of conventional ion-exchange methods. Owing to complexing origin of its selectivity, extraction chromatography is often the only choice for the separation strategy. Purification of medical isotopes produced in the Brookhaven Linac Isotope Producer (a proton accelerator operated in part by Medical Isotope Research and Production group (MIRP) at Brookhaven National Laboratory) entails separation from both the target material and the variety of co-produced radionuclides. Over the years extraction chromatography has been used at MIRP to facilitate separations in a number of production and analytical processes such as ^{86}Y from Sr, lanthanides, ^{83}Rb from ^{82}Sr. The talk will be focused on details and challenges of these separations.

NUCL 51

Control of iron in hydrometallurgical solutions using ion exchange resins

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Iron is often present as a contaminant in the hydrometallurgical recovery of base metals such as copper, zinc, nickel and cobalt. Iron is often controlled by precipitation or by electrolyte replacement. For example, in the copper solvent extraction process, copper is selectively transferred from a leach solution to an electrowinning solution. Iron is co-extracted to a minor extent in the copper system and may be transferred to the electrowinning solution. Iron may also be transferred by entrainment of aqueous solution in the loaded organic. The normal strategy in the copper industry is to dump contaminated electrowinning solution and replace with fresh acid and water. This limits the buildup of iron in the electrowinning solution and maintains a high overall current efficiency. This strategy is effective but in some cases very undesirable. A number of ion exchange processes have been developed for loading iron (as Fe(III)) from the contaminated electrowinning solution. This allows for an alternate purification strategy. The stripping of Fe(III) from the ion exhange resin (eg. Diphonix or Sulphonated Monophosphonic Acid resins) can be accomplished by reductive stripping of the Fe(III) using either a copper-catalyzed sulphur dioxide or a cuprous sulphate elution system. The technical development and commercial application of ion exchange for iron control will be reviewed with suggestions for future development.

NUCL 52

Diphonix: From Dallas to today

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The idea of Diphonix, a new ion-exchange resin, began as a gleam in the mind of Phil Horwitz arising from the work he and his Argonne group had done on thermally unstable complexants, a series of water-soluble methanediphosphonic acids. The question then became whether the critical diphosphonate ligand can be immobilized starting with a TUCS compound and in April 1989, at the ACS meeting in Dallas, he raised the issue with the present author. The initial reaction was that the vinylidene analogue would be too sterically hindered to allow polymerization but, as is often true in chemistry, an experiment is worth a thousand theories so we agreed to try. Working first with a highlly capable graduate student (now professor) Darrell Crick and later with a superb post-doctoral associate (now Dean of Faculty) Andrzej Trochimczuk, the monomer was coaxed into a polymer, it was made bifunctional, and Diphonix was born. In 1994, it received a R&D-100 award as one of the "100 most technologically significant new products." This is its story - from Dallas to today.

NUCL 53

Capture and release chemistry: Harvesting beryllium-7 from Brookhaven LINAC isotope producer’s 320 gallons of cooling water

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The ability to capture metals and/or radionuclides from large amounts of water is important for isotope production at BNL and FRIB, radioisotope waste treatment and environmental cleanup of metals. We developed a solid support based approach that allows multiple metal capturing groups to be used simultaneously to capture radionuclides and/or metals. In this application we synthesized and evaluated solid supports with the following metal capturing groups: sulfonic acid, iminodiacetate, pyridine amine, pyridine amine acid, or quaternary amine. The ability of the solid supports to capture metals from the Brookhaven LINAC Isotope Producer’s 320 gallons of cooling water was evaluated. The sulfonic acid solid support was found to be superior in the retention of Be-7, and one solid support (1.7x0.6 cm) retained 2 mCi of Be-7. The uptake of Be-7 over time was found to be linear in the first 24 hours with an equation of Y=4.11X (R^2=0.998), and the uptake of Be-7 was nearly identical at 24 and 168 hours. To harvest Be-7 from the BLIP water 38 solid supports were used to capture 65 mCi in 24 hours. The Be-7 was released from the solid supports in HCl, and an AG1 column was used for the final purification.

NUCL 54

Overview of solvent extraction technologies for recycle of used nuclear fuel and treatment of radioactive wastes

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Solvent extraction technology has been utilized to recycle uranium and plutonium from used nuclear fuel for nearly 70 years. The well known PUREX (Plutonium Uranium Reduction Extraction) process, or variations of the process, have been operated at commercial scale in several countries around the world. Over the past three decades, a number of new solvent extraction processes have been developed and in many cases, demonstrated for the separation of uranium, transuranic elements, trivalent actinides, and fission products. An overview of a number of these processes, demonstrating the significant influence of Dr. Phil Horwitz on this field will be given.

NUCL 55

Evolution from TRUEX to ALSEP

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This paper will describe the evolution of transuranic (TRU) separations in the United States from the TRUEX process to the ALSEP concept. The Transuranic Extraction (TRUEX) process was developed by Phil Horwitz and co-workers to separate the TRU elements from radioactive wastes. An early targeted application of TRUEX was pretreating radioactive waste stored in underground tanks at the Hanford Site in Washington state. These wastes consist mostly of non-radioactive components. The TRUEX process was investigated to concentrate the most hazardous radioactive components, primarily plutonium and americium, into a small mass for immobilization in borosilicate glass. In parallel, researchers in Europe pursued the Diamide Extraction (DIAMEX) process for separating TRU elements from commercial nuclear waste. Researchers at PNNL also investigated amide extractants in the late 1990s, leading to the development of a bicyclic diamide ligand with very high affinity for trivalent f-block ions. During the first decade of this century, work regarding the TRUEX process shifted focus to application in advanced closed fuel cycle options, and several successful tests of the process were conducted. However, TRUEX was one step in a multi-step process to remove the minor actinides americium and curium from commercial fuel. Subsequent steps were needed, particularly the Trivalent Actinide-Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Complexes (TALSPEAK) process. This spawned efforts to simplify the separations scheme by combining the functions of the TRUEX and TALSPEAK processes into a single process step. The first attempt was to simply combine the extractant used in the TRUEX process [octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide, or CMPO] with that used in TALSPEAK [di-(2-ethylhexyl)phosphoric acid, or HDEHP]. This met with limited success primarily because of strong interactions between CMPO and HDEHP. The system was improved by replacing HDEHP with the corresponding 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]). The interaction between CMPO and HEH[EHP] was less than that for HDEHP, but this interaction was still significant. It was discovered that the interaction between diglycolomide (DGA) type extractants and the acidic organophosphorus extractants is very weak. Replacement of CMPO with a DGA extractant has now led to a viable hybrid extraction system, referred to as the Actinide-Lanthanide Separation (ALSEP) concept.

NUCL 56

Developing the caustic-side solvent extraction process for cesium removal from legacy tank waste

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Developing a fully functional and robust solvent extraction process for industrial use requires a combination of scientific and technological advances. Identifying a selective extractant is just the start of research to develop a practical solvent and solvent cycle

that can put the extractant molecules to work. This presentation provides an overview of the chemistry of the Caustic-Side Solvent Extraction (CSSX) process and key steps in its development for cesium removal from legacy Cold War nuclear waste stored in underground tanks at the Savannah River Site (SRS) and Hanford Site. The CSSX process and its much more efficient Next-Generation descendent, NG-CSSX, employ calixarene-crown ethers for strong and selective cesium binding. To exploit the strong binding for strong extraction, a modifier is required, which evolved over the course of several years of development to an optimized fluorinated alcohol known as Cs-7SB. Stripping is accomplished with vitrification-friendly boric acid, which becomes almost quantitative when a strong organic base is employed to scavenge extractable anionic impurities. The SRS Modular CSSX Unit (MCU) has been running the CSSX and NG-CSSX chemistry since 2008 to treat over 5.6 million gallons of salt feed solutions. Since converting to NG-CSSX, the MCU has achieved decontamination factors exceeding 50,000, allowing it to treat higher ^{137}Cs activity and thereby effectively extend the operational lifetime of MCU until the full-scale Salt Waste Processing Facility (SWPF) comes on line starting in 2018. A benefit of the increased extraction power of NG-CSSX is the potential to increase throughput, which can potentially allow SWPF to accelerate its schedule and save billions of dollars. In addition, good performance has been obtained for Hanford type salt wastes, including the most challenging high-potassium compositions, and a flowsheet with a modular footprint is now feasible.

NUCL 57

Sixth period with Philip: Insights into the coordination chemistry of three metals with three extractants

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For many of the 32 elements with principal quantum number six—from the first stable, naturally-occurring monotope (Cs-133) and anthropogenic radiocesium-137 to the last, stable and heaviest naturally-occurring monotope (Bi-209) in the periodic table—a number of practical extraction processes are in routine use for chemical separations. In these, the basic concepts underlying the solvent extraction of the *s*-, *p*-, *d*-, and *f*-block elements in the sixth period can be understood at the most fundamental level in terms of metal-ligand interactions, namely coordination chemistry. The aim of this talk is to highlight the interactions of three cations—Cs^+ ($[Xe]6s^0$), Eu^{3+} ($[Xe]4f^6 6s^0$), Bi^{3+} ($[Xe]4f^{14}5d^{10}6s^2 6p^0$)—in complexes and solvates with dibenzo-crown ethers, tri-*n*-butylphosphate, and diglycolamide extractants. In the context of their extraction and recovery from nuclear wastes, the exceptionally innovative science of E. Philip Horwitz—the 2016 Glenn T. Seaborg Award Winner—is recognized as a renaissance in chemical separations. This presentation will review a tiny slice of his genius as it concerns the coordination chemistry of three period-six elements with three extractants in organic solutions and solid salts.

NUCL 58

Heavy actinide chemistry with Phil Horwitz

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While my interactions in graduate school with Phil focused on improvements to the Trivalent Actinide Lanthanide Separations using Phosphorus Extractants and Aqueous Komplexants (TALSPEAK) process, it is more recently that I have gained a deeper appreciation for Phil's work with the heaviest (*trans*-americium) elements. This presentation will consider Phil's efforts in heavy element chemistry and separations that are instrumental to current research efforts. Observations from current efforts in this area will be highlighted in the context of the previous work completed by our ACS National Awardee, Dr. E. Phil Horwitz.

NUCL 59

Separations, actinide coordination chemistry, and the butterfly effect: The inspiration and influence of Phil Horwitz

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In this talk, I will present a brief history of my work with Phil Horwitz, which includes actinide separations research at Eichrom Technologies and f-element coordination chemistry (lanthanides, Ac, Th, and U) at the University of Illinois Urbana-Champaign. I will then discuss how this early work in separations and coordination chemistry has evolved into my current research at the interface of these two fields. Recent results on the synthesis, f-element coordination chemistry, and bonding properties of amino bis(phenolate) ligands with pendant heaver ethers (S, Se, and Te) will be described, along with their relevance for lanthanide/minor actinide separations.

NUCL 60

Rapid methods for actinides and Sr-89/90 in environmental samples

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The need for rapid analyses in the event of a Radiological Dispersive Device (RDD), Improvised Nuclear Device (IND) or nuclear accident is well-known. The Savannah River Environmental Laboratory has published over 35 scientific papers on rapid radiochemical methods in the last 10 to 12 years to ensure laboratory readiness for emergency response samples and to improve efficiencies and reduce costs for routine sample laboratory operations. Rapid methods developed at the Savannah River Environmental Laboratory for the determination of actinides and Sr-89,90 for a range of environmental samples, as well as bioassay samples will be presented. Following rapid pre-concentration steps, actinides and Sr-89/90 are separated using extraction chromatographic resins to collect and purify the radionuclides for assay. Challenges associated with difficult sample matrices such soil and seawater samples will be discussed. The rapid analysis of solid building materials, such concrete or brick which may contain refractory particles following a radiological event, will also be addressed.

NUCL 61

Rapid separation of strontium from raw urine using a tandem of regenerated Eichrom columns

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In the event of a large scale exposure of radioactive materials, triage centers will be overwhelmed with the need to screen potential exposure victims. The conventional method of testing urine for radioactive strontium-90 intake requires lengthy solution preparation steps totaling more than 12 hours. To avoid this, we have devised a process based on extraction chromatography that quickly conditions the raw urine to facilitate the removal of quenching and fouling agents and permits the reuse of resin for ^{90}Sr separations. We described a flowsheet using Diphonix resin column in tandem with the Sr Resin column. Aqueous methane sulfonic acid (MSA) solutions were chosen as the carrier phase for the Diphonix resin, since nitric acid tends to nitrate aromatic constituents in urine resulting in strong coloration, and the presence of MSA has no effect on ^{90}Sr uptake by Sr Resin. Our approach uses the Diphonix resin to remove K^+ and Na^+ interferences to below 10 mM. With the alkali metals removed, competitive loading of the Sr Resin is avoided and its use to separate ^{90}Sr from ^{90}Y is possible. Using a combination of standard urine and surrogates we completed 20 consecutive cycles of the flowsheet. We prepared the Diphonix column by loading a slurry of the resin into a graduated polypropylene tube to a bed volume of 2 mL and bed height of 3.5 cm. The Sr Resin was prepared in a smaller graduated polypropylene tube to a bed volume of 0.2 mL and bed height equal to 0.6 cm. Inert frit or glass wool sealed the ends. The solutions were passed through the Diphonix column by gravity and pumped through the Sr Resin columns using a peristaltic pump. We developed the elution curve using ^{85}Sr tracer and frequent sampling of the eluate (514 keV photon). We saw no reduction in the performance of the Diphonix or Sr Resin as measured by the recovery of ^{85}Sr. ^{85}Sr recovery was consistently >95% in the Diphonix resin strip solution and

>95% after stripping the Sr Resin. The durability of the resin columns against this flow sheet suggests that it is possible to implement this in a semi-autonomous system. A scaled semi-autonomous system would allow the technique to be implemented in the triage setting to more quickly screen patients.

NUCL 62

Improved chemical separations: applications in oceanography

***Bill Burnett**, wburnett@fsu.edu.* Earth, Ocean and Atmospheric Science, Florida State University, Tallahassee, Florida, United States

Modern extraction chromatographic and other types of resins have made chemical separations of complex materials like seawater and sediments much easier. Resins developed by Phil Horwitz (Fig. 1) and commercialized by Eichrom Technologies have substantially advanced the analysis of these materials. Two examples will illustrate some of the benefits: (1) analysis of radium in seawater and groundwater; and (2) U/Th separations for geochronology.

MnO_2 Resin is prepared by a reductive precipitation of MnO_2 onto a macroporous resin substrate. In the pH range from 4-8, the resin surface has a net negative change and highly favors the adsorption of Ra^{2+} from natural waters to the exclusion of more common divalent cations such as Ca, Mg, etc. The resin can be used in either a batch or column mode and can be traced using ^{133}Ba. After preconcentration onto the resin, ^{226}Ra and ^{228}Ra may be determined directly via gamma spectrometry. Coupling a cartridge loaded with MnO_2 Resin to an automatic radon/thoron analyzer can be used for assay of ^{224}Ra (via ^{220}Rn) and ^{226}Ra (via ^{222}Rn).

U/Th separation for disequilibrium dating used to involve multiple ion-exchange and liquid-liquid extraction steps. Once the purified solutions were obtained, electrodeposition onto stainless steel planchets added several more hours to the sample preparation time. Now we can use a simple combination of the resins TEVA-UTEVA and Resolve filters to considerably shorten the process. Not only does this shorten the analysis time but also has improved the success rate.

Fig. 1. Phil says: "Bill, you should try our resins and make your life easier...", but Phil is thinking something different...

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Sequential separation of group II elements including Ra by reverse phase chromatography employing cation exchange resin in citrate media

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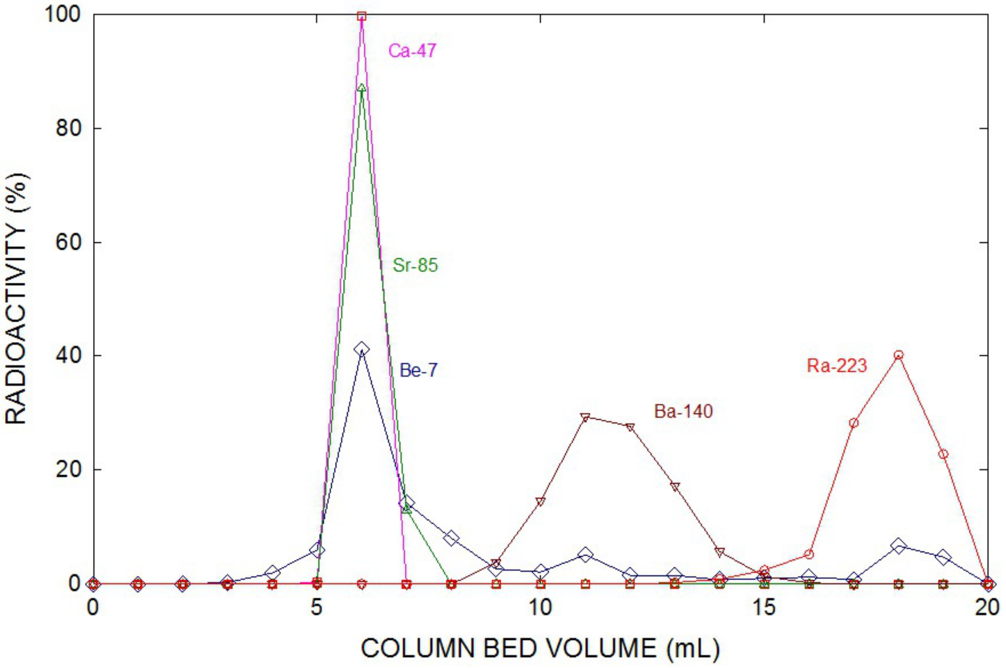
As a part of a general program to prepare highly pure samples of Ra-226, we have evaluated the application of reverse phase ion chromatography for sequential separation of Ra from other members of group II elements using cation exchange resin (BioRad AG50) in citrate media. Parameters studied have included the concentration of citrate ion, pH of the solution, and resin mesh size and cross-linking. Radioactive tracers of Be-7, Ca-46, Sr-85, Ba-140, and Ra-223 were used to determine separation performance and to develop the procedure. The most effective separation of Ra from Ba and other Group II metal ion was achieved using AG50x8, 200-400 mesh, resin in 0.32 M NH_4Cit at pH 5. Under the above experimental conditions the lighter member of group II ions forming stronger citrate complexes elute before Ba and Ra. Be-7 does not show a discernable pattern. Using a 1 mL resin bed volume (BV), it was possible to quantitatively separate 100 µg of Ra-226 from 10 mg of Ba by washing the column with 15 BV of 0.32 M NH_4Cit at pH 5, and then eluting purified Ra with 3 BV of 8 M HNO_3 .



Elution Profile of Group II Metal Ions from AG50x8 in 0.32 M NH4Cit at pH 5

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Solid-supported ionic liquids for metal ion separation and preconcentration: Where do we stand?

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Metal ion separations constitute an important part of numerous industrial processes and an essential first step in many chemical analyses. Over the last two decades, extraction chromatography (EXC), a form of liquid chromatography employing as the stationary phase any of a variety of extractants in an appropriate organic solvent sorbed on a solid support, has emerged as a powerful tool for such trace metal ion separations. Recent studies in which ionic liquids (ILs) have been evaluated either as extractants or as replacements for the molecular solvents normally utilized in liquid-liquid extraction suggest that a further improvement in the performance of EXC materials might be effected by the use of an IL as the basis for the stationary phase. In this presentation, approaches to the immobilization of ILs in/on a solid support, both alone and in combination with an extractant, are detailed, and the application of the resultant materials in various metal ion separations is described.

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Novel separation systems and the commandments of solvent extraction

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Phil Horwtiz, this year's Seaborg Award recipient, codified years of separation wisdom in his Commandments of Solvent Extraction. These four rules, extract the minor from the major, what goes up must come down, when all else fails change the diluent, and there is no substitute for luck, summarize key aspects of separation systems that are often overlooked when developing new materials and reagents for separations. Interestingly, biological systems often follow these same commandments when transporting, manipulating, and sequestering metal ions in living organisms. Using examples from actinide-binding proteins and peptides to illustrate Horwitz's Commandments and other separation concepts he advanced, the possible roles of biomolecules in sensing, binding and separating actinide elements in biological and technological systems will be considered.