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Novel mesoporous materials for actinide and lanthanide sequestration and separation

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We are designing, synthesizing, and testing reusable mesoporous materials for actinide and lanthanide sequestration, separation, and sensing. Our experimental-computational collaboration studies three types of materials with a high binding capacity for selected actinides and lanthanides: functionalized mesoporous silica, mesoporous carbon, and ferrihydrite. The affinity for target actinides of several ligands grafted to mesoporous silica, as well as their binding geometry, has been predicted by *ab initio* relativistic density functional theory (DFT) geometry optimization calculations, and compared to experimental batch sorption and X-ray absorption spectroscopy (XAS) measurements. Additionally, these batch studies have established the ability to reuse the materials as high-capacity sorbents. Ordered mesoporous carbon (OMC) has proven far superior to activated carbon in terms of Pu(VI) capacity and sorption kinetics. Batch and XAS studies of mesoporous and nanoparticulate ferrihydrite interactions with Pu(VI) have revealed interesting light-induced redox chemistry at the iron-oxide surface that may yield separation capabilities. We are also studying the effects of the presence of competing ions, as well as systematic ligand variation. We are exploring OMC-based electrodes offer a promising route for electrochemical separation and sensing of actinides and lanthanides.

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Radionuclide analysis based on lab-on-chip liquid-liquid extraction

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The analysis of radionuclides present in high and medium activity wastes is carried out according to operating protocols including the sequence of many steps of separation/purification. In order to improve these protocols, the microfluidic tools have their place. In particular the liquid-liquid extraction in microsystem shows various interests: very few solvent is consumed, the process can be automated and parallelized and the extraction and the stripping can be coupled on a single chip. Liquid-liquid extraction with continuous flow in microsystems has not been tackled until recently since only few chemical systems have been studied, in particular in the nuclear field. Thanks to the characteristics linked to the miniaturization (large specific area, short diffusion length, low reagents volumes), our objective is to control the fluid hydrodynamics for optimizing the contributions of diffusion and convection to the mass

transfer in solutions. An exhaustive bibliographical review about the liquid-liquid extraction of metal species on lab-on-chips and preliminary experimental results will be presented and discussed.

NUCL 3

Particle size limits, chemistry, and activities for Fukushima aerosols collected in Japan

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Aerosols collected 40 km from the Dai-ichi Nuclear Power Plant, Fukushima Prefecture, Japan were previously analyzed to determine their particle-by-particle activity distribution [Zeissler et al., 2012]. The current study builds on this earlier work by using various microanalytical methods to measure the chemistry and size of the collected particles. The chemical composition and particle size data are particularly relevant for understanding the transport and fate of the particles in the environment. Light and scanning electron microscopy with energy-dispersive x-ray spectrometry, elemental mapping by micro X-ray fluorescence (μ -XRF), autoradiography and nuclear counting methods were applied. Preliminary results indicate the collected particles are not associated with the larger chlorine, iron and calcium aerosols collected at the same time, and sizes for some Cs-bearing particles are at least 0.4 micrometers in diameter.

References

1. CJ Zeissler, LPG Forsley, RM Lindstrom, et al., 2012, J. Radioan. Nucl. Chem, doi:10.1007/s10967-012-2135-x.

NUCL 4

Using X-ray absorption fine structure spectroscopy to investigate the behavior of problematic radionuclides in nuclear waste

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X-ray absorption fine structure (XAFS) spectroscopy combines good signal to noise, elemental specificity, and sensitivity to changes in bonding. In addition, the energies of the characteristic X-ray lines for actinides and second-row transition metals are relatively high (>15 keV), which allows X-rays to penetrate the containment needed for radioactive samples. For these reasons, XAFS can be a very useful tool for investigating the chemistry of problematic radionuclides in nuclear waste. In this talk, the basics of XAFS will be explained, including the two main spectroscopic techniques: X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine

structure spectroscopy (EXAFS). While XANES and EXAFS are similar experimentally, the two techniques are useful for answering different questions about the chemical behavior of specific elements. These techniques will be used to investigate the behavior of technetium in the high level nuclear waste tanks at the Hanford Site, and to understand the behavior of technetium in a grout waste form.

NUCL 5

Challenges to performing quantitative non-destructive gamma-ray spectrometry analysis on non-traditional geometries for nuclear forensics

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This presentation will go through some of the challenges to performing quantitative non-destructive gamma-ray spectrometry analysis for nuclear forensics as well as our attempts to overcome these challenges. Some of these challenges include unusual matrices and geometries of the samples and the lack of standards available. A brief comparison of several different approaches to determining quantitative results for gamma spectrometry will be discussed; particularly, the traditional relative method and computational methods that have been developed, such as the FRAM and SNAP codes. Lastly, examples of how these different approaches are being utilized in the Actinide Analytical Chemistry group at Los Alamos National Laboratory will be demonstrated, along with a comparison of the results and uncertainties for those analyses. LA-UR-12-26010

NUCL 6

Characterization of γ -irradiated alkali uranyl peroxide nanoclusters

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Since the report of the first uranyl peroxide nanocluster compound in 2005, the class of polynuclear compounds has grown considerably and includes other coordinating ligands and in few cases neptunium. For example, clusters containing 24, 28, 32, 36, 40, 44, 50 and 60 $[\text{UO}_2(\text{O}_2)_3]$ units have crystallized as alkali metal salts. The formation of uranyl nanoclusters may offer a unique pathway to separate uranium from other chemical components of used nuclear fuels. For this pathway to be feasible, the uranyl nanoclusters must exhibit chemical and radiation stability. This paper reports results from initial studies characterizing uranyl nanoclusters by infrared and Raman spectroscopy and powder X-ray diffraction after varying doses of γ -irradiation from a ⁶⁰Co source.

This work is supported as part of the Materials Science of Actinides, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001089.

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WITHDRAWN

NUCL 8

Nanophase extractors for selective fission product sequestration

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Separation, sequestration and storage of the long-lived anionic fission products ^{99}Tc and ^{129}I are problematic due to their environmental mobility (i.e., anionic species) and redox sensitive speciation (e.g., Tc(IV)O_2 insoluble versus Tc(VII)O_4^- aqueous). Consequently, the separation and sequestration of these two fission products tend to drive waste processing and waste disposal design. One potential risk mitigation strategy for these fission products is to minimize their release by using sequestration agents. In this work we explored the use of a nanoscale “test-tube and cap” sorbent-based system for the separation and sequestration of anionic fission products in process and environmental waste streams (i.e., nanophase extractors). The nano test-tubes were fabricated using a well-developed silica nano-templating method along with silver solid solution and redox chemistries. Experimentally, the interior of the Si-nanotubes were functionalized with silver (Ag) moieties that are known to be selective for I^- and TCO_4^- removal. Batch sorption studies were then conducted to characterize the sorption behavior of a non-radioactive I^- isotope within the functionalized nanotubes. We have also shown that after I^- sorption the nanotubes can be capped with latex particles. These capped structures could potentially serve as stable waste forms for the long lived anionic fission products. Preliminary evaluation data will be presented on the separation, sequestration (i.e., secondary waste leaching) and storage behavior of these structures.

NUCL 9

Production and applications of very high specific activity Sn-117m

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Sn-117m is a 14 day half-life gamma (159 keV) and conversion electron (130 keV) isotope that has historically been produced in reactors at low (up to 20 Ci/g) specific

activities and used for bone pain palliation studies. Recently, this isotope has also found application in investigative efforts to image and treat vulnerable plaque. However, this application requires high (carrier-free) specific activity Sn-117m that can only be produced with accelerators. A new production method has, therefore, been developed that uses the Cd-116($\alpha,3n$) reaction with a 47 MeV alpha beam striking an electroplated Cd-116 target. Resulting yields were confirmed to be high (~0.15 mCi/ μ Ah) with minimal undesirable by-products. An ion exchange column method was used to isolate the Sn-117m resulting in a very pure high specific activity (~20,000 Ci/g) product. This isotope has subsequently been attached to biological targeting molecules and used in pre-clinical and clinical studies to treat vulnerable plaque.

NUCL 10

Sn-117m labeled annexin for vulnerable plaque

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Vulnerable plaque is responsible for over 60% of heart related deaths. Unlike normal plaque, it cannot be diagnosed by any technique including measuring the thickness of blood vessels. In this paper we report the synthesis and evaluation of high specific activity [Sn-117m]-DOTA-Annexin for the detection and potential treatment of vulnerable plaque. High specific activity Sn-117m was chelated to a bifunctional chelating agent and then purified using HPLC. Attachment of the chelate to annexin was accomplished by preparing the isothiocyanate version of the chelate and then reacting it with lysine residues on the annexin. Several analytical methods (cell binding, electrophoresis, gel permeation chromatography) were used to show that high purity [Sn-117m]-DOTA-annexin was produced that gave positive results in animal models. Human clinical trials are underway. In addition this paper will describe related work in the initial synthesis and evaluation of high specific Sn-117m chelated to DTPA and to a monoclonal antibody.

NUCL 11

Production of high specific activity Fe-55 to study radioparagenesis

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When a crystalline material is made with radioactive isotopes, the structure of the material is likely to change when the radioisotope decays to another element having a different valence and ionic radius. To study this effect, termed "radioparagenesis" the isotopes used must be a significant portion of the starting element mass. One system chosen to observe this effect is the transition of Fe₂O₃, hematite, to Mn₂O₃ employing

^{55}Fe . Commercial sources of ^{55}Fe are very low in specific activity. To produce high specific activity ^{55}Fe a natural nickel target was irradiated with protons at the Los Alamos Isotope Production Facility at the Los Alamos Neutron Science Center (LANSCE). The target was chemically processed to recover the iron isotopes which were subsequently oxidized to hematite for the experiment to observe the radioparagenesis effect.

NUCL 12

Production of thorium-229 with low energy protons

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The alpha emitters ^{225}Ac and ^{213}Bi are of great interest for α -radioimmunotherapy. Both radioisotopes are daughters of 7880-y ^{229}Th , currently obtained via decay of ^{233}U . Alternatively, ^{229}Th can be produced from ^{226}Ra in a nuclear reactor, or by proton irradiation of $^{230,232}\text{Th}$ either directly or through production of isobars that decay into ^{229}Th . To obtain the excitation functions for the relevant nuclear reactions, stacked foils of ^{232}Th were irradiated with 40 MeV protons from the ORNL 25 MV tandem electrostatic accelerator. The excitation functions of $^{232}\text{Th}[p,xn]^{(233-x)}\text{Pa}$ ($x=1-5$) reactions were determined by γ -ray spectroscopy, in some cases after chemical separation of the Pa fractions. The experimental threshold for the $^{232}\text{Th}[p,4n]^{229}\text{Pa}$ reaction is ~ 22 MeV, and the excitation function peaks at 162.5 mb. Results from benchmark tests conducted with Cu and Ni foils and differential cross-sections for the production of ^{229}Pa and other Pa isotopes from $^{230,232}\text{Th}$ will be presented.

NUCL 13

Theoretical approach to the production of ^{44}Ti ($T_{1/2}=59.1$ years) using high energy protons: Expanding ^{44}Sc availability

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While the direct production of the positron emitter ^{44}Sc ($T_{1/2}=3.97$ h) using $^{44}\text{Ca}(p,n)^{44}\text{Sc}$ has been accomplished the short half-life limits the radionuclide's widespread availability. The radioisotope ^{44}Ti ($T_{1/2}=59.1$ y) decays to ^{44}Sc and therefore can serve as parent nuclide in the $^{44}\text{Ti}/^{44}\text{Sc}$ generator. The $^{44}\text{Ti}/^{44}\text{Sc}$ generators have been produced in Europe using the $^{45}\text{Sc}(p,2n)^{44}\text{Ti}$ reaction. The feasibility of producing ^{44}Ti

with high energy protons using alternative nuclear reactions at BLIP (BNL) and IPF (LANL) is now under investigation.

In this work TALYS, ALICE2011 and Empire-III nuclear reaction codes have been used to calculate proton induced reaction cross sections on ^{nat}Cr and ^{51}V using proton energies up to 200 MeV. The development of a research $^{44}\text{Ti}/^{44}\text{Sc}$ generator would provide an opportunity to make ^{44}Sc more readily available for use in PET imaging. The research into radiolabeling chemistry of other Sc isotopes suitable for theranostic imaging and radiotherapy will benefit as well.

NUCL 14

Radiochemistry of yttrium-86 (^{86}Y) produced at the Brookhaven Linac Isotope Producer (BLIP)

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Yttrium-86 produced at BLIP by $^{86}\text{Sr}(p,n)$ reaction was evaluated for radiolabeling with a series of ligands; (*N*-[(*R*)-2-Amino-3-(*p*-isothiocyanato-phenyl) propyl]-*trans*-(*S,S*)-cyclohexane-1,2-diamine-*N,N,N',N'',N''*-pentaacetic acid (SCN-CHX-A"-DTPA), 2-(4-isothiocyanatobenzyl)-1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (SCN-DOTA), *S*-2-(4-isothiocyanatobenzyl)-1,4,7-triazacyclononane-1,4,7-triacetic acid (SCN-NOTA), diethylenetriaminepentaacetic acid (DTPA), 1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA) and 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetra(methylene phosphonic acid) (DOTP). The metal complexation behavior of DOTA, DTPA and DOTP was compared at various pH and concentration at 23°C and 80°C using molar ratio of metal to ligand of 1:1. SCN-NOTA, SCN-DOTA, SCN-DTPA, SCN-CHX-DTPA were conjugated to protein (P – i.e. bovine serum albumin and human immunoglobulin) at L:P molar ratio of 10:1 in pH 9 buffer. The purified conjugates were radiolabeled with ^{86}Y at pH 5 to 7 and their stability evaluated at 23°C and 4 °C. Optimum labeling of protein conjugates was observed at pH 5. Radiolabeling with three production batches of ^{86}Y were evaluated up to 4 days post EOB and the data used to set expiry dates for ^{86}Y .

NUCL 15

Thick target yield of Th-229 via low energy proton bombardment of Th-232

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Owing to its desirable properties, ²²⁵Ac is one of the more effective radioisotopes used in alpha radioimmunotherapy. Due to its 10-d half-life, it is more efficient to create its precursor, 7880-y ²²⁹Th. In this work, ²²⁹Th was produced via 40 MeV proton bombardment of a thick ²³²Th target at the ORNL 25 MV tandem electrostatic accelerator. Target, consisting of 23 foils (137 mg/cm²), was irradiated with 50 nA of protons for 90 hours. After 215 days, allowing for the decay of short-lived Ac and Pa isotopes and fission products, the target was chemically purified by a series of ion chromatography techniques. Th-229 was measured by γ-ray spectroscopy immediately after separation of the thorium fraction from the ²²⁸Th decay daughters and long lived fission products. The effective thick target cross section of ²²⁹Th is 122 mb at E_p=31 MeV. The effective cross-section as a function of proton energy will be presented.

NUCL 16

Production and separation of ⁶⁷Cu at Argonne National Laboratory

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The medical isotope ⁶⁷Cu holds great promise for the diagnosis and treatment of several types of cancer, most notably types of Non-Hodgkin Lymphoma. However, a regular, economical supply of this isotope is not currently available despite a noted demand for the isotope from medical researchers. To fill this gap, the research team at Argonne has focused on using electron linac produced bremsstrahlung radiation to drive the ⁶⁸Zn(γ,p)⁶⁷Cu reaction in a large metallic zinc target. This reaction has been evaluated and optimized at the bench scale. This has allowed for up to 2 mCi of ⁶⁷Cu to be distributed within 48 hours of irradiation. A solvent-free primary separation has been combined with anion exchange chromatography to minimize the contamination of the product with non-radioactive metals. Initial results to date and future plans will be presented.

NUCL 17

Design of an aqueous target isotope harvesting apparatus

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The Facility for Rare Isotope Beams (FRIB) will be a new national user facility that generates a host of isotopes that could be “harvested” for off-line use, without affecting the primary users of the facility. The underlying idea is that routine production of the secondary radioactive beams at FRIB will produce an abundance of other useful isotopes in the primary production target, thus it should be possible to radiochemically harvest significant quantities of these useful radioisotopes from the water cooling lines in the primary target area. The feasibility of harvesting useful long-lived radioisotopes from FRIB will be tested under similar conditions available now at the National Superconducting Cyclotron Laboratory (NSCL). The production and extraction yields of several important radioisotopes (⁶⁷Cu, ⁴⁸V, ⁸⁵Kr) that can be produced at the NSCL facility will be measured. The design and construction and first tests of an aqueous beam stop will be presented.

NUCL 18

First observation of gamma rays from the Th-229 nuclear isomer

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Th-229 is the daughter of U-233 by alpha decay. Approximately 2 percent of the alpha decays of U-233 populate the first excited state of Th-229. The energy of this level was previously determined, indirectly, by measuring the transitions feeding the excited state and ground state using micro-calorimetry. The energy of the Th-229 isomer was determined to be 7.8 ± 0.5 eV. This makes Th-229m the lowest energy nuclear state known with the corresponding photon in the vacuum ultraviolet. We have for the first time observed photons from the decay of the Th-229 isomer with a wavelength of about 173 nm (7.2 eV). The half-life was measured to be 6 hours, which is in good agreement with a theoretical estimate (5 hours) based on the transition between the same Nilsson orbitals in the Pa-233 decay scheme. We will describe the apparatus and measurements necessary to accomplish this first direct observation of the Th-229m gamma ray.

NUCL 19

Nuclear chemistry and the blue loop within massive stars

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We analyze the relation between nuclear chemistry in the core of stars of about 10 times the mass of our sun and the physical cooling mechanisms. In particular, we analyze an evolutionary stage of these stars, called the blue loop, during which a star shrinks and then expands again. We show that this stage is extremely sensitive to the rate at which carbon and oxygen are created in the core from helium reactions. In fact, novel cooling mechanisms can be efficiently constrained by the analysis of the blue loop.

NUCL 20

Level lifetimes in ^{94}Zr : From anomaly to resolution

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Measurements of ^{94}Zr with the $(n,n'\gamma)$ reaction revealed anomalous behavior unobserved in other nuclei. The $B(E2)$ value for the transition from the second 2^+ state at 1671 keV to the ground state was found to be larger than that from the first 2^+ state to the ground state. This nucleus thus became the only example where such an inversion of the $B(E2)$ strength occurs. Recently, we have carried out $(n,n'\gamma)$ measurements using metallic Zr, ZrO_2 , and $\text{Zr}(\text{OH})_4$ samples of natural isotopic composition. The lifetime of the second 2^+ state was determined by the Doppler-shift attenuation method and the $B(E2; 2_2^+ \rightarrow 0_1^+)$ was obtained; the results differ significantly from those published. A re-analysis of the original γ -ray data failed to reveal the source of this discrepancy; however, powder x-ray diffraction and scanning electron microscopy performed on each sample material, including that used previously, provide clues to the solution.

NUCL 21

Hydroxyl radical kinetics for metal-DTPA complexes: Size and metal charge dependence

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In order to establish a closed nuclear fuel cycle the separation of minor actinides (Am, Cm) from the lanthanides is essential. One proposed strategy is to use solvent extraction processes for this separation. The goal of this study was to determine the radiolytic stability of the TALSPEAK extraction ligand DTPA (diethylenetriaminepentaacetic acid) through its reaction kinetics with the hydroxyl

radical under acidic pH conditions. Rate constants were determined over a range of pH conditions using thiocyanate competition kinetics. Based on literature pK_a values and rate constant measurements at multiple pH's, rate constants for the partially protonated species DTPA- H_5 , DTPA- H_4^- and DTPA- H_3^{2-} of 2.69×10^9 , 3.40×10^9 and 3.26×10^9 $M^{-1} s^{-1}$, respectively, have been determined. Analogous kinetic parameters were also elucidated for Eu^{3+} , Lu^{3+} , Gd^{3+} , Er^{3+} lanthanide metal-DTPA complexes, as well as for metal complexes with different charges such as Ba^{2+} , and Hf^{4+} .

NUCL 22

Speciation behavior of americium higher oxidation states using XAFS and single crystal XRD analysis

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Fundamental understanding of key actinides chemistry such as americium (Am) is at the forefront of separations research. Characterization of higher oxidation states of Am has been performed using spectroscopy methods which have recently shown promise for determining Am speciation in these states. Am(V) and Am(VI) have been prepared by oxidation of Am(III) in acidic solution and determined by X-ray absorption fine structure spectroscopy. Initial experiments were performed using sodium bismuthate as the oxidizing agent and the oxidized Am species, as well as stereochemical arrangements of atoms in close proximity to Am, were evaluated using XAFS. Bismuth, Bi(V), has been synthesized with manganese, Mn(IV), in a crystal complex that showed oxidation of Mn(IV) to Mn(VII) as a precursor for the synthesis of oxidized Am(V) and Am(VI) crystals. Large single crystals of $NaBa_3BiO_6 \cdot M$, where $M = Mn(VII), Am(V,VI)$, were grown by precipitation from molten mixtures of alkali and alkaline earth metal hydroxides at $550^\circ C$ and analyzed by single crystal X-ray diffraction (XRD).

NUCL 23

Thermal stability study of the NG-CSSX solvent containing a new guanidine suppressor

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The Caustic Side Solvent Extraction (CSSX) process used at the Savannah River Site for the selective cesium removal from high-level salt waste has been markedly improved leading to the Next Generation CSSX (NG-CSSX) process. The NG-CSSX solvent involves the new and more soluble mono-crown calixarene extractant, MaxCalix.

The purpose of this study was to determine the effects of thermal degradation over time on NG-CSSX process. The NG-CSSX solvent prepared with N,N',N''-tris(3,7-dimethyloctyl)guanidine (TiDG) was left in contact with simulant waste over a period of four months at above-normal operating temperatures (35-37°C). The performance of the solvent was tested initially and then every 30 days after. Tests were carried out under standard operating conditions at 25°C with SRS-15 simulant waste, 25mM NaOH scrub solution, and 10mM H₃BO₃ strip solution.

This research was sponsored by the Office of Technology Innovation and Development, the Office of Environmental Management, and the U.S. Department of Energy

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Determination of stability constants for the complexation of lanthanides and actinides by amino acids

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The TALSPEAK process continues to be an important solvent extraction system for separating trivalent lanthanides from the minor actinides (Am³⁺ and Cm³⁺). The complexity of the chemical interactions that govern this separation system (both aqueous and organic) have motivated numerous fundamental studies aimed at furthering the understanding of the separation. Recent work has demonstrated the successful Ln³⁺/Am³⁺ separation using amino acid buffers (e.g., L-alanine, L-arginine, L-histidine, and L-methionine) at pH 2. We have successfully modeled the aqueous-modified TALSPEAK system (pH 1.6~3.2) when L-alanine was used as the aqueous phase buffer. Attempts to model the other amino acid-buffered TALSPEAK systems illustrated the need for additional thermodynamic data (e.g., stability constants) for the Ln³⁺/An³⁺/amino acid complexes. In this study, multiple analytical techniques have been used to determine the stability constants for Ln³⁺/An³⁺ complexes with L-alanine, L-arginine, L-histidine, and L-methionine and used to model the appropriate amino acid-buffered TALSPEAK systems.

NUCL 25

Radiochemistry at the Colorado School of Mines: Preliminary results

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In August of 2012, a radiochemistry research program was initiated at the Colorado School of Mines (MINES) that serves both the Department of Chemistry & Geochemistry and the Nuclear Engineering Program. Current infrastructure at MINES includes dedicated radiotracer wet lab facilities on campus and capabilities for higher

level work in Building 15 at the Denver Federal Center (DFC, 15 minutes from MINES campus). Building 15 houses a low-enriched uranium-fueled 1 MW TRIGA reactor operated by the US Geological Survey. A Memorandum of Understanding (MOU) exists between the USGS and the Colorado School of Mines, and the collaborative research benefits both organizations in academic and basic research efforts. This presentation will focus on the trajectory and current research capabilities of the radiochemistry program. Preliminary results from research activities within the research group will also be presented. Research is supported by the NRC Faculty Development Grant.

NUCL 26

Teasing out the details of TALSPEAK separations using multiple modes of analysis

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The TALSPEAK process for lanthanide/actinide separations was developed at ORNL in the 1960s and this and related separations methods have seen significant process development research during the intervening years. Recent work in this lab has focused on improving understanding of the fundamental chemistry that underpins this process. To address several interesting anomalies that are known to plague TALSPEAK and TALSPEAK-like separations, we have applied a variety of analytical methods to the characterization of solvent-solute and solvent-solvent interactions in conventional TALSPEAK separations systems. The objective is to gain fresh insights into the chemical processes that drive (and limit the application of) this moderately versatile process. In this presentation, the coordination of observations from NMR, ESI-MS, neutron scattering, radioanalytical chemistry and optical spectroscopic studies are combined with new thermodynamic data to provide fresh insights into lanthanide-actinide separations systems based on aqueous complexing agents. Work supported by the U.S. Department of Energy, Office of Nuclear Energy, NEUP and Sigma Team for Minor Actinide Separations programs.

NUCL 27

Effects of fuel components on Am, Cm, and Pu sorption on DGA resin

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In a reprocessing facility, it is important to obtaining material balance and accountancy in all feed, process and waste streams in as near real time as possible. Current techniques for analyzing samples are time and labor intensive and often not well suited for situations in which a rapid sample analysis is required and/or a large number of

samples needed to be analyzed. To address this issue the usefulness of DGA extraction chromatography resin is being investigated due to its high affinity towards trivalent actinides. Even though it is known that Am, Cm, and Pu are retained on DGA resin to a high degree, the dissolved fuel and raffinate will have a much more complex compositions than previously studied samples. Their behavior might therefore potentially deviate from normal sorption characteristics. For this reason, the interference and synergistic effects of fuel constituents on Am, Cm, and Pu sorption is being investigated to elucidate the characteristics of DGA resin. The effects of Zirconium, Cesium, Strontium, and Neodymium in nitric and hydrochloric matrixes will be discussed.

NUCL 28

Study of the interaction between Cyanex-923 and Cyanex-272, HEH[EHP], and HDEHP

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To reduce the cost and complexity of separations for closed nuclear fuel cycles, solvent extraction processes based on combined extractants are being considered. Unfortunately, strong interactions between the extractants have introduced complications in process development. In this work, ^{31}P NMR and FTIR have been used to characterize new combinations of extractants that might be suitable for use for trivalent actinide/lanthanide separations. Adducts between Cyanex-923 and HEH[EHP] or Cyanex-272 ($\log K_{\text{HEH[EHP]}} = 2.21$, $\log K_{\text{Cyanex-272}} = 1.44$) were found to be weaker than adducts of HDEHP with either Cyanex-923 or CMPO ($\log K_{\text{C-923}} = 2.79$, $\log K_{\text{CMPO}} = 3.07$). Most importantly, the strength of the interaction correlates with the acidity of the cation exchanging extractant. The weak interactions between Cyanex-923 and HEH[EHP] (and Cyanex-272) suggest that this combination could offer fresh options for combined extractant systems. Work supported by the USDOE FCR&RD program, Sigma Team for Minor Actinide Separations program.

NUCL 29

Characterization of americium(III) and lanthanide(III) complexes in mixed solvent extraction systems containing a malonamide and a dialkylphosphoric acid

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In order to further reduce toxicity of nuclear waste, the French *Commissariat à l'énergie atomique et aux énergies alternatives* (CEA) is developing processes that allow separation of minor actinides from fission products. The DIAMEX (Diamide extraction) -

SANEX (Selective actinide extraction) process is based on a mixture of two organic extractants: a malonamide, the N,N'-dimethyl-N,N'-dioctylhexylethoxymalonamide (DMDOHEMA) and a dialkylphosphoric acid, the di(2-ethylhexyl)phosphoric acid (HDEHP), dissolved in an alkane. The mechanisms of its extraction process are still not completely understood. Various complementary analytical techniques were used to identify and characterize americium(III) and lanthanide(III) metallic complexes formed in the organic phase after solvent extraction (UV-Visible, Infrared, NMR and Time-Resolved Laser-Induced Fluorescence spectroscopy, as well as Electrospray Ionization Mass Spectrometry). These speciation studies were performed under a variety of experimental conditions (influence of the extractants concentration, acidity of the aqueous phase...) and mixed species including the two extractants were observed.

NUCL 30

Recent advances in radioanalytical chemistry for actinide analysis

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This presentation will discuss some of the recent advances in analytical radiochemistry for actinide materials that have been accomplished by the Actinide Analytical Chemistry Group (C-AAC) and their collaborators at Los Alamos National Laboratory. The analytes/radionuclides requested and sample matrices present significant challenges. The supported programs range from nonproliferation, to nuclear forensics to heat source development. Some of the projects that will be described include neutron spectrometry, new methods developed for the analysis of ²³⁸Pu and ²³⁷Np, separation science, non-traditional gamma spectrometry methods, including the development of a two-dimensional gamma mapping system and the analysis of low-level actinides in complex matrices. Advances and applications of FRAM and SNAP codes for gamma spectrometry will also be discussed. Many of these advances have helped expand the analytical capabilities of C-AAC or have modernized older traditional methods while maintaining the quality of results necessary for good analytical chemistry laboratory. LA-UR-12-26030

NUCL 31

Analytical applications of radiochemical extractants for cesium isotopes

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Tank closure at the Savannah River Site has created an ongoing need to characterize inventories of waste tank heels. Cs-137 is one of the most predominant beta-emitting isotopes in SRS radioactive waste inventories. The high abundance of this isotope in waste streams can be problematic when quantifying other, significantly less abundant isotopes. The dose associated with Cs-137 is also problematic when large volumes of the matrix are required in order to meet sensitivity requirements. Cesium removal protocols are often required for radiochemical separation methodologies conducted on SRS high activity waste matrices in order to reduce dose to laboratory personnel, reduce analytical interferences, and improve sensitivity.

Properties and applications of several specialized Cs-extractants utilized for numerous radiochemical separation protocols on high activity residue will be reviewed.

NUCL 32

Metal-organic frameworks for strontium and actinide separations in high-level nuclear waste

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New materials have been prepared for the removal of strontium and actinides from high-level nuclear waste, with initial focus on waste stored at the Savannah River Site. Metal-organic frameworks (MOFs) and MOF templated materials containing metals such as Al, Fe, and Ti, have been synthesized and evaluated for strontium and actinide removal under highly alkaline conditions. The MOF serves as a precursor material, and decomposes upon exposure to the highly alkaline conditions of the waste forming a porous metal oxide or hydroxide which serves as the active material. In addition the MOFs have been used as templates to form core-shell mixed metal oxides, which have also shown promise for removal of strontium and actinides from high-level waste.

NUCL 33

Development of TIMS procedure for plutonium extracted by the H2DEH[MDP] and HDEHP polymer ligand film (PLF) system

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A Polymer Ligand Film (PLF) has been developed to be used for rapid extraction of plutonium. The thin film matrix was prepared by incorporating plutonium extraction ligands into a polymer support system. Previous studies by our research group have

demonstrated the effectiveness of H2DEH[MDP] and HDEHP ligands in the extraction of plutonium. After the plutonium was extracted by the PLF, it was directly counted on a solid state alpha detector without further chemical process. This new technique was mainly designed to be used as a screening method before running a more accurate analysis, such as TIMS. However, since the PLF method is a relatively new technique in plutonium extraction, prior to this there was no procedure that was established for the TIMS analysis. This paper will present a TIMS analysis procedure for the PLF samples. The most important component in the TIMS procedure is to first efficiently back-extract plutonium from the PLF. This was accomplished by using either isopropanol or nitric acid. Extracted plutonium was then processed and analyzed by TIMS for plutonium isotopic ratio measurement.

NUCL 34

Evaluation of the PuO₂ oxygen isotopic exchange mechanism using CeO₂ as a surrogate

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²³⁸PuO₂, the fuel used in Radioisotope Power Systems, undergoes a secondary (α,n) reaction with the naturally occurring ¹⁷O and ¹⁸O isotopes. Neutron radiation is a significant concern for worker dose rates and spacecraft components. Isotopic exchange with ¹⁶O is currently used to minimize the (α,n) reaction, but the mechanism and thermodynamics of this process are not well understood. Using a homebuilt vacuum chamber and atmospherically controlled reaction vessel, we have evaluated the oxygen exchange mechanism on CeO₂, a cold surrogate, and found that the rate of the reaction has a first order dependence on the specific surface area of the particles and on the fraction of the reaction remaining. Rate constants, activation energy, and mechanistic data will be discussed. A comparison of the exchange data and time to equilibrium with previous PuO₂ reports suggests that the mechanistic and thermodynamic data obtained here is a good approximation of PuO₂ behavior.

NUCL 35

Hot atom chemistry provided the foundation for understanding target chemistry and radiopharmaceuticals

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Hot atom chemistry is a topic that has faded from many radiochemistry textbooks, but it played a pivotal role in the development of radiopharmaceutical chemistry and provided the educational background for many of the pioneers in the field, including Professor Michael J. Welch. It provides some important lessons that are relevant to current

understanding of the chemistry that takes place in cyclotron targets and during the synthesis and decomposition of radioactive molecules. This presentation will review the essentials of hot atom chemistry applied to radiopharmaceuticals. Illustrations will be taken from the career of Professor Welch and several of his students.

NUCL 36

Development of a system to purify the long-lived positron emitter Zr-89 from irradiated yttrium target

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Better access to high-purity, long-lived Positron Emission Tomography radionuclides is needed for medical imaging. Zirconium-89 (⁸⁹Zr) is a positron-emitting radionuclide ($t_{1/2} = 78.4$ hr) that can be used to image multi-day physiologic processes. This radionuclide is produced from naturally monoisotopic yttrium-89 via a (p,n) reaction. PNNL has assembled a prototype automated fluidic system that uses a tandem column separation method to purify ⁸⁹Zr from the dissolved ⁸⁹Y target, using longer-lived ⁸⁸Zr and ⁸⁸Y radiotracers for method development. Our collaborators at the University of Washington are optimizing target design and cooling to maximize ⁸⁹Zr production using their 11 MeV and 50 MeV cyclotrons. They are minimizing the amount of ⁸⁹Y foil required for ⁸⁹Zr production, evaluating commercially available 99.9+% pure ⁸⁹Y ranging from 0.1 to 1 mm in thickness. Final testing will assure high labeling yield of the ⁸⁹Zr produced by this method via labeling of desferyl-derivatized proteins.

NUCL 37

Radioisotope production beamlines for SPECT and PET: Tens of meters to tens of centimeters

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SPECT radioisotope production beamlines have been utilized on H- commercial cyclotrons to transport extracted high current proton beams of kinetic energies in excess of 25 MeV a distance of ten meters or more to shielded target bunkers. This arrangement resulted in relatively low residual activity to the cyclotron and beamlines (a boon to maintenance personnel), and permitted steering, focusing and optimization of the beam spot on target. Commercial PET cyclotrons traditionally have not been provided with beamlines, however, the current trend is towards compact and even micro-beamlines that displace the high activity targets just far enough from the cyclotron to permit use of target shielding to limit dose exposure to cyclotron maintenance personnel while simultaneously facilitating beam steering and focusing to optimize

beam on target as proton currents have grown from 20 micro-amperes to 150 micro-amperes or more on target in the kinetic energy range 10-19 MeV. This paper describes best practices in SPECT and PET beamline design, and the evolution towards micro-beamlines for commercial PET radioisotope production.

NUCL 38

Cyclotron produced Tc-99m from Mo (II) compounds: A viable alternative to generator produced Tc-99m

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Tc-99m, the most widely used radionuclide in diagnostic nuclear medicine is available via decay of Mo-99 in a radioisotope generator. Most Mo-99 is produced from Highly Enriched Uranium (HEU). Recently, problems have arisen in the supply of Tc-99m which can be traced back to the ageing reactors used in the production of Mo-99. Additionally, recent legislation has been passed that will limit the export of HEU, further limiting the availability of Tc-99m. Several groups have investigated various target materials and the use of medical cyclotrons for the production of Tc-99m. Tc-94m has also previously been produced on medical cyclotrons using enriched Mo-94 as MoO₃ albeit only in small activities. The small activities produced are as a direct result of the low melting point and conductivity of the oxide target material which limits the beam current that can be used to irradiate the target. This essentially precludes the use of the oxide for any large activity production of Tc-99m. While Mo metal as a target material offers high conductivity and melting point, several challenges are presented in the preparation of molybdenum metal targets. Our group has investigated alternative Mo (II) compounds for ease of target preparation to facilitate large routine production of Tc-99m on a medical cyclotron. The use of these compounds also facilitates the facile separation of the radionuclide from the target material via a thermo-chromatographic technique, thus enhancing the recycling of the expensive Mo -100 target material.

NUCL 39

Production of ^{95m}Tc for the Compton camera imaging

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Technetium-99m is the most successful medical isotope, and many kind of labeled compounds were developed for various diagnosis use. Recent years, with the development of the Compton camera which can realize high position resolution, technetium isotopes emitting high energy gamma-rays are required. In this study, technetium-95m which emits some gamma rays around 800 keV was produced by the

$^{95}\text{Mo}(p,n)^{95m}\text{Tc}$ reaction. A 300-700 milligrams of $^{\text{nat}}\text{MoO}_3$ targets were irradiated with 15 MeV proton beam for 7 hours at the Tandem accelerator. Averaged beam currents were 1.2 mA. After a week cooling time, about 700-1000 kBq of ^{95m}Tc were extracted from the irradiated MoO_3 target after a chemical separation. 1) Using purified ^{95m}Tc , two kinds of labeled compounds, ^{95m}Tc -MDP (methylene diphosphate) and ^{95m}Tc -DTPA (diethylenetriamine pentacetic acid), were synthesized. In order to examine quality of the labeled compounds obtained in this study, thin-layer chromatography (TLC) method was carried out. A spot of solution of the labeled compound was placed at the edge of the TLC plate, and the plate stood up-right in a solvent. Two kind of solvents, Methyl ethyl ketone (MEK) and physiological saline were used. After about 10 min dipping time, TLC plates were dried and taken autoradiography images using imaging plates for 12 hours. Results of labeling experiments and imaging by the Compton camera will be discussed.

Reference

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NUCL 40

Cyclotron production of ^{89}Zr in a solution target

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Solution targets are interesting for cyclotron production of radiometals since they can be used with self-shielded cyclotrons and avoid complicated solid target processing steps. We developed a solution target method for production of ^{89}Zr by proton bombardment of aqueous solutions of yttrium salts. Initial results showed significant rates of evolution of H_2 and O_2 indicating radiolysis and/or electrolysis of water. In this study, we investigated the mechanism of gas evolution (GE). A niobium target containing yttrium solutions was irradiated for 5 min with protons (14 MeV, 25mA). GE was dramatically lower for a 1.7M $\text{Y}(\text{NO}_3)_3$ solution ($0.317 \pm 0.005 \text{L/h}$) compared to a 1.7M YCl_3 solution ($2.35 \pm 0.14 \text{L/h}$) ($p < 0.01$). Addition of 1N HNO_3 decreased GE by 37% and 53% in $\text{Y}(\text{NO}_3)_3$ and YCl_3 solutions, respectively, consistent with the effect of acid on radiolysis. However, addition of ethanol (50mM), a free radical scavenger, had little effect on GE from the $\text{Y}(\text{NO}_3)_3$ solution, contraindicating radiolysis. Interestingly, 1.7M NaNO_3 showed higher GE ($1.13 \pm 0.41 \text{L/h}$) relative to 1.7M $\text{Y}(\text{NO}_3)_3$, suggesting the cation also is important. These findings do not provide a conclusive explanation for the mechanism of GE, and further studies under conditions favoring or disfavoring radiolysis will be required to elucidate the mechanism.

NUCL 41

Production of copper-64: Life-cycle assessment

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The large scale production of ^{64}Cu via the nuclear reaction $^{64}\text{Ni}(p,n)^{64}\text{Cu}$ was first extensively studied by Welch *et al.* This work strongly influenced much of the research and design of current ^{64}Cu production processes implemented in cyclotron facilities around the world, including the Sir Charles Gairdner Hospital, in Perth Australia.

Our study investigates the efficiency of a novel radiochemical separation process for ^{64}Cu from enriched ^{64}Ni , using a single anion exchange column and low concentrations of hydrochloric acid (0.2 - 0.3M) in alcohol mixtures. The method is fast, using minimal reagents, and affords simultaneous cleaning of the ^{64}Ni for recycling and replating. The final products, ^{64}Ni and ^{64}Cu , isolated from a number of irradiation cycles, were analysed for metallic impurities by ICP-MS. Production yields for ^{64}Cu from recycled ^{64}Ni targets were assessed. The radiolabelling efficiency of the ^{64}Cu was also evaluated using the Cu(II) selective chelator, DiamSar.

NUCL 42

Solution target systems to produce radioisotopes at PET facilities

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Technetium-99m is the most widely used medical radionuclide, accounting for over 70% of nuclear medicine procedures (70,000 procedures daily in the US). Serious supply and proliferation issues associated with conventional "HEU fission Mo" generators are leading to intense research into alternative production methods. We have developed a technology for use on an accelerator employing the reaction $\text{Mo-100}(p,2n)\text{Tc-99m}$ with a target solution (molybdate) which has several advantages: Uses the same fluid targetry, cyclotron and infrastructure as presently used for PET isotope production; employs a newly developed automated chemistry unit designed to use a disposable kit to extract the Tc-99m; recycles the Mo-100 for repeated use and processing losses are

minimized. The Tc-99m is produced in high activity concentration and purity and had been used to label a sestamibi kit efficiently. This method is now being adapted to produce and purify other isotopes such as Cu-64, I-124, Re-186 and Ac-225.

NUCL 43

Production of Zn-63 via proton irradiation of Cu-63 nitrate solution

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Abnormalities of zinc homeostasis are indicated in a variety of human diseases. To provide a PET imaging agent for zinc, we investigated production of Zn-63 ($t_{1/2} = 38.5$ min) via the $^{63}\text{Cu}(p,n)^{63}\text{Zn}$ reaction. A solution target (Bruce Technologies) was used for rapid processing. Isotopically enriched Cu-63 (>99%, 0.5 g) was dissolved in conc. HNO_3 and diluted with water to a final volume of 3 mL. Irradiation for 10 min at 20 μA yielded 1.9 GBq of Zn-63 (decay-corrected to EOB). Zn-63 was purified by cation exchange chromatography (AG 50W-X8, H^+ form) using 0.05 N HCl-85% acetone as the eluent. The eluate was neutralized with NaHCO_3 , trapped on a Waters CM Sep-Pak, washed with water, and eluted with 1.5 mL 3.8% sodium citrate. The saturation yield was ~ 0.5 GBq/ μA after purification, with copper content < 1 $\mu\text{g/mL}$. Nonradioactive Zn levels were initially significant (> 5 $\mu\text{g/mL}$) due to Zn in the target material, but decreased as the target material was recycled.

NUCL 44

Cyclotron production of $^{99\text{m}}\text{Tc}$ in Canada

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A collaborative initiative, between Advanced Cyclotron Systems, University of Alberta and University of Sherbrooke has been established to evaluate the viability of commercial production of $^{99\text{m}}\text{Tc}$ via the $^{100}\text{Mo}(p,2n)^{99\text{m}}\text{Tc}$ reaction using high power, 24 MeV cyclotrons. Up to 2 TBq of $^{99\text{m}}\text{Tc}$ can be produced in two 6-hour bombardments with a 500 μA proton beam. This amount would produce up to 800 patient doses of $^{99\text{m}}\text{Tc}$ -radiopharmaceuticals, fulfilling the daily $^{99\text{m}}\text{Tc}$ requirements for a large metropolitan area. National Resources Canada contributed 18 million dollars to

establish two pilot cyclotron facilities, which will demonstrate the technological, regulatory and commercial foundation for high-yield, cyclotron-based ^{99m}Tc production. These facilities will become a viable alternative source of ^{99m}Tc between 2014 and 2016. Network researchers are currently focusing on developing high power cyclotron targetry and the separation technology as well as addressing regulatory requirements for Health Canada approval of cyclotron produced ^{99m}Tc for clinical use.

NUCL 45

Award Address (Glenn T. Seaborg Award for Nuclear Chemistry sponsored by ACS Division of Nuclear Chemistry and Technology). Exploring and understanding actinide science via systematic correlations and electronic configurations together with theoretical considerations

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Electronic configurations and the respective bonding of the actinide series are complicated and continue to be probed via new techniques and considerations. But scientific advances with these elements are also complicated by their radioactivity and scarcity, especially with the higher members. These elements are prime candidates for fundamental science, especially with regard to the changing role of their 5f electrons both in progressing across the series or when variable experimental conditions are involved. Important correlated properties include crystal structures, atomic volumes, their enthalpies of sublimation and solution, and the electronic and bonding changes forced by pressures and/or high temperatures. These changes should also be evaluated in conjunction with theoretical concepts. Such studies with actinides have provided unique insights into their electronic make up and bonding, but often new findings can suggest that additional concepts/conclusions must be considered. The presentation will provide an overview of the present status regarding these elements.

NUCL 46

Thermodynamic properties of the actinides beyond curium: A status report

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The status of our knowledge of the actinides beyond curium will be summarized and the most important contributions of Dick Haire in the field will be evoked. The author will also recollect his collaborations with Dick throughout the years.

NUCL 47

Recent thermochemical studies of fluorite-structured oxides containing, U, Th, Ce, Zr, and Hf

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Oxides based on the fluorite structure are important both in nuclear energy and as solid electrolytes, catalysts, and thermal barrier coatings. Experimental thermochemical data on the energetics of doping these oxides with trivalent rare earth elements are summarized. The data clearly show the competition among phase transitions, strain energy, and defect clustering in determining the thermodynamics of mixing and the extent of solid solution.

NUCL 48

Actinide science the Richard G. Haire way: Inspiring, innovative, energetic, and sleeves-up

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Soft x-ray synchrotron radiation (SR) methodologies are being developed at the Advanced Light Source (ALS) of LBNL to improve modern electronic structure theories for actinide elements and to aid in the design of special-purpose actinide materials and ligands. We have begun by measuring X-ray absorption spectra (XAS) with a scanning transmission x-ray microscope (STXM) for a seminal family of organometallic transition metal and actinide metallocene compounds. These efforts are complemented by theory and also by x-ray emission spectroscopy (XES) and resonant inelastic x-ray scattering (RIXS) measurements, which provides improved knowledge of *f*-orbital composition, oxidation state, and electronic structure. For example, Cm 5*d* RIXS spectra from curium oxide show 5*f*-5*f* intra-atomic transitions at energies 1-4 eV below excitation. Differences between RIXS features and calculated spectra yield evidence for Cm(III). The prospects for future studies of *f*-element materials in the soft x-ray region will be critically discussed.

NUCL 49

Evaluating orbital mixing in $\text{UO}_2\text{Cl}_4^{2-}$ vs. $\text{U}(\text{N}^t\text{Bu})_2\text{Cl}_4^{2-}$ using Cl K-edge XAS and TDDFT

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The linear actinyl ions, AnO_2^{2+} dominate the chemistry of light actinides in their hexavalent oxidation states, and have played a central role in discussions surrounding covalency between $An=O$ and $An-Cl$ bonds in the actinide series. With the discovery of the family of trans diimido $U(NR)_2^{2+}$ containing compounds where $R = Bu^t$, Ph, 2,6- $Pr^i_2C_6H_3$, 2,6- $(CF_3)_2C_6H_3$, we have the unique opportunity to assess the similarity in electronic structure between the isoelectronic AnO_2^{2+} and $An(NR)_2^{2+}$ units. All of these complexes contain short $U=N$ bonds in the range 1.85 – 1.88Å. Hybrid DFT electronic structure calculations indicate a formal U-N triple bond similar to that observed for UO_2^{2+} , with axial $U=O$ and $U=N$ bonds composed of $6d_\sigma$, $6d_\pi$, $5f_\sigma$, and $5f_\pi$ interactions. The comparative equatorial U-Cl bonding was explored through Cl K-edge XAS spectra of the $UO_2Cl_4^{2-}$ and $U(N^tBu)_2Cl_4^{2-}$ ions. Curve fits of the peaks reveal a very small % Cl $3p$ mixing whose interpretation will be discussed.

NUCL 50

Toward applications in an advanced nuclear energy system: Properties and behavior of nanoscale uranium-based cage clusters in aqueous solution

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As part of the Energy Frontier Research Center “Materials Science of Actinides”, more than 80 uranyl peroxide cage clusters have been synthesized in aqueous solution and crystallized for structure characterization. These clusters have diameters as large as 3 nm, and as many as 124 uranyl polyhedra. This presentation will focus on the Center's ongoing studies of the behavior of selected clusters in aqueous systems, as characterized by small-angle X-ray scattering (SAXS), dynamic light scattering (DLS), electrospray ionization mass spectrometry (ESI-MS), and nuclear magnetic resonance spectroscopy (NMR). Experimental evidence indicates that uranyl peroxide cage clusters can persist in solution for months as apparently stable entities, and they present complex aggregation behavior under changing solution conditions. Controlled deposition from solution can lead to nano-scale hybrid materials with well-defined structures.

NUCL 51

Plutonium and beyond: Understanding structure and bonding in transuranium borates

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The chemistry of actinide borates from thorium to californium has been developed over the past three years. In this talk the synthesis, structure, spectroscopy, and bonding in transuranium borates will be discussed with a focus on bonding differences that occur between neighboring trivalent actinides (e.g. Pu(III), Am(III), Cm(III), and Cf(III)). We will discuss how bonding changes can be exploited in separation technologies.

NUCL 52

Comparison of plutonium oxides from diverse process streams

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Production of plutonium oxide in support of mixed oxide (MOX) nuclear fuels remains a primary goal of the Advanced Recovery Integrated Extraction System (ARIES) at Los Alamos National Laboratory. An integral step in this process is the Direct Metal Oxidation (DMO) of plutonium primary “pits”. This certified production of plutonium oxide must meet DOE-STD-3013 requirements to ensure safe transport and long-term storage goals. Acceptable material is verified by the following physical and chemical measurements: thermogravimetric analysis (TGA), elemental analysis, specific surface area, particle size determinations, and bulk and tapped density. Plutonium oxide in various stages of the ARIES process, muffle furnace-oxide, and oxide produced under atmospheric conditions were analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) to confirm particle size, characterize fine-structure detail, and identify elemental constituents. Plutonium oxides derived from multiple process streams were compared utilizing these analytical techniques. Property-process relationships will be discussed.

NUCL 53

Development of chloride assay techniques for actinide processes

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Los Alamos National Laboratory safely and efficiently processes actinide materials to fulfill programmatic needs. Ion exchange effluents and precipitation filtrates are processed using a thermosiphon evaporator system for recovery and reuse of nitric acid as well as volume reduction of waste. Certain actinide residues have chloride content

that may be reduced by pretreatment prior to dissolution but even low concentrations of free chloride ions in the nitric acid process solutions can contribute to corrosion in the stainless steel evaporator, leading to premature equipment failure. For this reason, a plan to implement inline analysis for chloride within the plutonium processing facility at LANL was developed. Chloride assay techniques were compared on the basis of three considerations: (1) compatibility with current facility infrastructure, (2) reducing volume of waste generated, and (3) improved detection limits for chloride. Results and implementation of these techniques into the LANL processing facility will be discussed. LA-UR 12-26006

NUCL 54

Improving the PRESAGE polymer radiosensitivity for 3D characterizations

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RadBall® is a novel, passive, radiation detection device that provides 3D mapping of radiation from areas where measurements have not been previously possible due to lack of access or extremely high radiation doses. This kind of technology is beneficial when decommissioning and decontamination of nuclear facilities occur. The key components of the RadBall® technology include a tungsten outer shell that houses a radiosensitive PRESAGE® polymer. The 1.0-cm thick tungsten shell has a number of holes that allow photons to reach the polymer; thus, generating radiation tracks that are analyzed to characterize the radiation sources within the contaminated area being considered. Facilities being mapped frequently have to be shut down to minimize radiation exposures to its workers; therefore, reducing the mapping or characterization time is significant. The objective of this study was to reduce the RadBall® deployment time by increasing the radiosensitivity of the PRESAGE® formulation.

NUCL 55

Field alpha spectrometry tool (FaST) development using polymer ligand extractants (PLEs) for sample collection

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The Field Alpha Spectrometry Tool (FaST) is an instrument designed for rapid, field-based measuring of alpha-decaying species. The enabling technology for this instrumentation relies on polymer ligand extractants (PLEs). PLEs have been shown to selectively extract actinide analytes from solution onto a substrate material. The

substrate material can be directly measured with an alpha spectrometer with high resolution. The ability of PLEs to efficiently and selectively extracting certain actinides onto a substrate that facilitates measurement of high-quality spectroscopic data lends the technology as a first field-based alpha measurement tool. The primary objective of the FaST project is to integrate this unique capability into a field-deployable instrument. This will enable field-based alpha spectroscopy measurements. This paper will discuss the development of fieldable techniques and their interface with the fieldable instrumentation. (LAUR-12-25996)

NUCL 56

Effects of changing the eutectic melt composition on the electrochemical properties of europium(III) chloride under pyroprocessing conditions

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The effects of changing the eutectic melt compositions on the electrochemical properties of EuCl_3 under pyroprocessing conditions have been studied. Even though several studies on the electrochemical properties of europium in eutectic melts can be found in the literature the results cannot be easily compared because of differences in experimental setup. This has led to an inability to compare the effects that changing the eutectic melt composition has on the electrochemical properties of EuCl_3 . To fill this gap we looked at the properties of EuCl_3 within different eutectic mixtures (LiCl/NaCl , LiCl/KCl , LiCl/RbCl , and LiCl/CsCl) over a range of temperatures ($370^\circ\text{C} - 800^\circ\text{C}$) using different electrochemical techniques. This paper will discuss the observed trends in the diffusion coefficients and standard redox potential over the temperature range, and will also compare the different melt compositions with one another.

NUCL 57

Characterizing functionalized dipicolinate complexes of actinides and lanthanides using optical spectroscopy

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Developing an optimized solution to the challenge of separating trivalent actinides from lanthanides in advanced nuclear fuel reprocessing schemes has so far proven a difficult task. Dipicolinic acid (pyridine-2,6-dicarboxylic acid, DPA) exhibits good potential for application in $\text{Ln(III)}/\text{An(III)}$ separation, but suffers limited solubility in acidic media. This research focuses on two main goals: 1) overcoming the acidic media solubility limit and,

2) establishing that the new derivatives retain their complexing strength and An/Ln selectivity. To address these goals four dipicolinic acid derivatives have been synthesized including 4-(hydroxymethyl)pyridine-2,6-dicarboxylic acid (4-HMDPA), N,N,N-trimethyl-4-pyridinemethanaminium-2,6-dicarboxylic acid (QDPA), 4-(4-morpholinyl)-2,6-pyridine dicarboxylic acid (mor-DPA), and 4-(N-methylpiperazine-1-yl)-2,6-pyridine dicarboxylic acid (mPIP-DPA). Spectrophotometry and potentiometry have been utilized to evaluate the chemical characteristics and to determine stability constants of lanthanide and actinide complexes with these ligands.

Work supported at WSU and at PNNL by the U.S. Department of Energy, Office of Nuclear Energy FCR&D program, Sigma Team for Minor Actinide Separations.

NUCL 58

Photonic crystals for enhanced light outcoupling of scintillation based detectors

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The sensitivity of scintillation based detectors is maximized with increased photon yields. These are critically limited by total internal reflection within the crystal, leading to an undesirable decrease in the energy resolution of the counter. In this work we studied the use of photonic crystals (PhCs) to minimize total internal reflection in high refractive index scintillators. Efficient light extraction is achieved through periodic 2-dimensional nanoscale patterns, which inhibit light propagation along directions along the surface. A computational technique was used to design a PhC pattern to produce a photonic band gap in an indium tin oxide / bismuth germanate system. A convenient and low-cost approach was used for the preparation of a large-area PhC by adopting highly-ordered porous anodic alumina membranes as selective dry-etching masks for pattern transfer. The light output yield of a PhC-modified scintillator was characterized using γ and x-ray sources relative to flat surface and random-patterned crystals.

NUCL 59

Mass yield and cross section measurements for proton induced fission at 10-15 MeV of nat. U

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Improvements in the fidelity of nuclear forensic exercise samples require the development of analytical reference materials with the end goal of establishing a realistic exercise sample. This will inevitably test the laboratory analysis and data evaluation communities, via truly coupled, end-to-end “unknown sample” exercise. The production of such a sample requires an accurate knowledge of cross sections and fission yields of possible reactions that may be used to obtain fission products and/or short-lived actinide isotopes. Due to the limited amount of nuclear data and the large uncertainties associated with the reported values of proton-induced fission on nat. U and/or U-238, a series of experiments were performed at the Center for Accelerated Mass Spectrometry to measure the fission mass yields and the cross sections for nat. U in the proton energy range of 10-15 MeV. Preliminary data from these experiments will be presented.

NUCL 60

Isostructural extended series of lanthanide 2-nitroterephthalates

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Our investigations into various sets of lanthanide compounds indicate that increasing strain on the crystal lattice, induced by reduced ionic radii, can be alleviated by a reorganization of the crystal structure. Comparing purely inorganic lanthanide complexes and lanthanide compounds with organic components implies that the rigidity of the ligand systems has a significant impact on the crystal lattices' abilities to absorb tensions caused by decreasing ionic radii. It seems that compounds incorporating small, highly rigid, polyatomic anions, such as lanthanide hydroxysulfates, more likely reorganize their crystal structure with reduced space for coordination. Compounds incorporating monoatomic anions, such as lanthanide bis-hydroxychlorides, or extended organic systems with higher degrees of flexibility, e.g., lanthanide terephthalates, rather absorb increasing strain without significant changes in the crystal structure. Most recently we have synthesized an extended series of lanthanide 2-nitroterephthalates, $\text{Ln}_2(\text{TPNO}_2)_3(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ (Ln = Pr - Lu, except Pm). All of these complexes are isostructural and crystallize in the monoclinic crystal system with space group C2/c, and the coordination number 8. The more flexible 2-nitroterephthalate entities seem to allow the unobstructed decrease in size of the LnO₈-coordination polyhedra along the series as Ln³⁺ ionic radii become smaller towards the heavier Ln-elements. Hence, the structural parameters of the crystal lattice adjust gradually without noticeable strain buildup along the entire series. Besides structural and spectroscopic characterization we applied thermogravimetric analysis and learned that these compounds lose the interstitial water at 180°C.

NUCL 61

Synthesis and characterization of multilayer Ln(²²⁵Ac)PO₄ nanoparticles for targeted alpha therapy

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In vivo α-generator radionuclides such as ²²⁵Ac can deliver multiple α-particles to a single receptor site, dramatically amplifying the delivered radiotherapeutic dose. In this case, conventional bioconjugate constructs are of limited use as the high recoil energy of the daughters severs metal-ligand bonds, separating α-emitting daughters from the targeting agent. In this work, we demonstrate that a multilayered nanoparticle-antibody conjugate can deliver multiple α radiations from ²²⁵Ac at a receptor site. This approach combines the radiation resistance of crystalline lanthanide phosphate to encapsulate and sequester ²²⁵Ac and its decay daughters; the magnetic properties of gadolinium phosphate for ease of separation; and the established surface chemistry of gold for attachment of targeting antibodies to nanoparticles. The nanoparticles were characterized by electron microscopy, radiotracer measurements, and neutron activation analysis. Nanoparticles conjugated to mAb 201b (thrombomodulin receptor) were used to determine biodistribution, pathology, and treatment efficacy on a murine EMT-6 tumor model.

NUCL 62

Radiochemical study of Re/W sorption behavior on a strongly basic anion exchange resin

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Rhenium-186 is a beta-emitter with a high potential for therapeutic applications. It emits therapeutic beta particles accompanied by a low energy γ-ray, which allows for *in vivo* tracking of the radiolabeled compound and dosimetry estimates. The current reactor production pathway ¹⁸⁵Re(n, γ)¹⁸⁶Re produces low specific activity ¹⁸⁶Re, thereby limiting its therapeutic application. Work is underway to develop an accelerator-based

method to produce high specific activity ^{186}Re . To optimize the separation method, batch studies have been performed to characterize the sorption capabilities of AG 1-X8 anion exchange resin. Basic (NaOH) and acidic (HNO_3) matrices were used to determine the equilibrium distribution coefficients for rhenium and tungsten. The resin exhibits the best affinity for rhenium at slightly basic conditions and little affinity for rhenium above moderate acid concentrations. Tungsten has low affinity for the resin above moderate basic concentrations. An additional study was performed to examine the effect of tungsten concentration on rhenium sorption, which showed the presence of significantly higher concentrations of tungsten was not detrimental to rhenium sorption.

NUCL 63

Effect of pellet geometry on specific activity of nickel-63

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Nickel-63 is routinely produced at the ORNL HFIR with a specific activity (SA) of ~15 Ci/g by irradiating 86.31 % enriched ^{62}Ni for 2 years. Project goal is to examine the effect of neutron depletion on ^{63}Ni SA. Because of rather high neutron capture cross-section of ^{62}Ni ($\sigma_{\text{th}} = 14.5 \text{ b}$, $I^0 = 6.6 \text{ b}$), it is thought that ^{63}Ni of higher SA can be produced using thinner target. To verify, three sets of ^{62}Ni targets (83% enriched) with different thicknesses; solid pellets (O.D. ~6 mm) and two in form of rings (6 mm O.D., 2 and 4 mm I.D.), were prepared and irradiated at center position of flux trap of HFIR for 2 h. Results indicated a slight increase in SA, ranging from 9.3 mCi/g for solid target to 9.6 and 9.9 for 2 and 4 mm I.D. rings. Detailed data will be presented, along with model calculations of neutron depletion.

NUCL 64

Next generation of hexa-aza bicyclic cages: Probes for molecular imaging

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The 1-*N*-(4-aminobenzyl)-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane-1,8-diamine ligand (Sara) was the first bi-functional hexa-aza bicyclic cage used for ^{64}Cu radiolabelling of proteins for positron emission tomography (PET). Since its first

application in molecular imaging, there has been increasing interest to develop other hexa-aza cage ligands with functional groups for reaction with different active groups on proteins, peptides and nanomaterials. Here we present the synthesis of over 15 new substituted hexa-aza cages via reductive amination of the substituted aldehyde with the Cu(II) diamsar (3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane-1,8-diamine) and the new method using metal free diamsar. The latter affords the synthesis of a range of new ligands not previously possible. Hexa-aza cages incorporating functional groups such as isothiocyanate, nitro-, maleimide, hydroxy, halogens, ortho- and meta- amino and alkyl groups have been isolated. Their metal complexation behaviour with a range of transition metal radioisotopes (i.e. ^{64}Cu , ^{57}Co , ^{65}Zn , ^{109}Cd) has also been investigated over a range of pH and metal/ligand concentrations.

NUCL 65

Comparing protein radiolabelling of the new NCS-SARAR with NCS-NOTA and NCS-DOTA using copper-67 produced at the Brookhaven Linac Isotope Producer (BLIP)

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Copper-67

(^{67}Cu) produced at BLIP was evaluated for radiolabeling of proteins with a series of bi-functional ligands (**L**), 2-(4-isothiocyanatobenzyl)-1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (SCN-DOTA), S-2-(4-isothiocyanatobenzyl)-1,4,7-triazacyclononane-1,4,7-triacetic acid (SCN-NOTA), and the new *N*¹-(4-isothiocyanatobenzyl)-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane-1,8-diamine (NCS-SARAR). The SCN-NOTA, SCN-DOTA, SCN-SARAR were conjugated to proteins (**P**) (bovine serum albumin (BSA) and human Immunoglobulin-G (IgG)) with **L**:**P** molar ratios of 1, 10, 50 and 100 in pH 9 buffer for 1 hour at 23°C. The radiolabeling efficiencies of the conjugates with ^{67}Cu and ^{57}Co (external supplier) at pH 7 were determined, and the optimum **L**:**P** ratio was 10. The number of ligands attached to the protein measured using solutions of Cu(II) and Co(II) (doped with ^{67}Cu and ^{57}Co , respectively) was calculated to be ~0.8 for BSA and ~1.7 for IgG. Radiolabeling efficiency of three ^{67}Cu production batches were compared at 1 to 7 days post EOB. The data was used to establish expiry dates for BLIP produced ^{67}Cu .

NUCL 66

ORNL and its isotope mission

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For over 65 years ORNL has produced both radioactive and stable isotopes that have been used for research as well industrial applications. Although ORNL's original mission was to support the Manhattan project with the production and separations of ^{239}Pu in 1944; its name has been synonymous with isotopes. In the June 1946 issue of Science ORNL published its first radioisotope catalogue and its first shipment of reactor produced isotope, ^{14}C , was sent to the Barnard Free Skin and Cancer Hospital of St. Louis, MO, two months later. From new element discoveries of Promethium to super-heavy element 117 and from calutron separations to electromagnetic isotope separation, ORNL continues to explore research into the development of new isotopes and their production.

NUCL 67

Development of a teaching-hospital based PET radiometal isotopes production and investigational facility in Perth, Australia: Strategic relevance for national biomedical research

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Perth, Australia is one of the world's most isolated cities, and while 'conventional' PET isotopes must be synthesized and utilized locally, this is not so for several PET radiometals. Following establishment of a sole-supplier regional PET-radiopharmaceuticals service our group strategically pursued radiometal isotopes, when no sources were readily available in Australia; exemplifying what is achievable when a medical cyclotron is embedded in a major medical physics/engineering department.

An 18/9MeV cyclotron was installed in 2003 for clinical PET. Subsequently, publications by the Michael J. Welch group (plus a notable discussion with him at WTTC12, 2008) inspired our cyclotron team that PET radiometal isotopes were an 'horizon' topic. Local design and construction of solid-targetry engineering & chemistry systems were implemented, enabling routine production of ^{61}Cu , ^{64}Cu and ^{89}Zr as certified products for

shipping to collaborators Australia-wide. Research utilizing novel radiopharmaceuticals is underway, for preclinical oncologic imaging and first-in-human clinical trials.

NUCL 68

Simple approach to high sensitivity trace metal analysis

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Measurement of trace metal contamination is critical in the production of radiometals. ICP-MS provides these data with high sensitivity and specificity, albeit at high cost. TETA titrations provide high sensitivity and low cost but low specificity. We are developing a method to obtain these data with high sensitivity and high specificity but at relatively low cost. The method is based on a novel molecule comprised of a chelator (e.g., DOTA) and a fluorophore (e.g., fluorescein). The chelator complexes the metals present in the radiometal sample, and the fluorophore provides a high sensitivity signal for fluorescence detection while simultaneously increasing the complex's lipophilicity, facilitating HPLC separation of the metals present in the sample. Recent proof-of-concept studies in our laboratory demonstrate that, using this system, we are able to detect Cu at concentrations as low as 10 ppb, more than adequate for the measurement of trace metals in typical samples of Cu-64.

NUCL 69

Automated ¹⁸F labeling of sucrose for transporter studies in plants via PET

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An automated radiochemical process to fluorinate sucrose at the 6' position of the fructosyl unit of the molecule with ¹⁸F is being developed. The 6' position is among the most accessible hydroxyl groups available for fluorination that leaves the glucose hydroxyl groups intact. The ¹⁸F-sucrose tracer will be used to investigate the local storage and transport of sucrose by sucrose transports, *specifically SUT1*, in both mutant and wild-type maize (*Zea mays*) leaves via positron emission tomography (PET). The ¹⁸F-fluoride from a GE PETtrace is transferred to the automated chemistry system in the shielded cell. The sample is dried multiple times in the reaction cell to

remove water from the Kryptofix 222 and QMA elution solution. 6'-O-Trifluoromethanesulfonyl-2,3,4,6,1',3',4'-hepta-O-benzoylsucrose (triflated sucrose) is then added and refluxed under argon for 30 minutes after which potassium carbonate in methanol is added to quench the reaction. The ^{18}F -sucrose product is then separated and purified by HPLC. Results of the automated synthesis process will be presented along with results from the initial tracer studies.

NUCL 70

Influence of chemical pressure on various luminescence properties of curium(III) and europium(III) ions in rare-earth hydroxides: A time-resolved laser fluorescence spectroscopy (TRLFS) study

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TRLFS is a powerful tool for detection and characterization of curium(III) at trace-levels in various chemical environments. With its $5f^7$ electron configuration, Cm^{3+} has several favorable luminescence properties; e.g., a single-emission band which is sensitive to the local environment, and a long emission lifetime which amounts to several milliseconds in the absence of water or hydroxide ligands. Because these ligands significantly shorten the lifetime, their number may be calculated. An equation to calculate the hydration number is known,¹ though no such equation exists for hydroxide ions. Here, we report a systematic TRLFS study on Cm^{3+} and Eu^{3+} in rare-earth hydroxides, $\text{M}(\text{OH})_3$ and MOOH . The emission spectra and the lifetimes depend on the M^{3+} ionic radii, which influence the 'chemical pressure', the crystal-field strength, and the electron-phonon coupling. Results are also presented for Eu^{3+} in polynuclear hydroxo clusters.

(1) Kimura, T.; Choppin, G. R. *J. Alloys Compd.* **1994**, 213/214, 313.

NUCL 71

Optical spectroscopy of Es(III) and Bk(III) doped in borosilicate glasses: Ten years later

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The optical spectroscopy of glasses doped with the transuranium elements Es and Bk were followed for a decade. When Es(III) was doped in borosilicate based glasses a blue self-luminescence (SL) band having a maximum at ~ 455 nm appears with minor

bands at 650 and 730 nm. These bands are believed to arise from defect centers that are produced by alpha-particles and recoiling atoms. The photoluminescence spectra also display the longer wavelength bands that show unusual excitation power dependence. Ten years later some of the original photoluminescence bands persist and other new bands emerge. The trivalent state of Bk also exhibits primarily two emission bands, centered at 650 and 740 nm. The relative intensities of these two bands exhibit an unusual dependence on excitation power, where at low power levels, the later band dominates and at high power the former dominates. The overall feature persists ten years later indicating that the bands at 650 and 730 nm originate from the non-bonding oxygen hole centers (NBOHC), and Si-micro cluster sites, respectively as suggested originally. Details of these investigations are discussed in this presentation both for Es and Bk systems.

NUCL 72

Optically excited near-infrared photoluminescence from NpO_2^{2+} in $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$

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Previously we reported near-infrared fluorescence emission and excitation spectra from neptunyl and plutonyl ions. Here we present additional results on the $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ system doped at different concentrations into an isostructural, crystalline uranyl host. Spectra were measured from single crystals of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ and from crystals of $\text{Cs}_2\text{UO}_2\text{Cl}_4$ doped with the neptunyl ion at concentrations ranging from 3% to 50%. The Np near-infrared luminescence is stimulated by excitation of either ligand-to-metal charge-transfer or intra-5f transitions of the Np. There are indications of energy transfer to luminescent excited states of neptunyl following excitation of the uranyl ion in the host crystal. At low Np concentrations, green luminescence typical of uranyl is observed. Increase in Np concentration leads to quenching of the green uranyl emission coincident with stimulation of the Np near-infrared emission. In this presentation, we will describe the observed transitions, as well as decay kinetics and the excitation spectra in the visible and near-infrared spectral regions. LA-UR 12-26052

NUCL 73

Luminescence study of divalent samarium sites in a variety of barium borate systems prepared by air firing of samarium-barium tetraborate coprecipitates with boric acid

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The coprecipitate of 5 mole percent samarium in barium with sodium tetraborate has been found to produce five characteristic divalent samarium environments upon firing of the product in air with 0-80% additional boric acid by mass. Four of the systems appear to result from the formation of various polyborates, only one of which (the octaborate) has been previously identified. The fifth characteristic emission spectrum observed from these samples was more unusual. The emission features of this spectrum correlate exactly with those reported to be characteristic of samarium-doped strontium tetraborate. Since strontium was not present in the sample, it is believed that the emission associated with this site must be attributed to a pure samarium borate phase.

NUCL 74

Electronic and vibronic interactions of actinyl in complexes and compounds

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Ion-ligand interactions of uranyl and neptunyl in complexes and compounds have been investigated in optical spectroscopic experiments and theoretical calculations. Luminescence, excitation and absorption spectra are theoretically analyzed and simulated to assign the electronic states of different configurations and to characterize the electronic and vibronic transitions of different origins commonly known as ligand-to-metal charge transfer and f-f transitions. Both types of electronic transitions involve states of mixed orbitals, and provide information on interactions between electrons in $An5f(6d)$ and $O2p(2s)$ orbitals within an actinyl ion and between the actinyl ion and its surrounding ligands. The calculations of electronic energy levels are performed using an effective operator method which was developed based on the theory of configuration coupling in the framework of Hartree-Fock formulation. The simulation of intensities of the Frank-Condon type of vibronic transitions is based on a modified model of Huang-Rhys theory of ion-phonon interaction. The calculations and simulations of optical spectra have achieved unprecedented success in analysis of complex optical spectra of high resolution; these therefore provide a quantitative understanding of actinyl electronic interactions in terms of electron repulsion and exchange interactions, spin-orbit coupling and crystal-field interaction. The method we developed for empirical simulations of optical spectra has been used for correlating electronic interactions and structural properties. It is an effective method for spectroscopic measurement of changes in $O=An=O$ bond length which is influenced by the equatorial ligand geometry and local electrostatic field.

NUCL 75

Synthesis and chemical stability of actinium-fullerenes

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Due to their chemical and thermodynamic stability, fullerenes could play an important role in encapsulation of radionuclides. In this abstract, we report the first synthesis of the actinium endohedral fullerenes. The α -emitter ^{225}Ac ($t_{1/2} = 10$ d) was contained in fullerenes by the d.c. arc discharge/catcher method in a He atmosphere. Endohedral ^{225}Ac and the bulk of C60 was dissolved from the catcher electrode (a Pt disk cover with a thin layer of C60) in toluene under N_2 and converted to malonic ester derivative. Cage stability was enhanced significantly by coupling the fullerene surface with organic adducts. Repeated washing of the organic phase with dilute HNO_3 demonstrated that a small fraction of ^{225}Ac (~1 %) could not be removed from the organic phase and presumably were inside the fullerenes. The 4.8-m Fr- 221 (α -decay daughter of ^{225}Ac), however, was observed to leak from the cage as the results of the nuclear recoil process.

NUCL 76

Electronic structures of group VI and VII actinide compounds

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Theoretical treatment of the electronic structures and properties of actinide compounds is challenging due to the need for inclusion of relativistic effects, and the presence of f and/or d orbitals that are partially filled. Computational methods are being evaluated through comparisons with experimental results. Gas phase data are most suitable for this purpose. Using multiple resonance techniques, our recent gas phase studies have focused on the electronic structures of the oxides, sulfides fluorides and nitrides of Th, Hf and U. Comparisons between isoelectronic species indicate that relativistic effects play a relatively minor role in the ionic bonding of ThO , ThO^+ , ThF and ThF^+ . The first electronic spectra for UF/UF^+ , ThN/ThN^+ and ThS/ThS^+ will be presented, along with the results from high-level electronic structure calculations. Systematic trends in the patterns of electronic states and their correspondence with ligand field theory models will be discussed.

NUCL 77

Stimulated dissociation of gas-phase uranyl complexes using electrons and infrared photons

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A number of prior studies have demonstrated the utility of electrospray ionization for generation of gas-phase ions containing actinide elements (eg. U, Np and Pu). Studies of the structure and intrinsic reactivity of these ions have been conducted primarily using tandem ion-trap mass spectrometry (ITMS), collision induced dissociation (CID) and infrared photodissociation (IRMPD). Here we present further study of the fragmentation of gas-phase uranyl complexes as induced by absorption of infrared radiation (IRMPD) or capture of energetic electrons (electron capture dissociation or ECD). The present experiments were performed under the ultra-high vacuum conditions of a Fourier-transform ion-cyclotron resonance mass spectrometer to probe fragmentation pathways without the influence of the adventitious water present in ion trap instruments. Fragmentation of uranyl-acetone and uranyl-acetonitrile complexes by IRMPD and ECD in FT-ICR experiments will be presented, and compared to observations from previous experiments conducted using CID and ITMS.

NUCL 78

Spectroelectrochemical sensor for detecting metal ions in harsh environments

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A novel sensor that combines electrochemistry, spectroscopy, and selective partitioning into a film has been developed. The sensor consists of an optically transparent electrode (OTE) coated with a selective film. Sensing is based on the change in optical signal for attenuated total reflectance at the OTE that accompanies electrochemical modulation of analyte that has partitioned into the film. Selectivity for the analyte relative to other solution components is obtained by choice of film material, electrolysis potential, and wavelength for optical monitoring. Detection by absorbance and fluorescence has been demonstrated. The sensor has selectivity and ruggedness for applications that involve complex samples in harsh environments such as the determination of ferrocyanide in nuclear waste. The sensor is also suitable for environmental applications such as detecting metal ions in subsurface water at the Hanford Site.

NUCL 79

Development and deployment of a deep-sea Raman instrumentation for in situ analysis

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We have developed, deployed, and tested a Raman spectroscopic probe for study of the geochemistry of sediment pore waters. The Raman technique has already been used successfully for in situ measurements of targets of scientific interest including gas and hydrothermal vents and complex gas hydrates, but sediment geochemistry has so far been an intractable problem since the sediments themselves are strongly fluorescent and typically only very small sample volumes are obtainable. The 35 cm long probe extracts pore fluids through a 10 micron sintered metallic frit and draws the sample through a 2 mm diameter channel into a sapphire windowed optical cell within which the laser beam is focused and the spectrum recorded. The unique features of this mode of detection include observation of the sulfate gradient in marine pore waters as an indicator of diagenesis, direct measurement of the dissolved sulfide species H_2S and HS^- , and measurement of dissolved methane; all of which are of primary geochemical interest. This paper outlines the technology and techniques used to accomplish in situ measurements in harsh environments that could possibly be adapted to other applications.

NUCL 80

Online process verification with the multi-isotope process monitor

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The Multi-Isotope Process (MIP) Monitor combines gamma spectroscopy and multivariate analysis for online monitoring of nuclear reprocessing facilities. The MIP Monitor evaluates the distribution of a suite of isotopes present in feed, product, and waste streams to detect deviations from nominal operation. Multivariate analysis methods common in chemometrics, such as principal component analysis and partial least squares regression, act as pattern recognition techniques, which can detect small deviations from the expected, nominal condition. By targeting gamma-emitting indicator isotopes, the MIP Monitor approach is compatible with the use of small, portable, relatively high-resolution gamma detectors that may be easily deployed throughout a new or existing facility. Researchers at Pacific Northwest National Lab have developed the MIP Monitor and applied it to simulated spectra representative of light water reactor fuel reprocessing and to bench-scale testbeds. This presentation will give an overview of the MIP Monitor concept and present the results to date.

NUCL 81

Colorimetry of Pu process solutions – getting the most out of univariate measurements

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When actinide processing solutions are analyzed spectroscopically, they often exhibit deviations from linear Beer's Law behavior. For example, changes in solution acidity or concentration of certain anions will change the distribution of actinide complexes, altering the absorption spectrum. The deviations can be addressed through multivariate spectroscopy and chemometric analysis. However, there are monitoring scenarios where spectrophotometry is not feasible. Budget constraints or issues with legacy equipment and maintenance can force the use of filter photometers, which produce a univariate measurement. Using the right filters can reduce the sensitivity to process conditions and simulate some of the advantages of the multivariate approach. We describe a computational technique to predict colorimeter performance and its use to develop a method to analyze Pu(IV) nitrate solutions under a wide span of nitric acid and Pu concentrations. We discuss the improved robustness of this method as well as specific examples of its limitations.

NUCL 82

Cryogenic laser fluorescence spectroscopy investigation of U(VI) sorption on quartz-chlorite mixtures

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Uranium is a major subsurface contaminant at many US DOE sites. Subsurface sediments are heterogeneous mixtures of mineral phases, and evidences have suggested that multiple uranium hosts exist. However, spectroscopic investigation of U(VI) sorption on mineral mixture/assemblage is limited. In this work, batch sorption and cryogenic laser-induced time-resolved fluorescence spectroscopy investigation of U(VI) sorbed on a series of quartz-chlorite mixtures at varying quartz:chlorite mass ratios have been performed at field-relevant uranium concentrations (5×10^{-7} M and 5×10^{-6} M) in pH 8.1 synthetic groundwater. Our results indicated that the fluorescence spectra of U(VI) sorbed on the quartz-chlorite mixtures can be simulated by those of U(VI) sorbed on the pure mineral phases. However, the measured U(VI) sorption K_d values on the mineral mixtures were consistently lower than the calculated ones based on linear addition of the K_d values on the pure phases although the differences were small.

NUCL 83

Optical measurement technologies for advanced small modular reactors

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Advanced Small Modular Reactors (aSMRs) promise sustainable, economically viable, safe, reliable, proliferation resistant, and carbon neutral energy sources. These designs

also represent a revolutionary advancement in sustainability and their small modular size significantly departs from the massive scale of past nuclear power generation systems. Operation temperatures within aSMR designs are significantly higher than inside conventional reactors, and hence will require new instrumentation and control architectures for plant operation and management. In-vessel reactor sensing and monitoring will require understanding and overcoming the significant technical challenges presented by extremes of high temperature, pressures, corrosive environments, and radiation flux. The future viability of aSMRs depends on solutions to this problem.

Optical-based sensing, measurement, and process control has a long history in extreme environment applications. We review the feasibility of using optical sensing technology for in-vessel aSMRs measurements. Current technology gaps are identified and enabling engineering solutions and materials advancements are considered.

NUCL 84

Development of a fiber optically coupled Raman telescope for nuclear waste tank analysis

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A novel, compact fiber optically coupled Raman probe with a telescope focusing and Raman collection front optics is developed as an analytical tool for nuclear waste storage tanks. The Raman telescope probe incorporates an electronic focusing mechanism and a video image that allows the remote optimization of the Raman probe focus into the sample. The Raman telescope can be used as a standoff detection and mapping tool for solid waste materials remaining in nuclear waste tanks. This paper will describe the development of the Raman probe and telescope and a high throughput Raman instrument.

NUCL 85

Dual-remote Raman technology for in-situ identification of nuclear tank waste

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A new Raman spectroscopic system for in-situ identification of the composition of the solid nuclear tank waste is being developed by collaborative effort between Pacific Northwest National Laboratory (PNNL) and EIC, Inc. The recent advancements in the

Raman technology allow probing the chemical composition of the tank waste without sample collection. In the newly tested configuration, the Raman probe is installed on the top of the tank riser and sends the incident laser beam to the bottom of the tank, 20 – 70 feet away. The returning light containing chemical information is collected by the Raman probe and transmits it via fiber optic cable to the spectrometer located outside the tank farm area. This dual remote technology significantly expands currently limited options for the safe rapid in-situ identification of the solid tank waste needed for the retrieval decisions.

The developed Raman system was extensively tested for acceptability prior tank farm deployment. This testing included calibration of the system with the respect of the distance between the Raman probe and the sample, incident laser beam angle, and presence of the optical interferences. The Raman system was successfully deployed to the nuclear waste Tank C-111 at the US DOE Hanford site. As the result of this deployment, several constituents later confirmed to be present in the hardpan at the bottom of Tank C-111 were identified.

NUCL 86

Development of a novel, integrated fiber optic Raman and turbidity probe for in situ use in nuclear waste solutions

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Stored nuclear waste must be retrieved from storage, treated, separated into low- and high-level waste streams, and then processed for eventual disposal. Before waste retrieval can be done, waste composition will need to be characterized. There is also a need for active monitoring of the dynamic chemistry of the waste during storage since the waste composition can become highly corrosive. An integrated Raman and turbidity fiber optic probe head was developed for use in nuclear waste solutions. The sensor allows the simultaneous chemical identification of nuclear waste and determination of the clarity of the waste solution using a common laser excitation source. A partial least square algorithm employing both the Raman and turbidity data was developed to accurately predict the concentrations of analytes in the waste solution.

NUCL 87

Radium-228 as a target for production of thorium-229 in a nuclear reactor

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Among prospective α -emitters, ^{225}Ac ($t_{1/2} = 10.0$ d) is of major interest for Targeted Alpha Therapy, where ^{225}Ac is the decay product of long-lived ^{229}Th ($t_{1/2} = 7880$ y). Currently, ^{228}Ra ($t_{1/2} = 5.75$ y, first α -decay of ^{232}Th) is being considered as target for production of ^{229}Th via $^{228}\text{Ra}[n,\gamma]^{229}\text{Ra}(t_{1/2}=4.0$ m, β^-) $^{229}\text{Ac}(t_{1/2}=62.7$ m, β^-) ^{229}Th nuclear reaction. The goal of this project is to recover ~ 2 μg of ^{228}Ra from 5 kg of 30-y old ^{232}Th , purify and prepare ^{228}Ra target for irradiation at the ORNL-HFIR for measurement of the effective cross-section for the above reaction. Based on a 36 barn reported thermal neutron cross-section of ^{228}Ra , the predicated ^{229}Th yield is ~ 0.04 mCi per mg of ^{228}Ra for a 50-d irradiation at a thermal neutron flux of 2×10^{15} $\text{n}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$. A comparison of the experimental and theoretical data will be presented.

NUCL 88

Evaluation of nuclear data for reactor production of thorium-229

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The rapidly increasing interest in the medical applications of bismuth-213 and actinium-225 coupled with the limited availability of their parent isotope thorium-229 necessitate investigation of alternative production routes for ^{229}Th as well as the medically important decay daughters, ^{225}Ra and ^{225}Ac . The theoretical evaluation of potential production using reactor approaches is greatly hampered by the lack of certain neutron capture cross-section data for intermediate radionuclides and large uncertainties in some of the existing cross-section data from the 1950's and 1960's. To obtain this data, a series of dilute targets of radium-226, radium-228, thorium-228 and actinium-227 have been irradiated at the ORNL High Flux Isotope Reactor (HFIR), followed by chemically separating and purifying trace amounts of ^{229}Th by-products. Details of this work and initial data will be presented.

NUCL 89

Nuclear data for reactor production of barium-131

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Cesium-131 ($t_{1/2}=9.69$ d, 100% EC) is the most recent addition to the arsenal in the fight against prostate cancer. It is generated from the EC-decay of 11.5-d ^{131}Ba , which is produced by neutron irradiation of ^{130}Ba target in a nuclear reactor. For large scale production, knowledge of ^{131}Ba burn-up cross-section is essential. Due to a short half-life, the burn-up cross-section of ^{131}Ba can only be measured empirically by superimposing theoretical calculations on experimental data. To this end, six sets of targets consisting of mg quantities of $\sim 35\%$ enriched ^{130}Ba target was irradiated at

ORNL HFIR at a thermal neutron flux of $1.8 \times 10^{15} \text{ n.s}^{-1} \cdot \text{cm}^{-2}$ (th/epi=31) for 3 to 26 days. Preliminary data indicates that the burn up cross-section of ^{131}Ba is not significant. These results together with new measurements of the thermal and epithermal cross-sections for the $^{130}\text{Ba}[n,\gamma]^{131}\text{Ba}$ reaction and a new half-life for ^{131}Ba will be presented.

NUCL 90

Production of promethium-147 via neutron capture of neodymium-146

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Promethium-147 is a low-energy Beta emitter usually obtained from spent nuclear fuel fission products. It can also be produced via neutron bombardment at ORNL-HFIR of mg quantities of highly enriched (86%) ^{146}Nd for 3-5 days via the reaction $^{146}\text{Nd}[n,\gamma]^{147}\text{Nd}$ ($t_{1/2}=11 \text{ d}$, β^-) ^{147}Pm . It is then allowed to decay from ^{147}Nd (120.5 keV gamma ray at 0.4% intensity) to ^{147}Pm (120.26keV gamma ray with $2.85 \times 10^{-3}\%$ intensity). Using the least-square algorithm ('CLSQ'), we found this decay period needed to be at least 150 days in order to observe the less intense gamma ray from ^{147}Pm . CLSQ is capable of fitting decay to resolve short and long-lived isotopes. This result, together with the experimental yield of ^{147}Pm , chemical separation of Pm from Nd target, and an estimate of the upper limit of ^{146}Pm impurity in ^{147}Pm preparation, will be presented.

NUCL 91

Producing high specific activity radiolanthanides for medical purposes

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Radioactive lanthanides are an important tool in the medical field. For example, the samarium isotope of ^{153}Sm has been proven to have desirable characteristics for treatment of bone cancer. However, for medical purposes, the radioactive isotopes must be produced at high specific activity, i.e. low concentration of inactive carrier, so they are beneficial for the therapy but the concentration of the metal ions does not exceed the maximum sustainable by the human body. The objective of our research is to produce radioactive lanthanides with high specific activity in a small-scale research reactor using the Szilard-Chalmers method. At the start of his career Michael Welch was a "Hot Atom Chemist" relying on the Szilard-Chalmers effects, and he definitely followed this extensively throughout his career. We will present methods for preparation

of the material used for irradiations and the results of enrichment factors and extraction yields in radioactive lanthanide solutions.

NUCL 92

Scale-up of erbium and thulium separation for Tm-171 production

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According to the National Nuclear Science Administration, investigations leading to more accurate determination of low energy cross sections of stable and unstable nuclei and corresponding reaction rates for neutron-, γ - and ion-induced reactions is one of the major research areas in low-energy nuclear science. One of these unstable nuclei of interest is ^{171}Tm , which is part of a reaction network that was used as radiochemical detector to monitor the performance of nuclear devices. ^{171}Tm also plays an important role in astrophysics, as a branching point in the s-process of stellar nucleosynthesis. ^{171}Tm will be produced through neutron capture on stable ^{170}Er followed by beta decay. For the neutron capture cross section measurements, milligram amounts of ^{171}Tm need to be separated from hundreds of milligrams of irradiated erbium target. The separation was previously optimized on the analytical scale. The scale-up of the method to the expected target mass will be presented.

NUCL 93

Enrichment of stable isotopes using an electromagnetic isotope separator

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A modernized electromagnetic isotope separator (EMIS) has been designed, built and tested at Oak Ridge National Laboratory as part of a recent effort by the U.S. Department of Energy, Nuclear Physics Program to reestablish a domestic capability to produce enriched stable isotope products. This presentation will discuss the results obtained using the first prototype EMIS which consists of a Freeman-type ion source, an ion optics subsystem that includes a magnetic quadrupole doublet and a 60 degree, large pole gap sector magnet and a custom built isotope collection system. The current initiative envisions increasing the throughput of the EMIS through spiral development of improvements to the ion source to increase ion current while maintaining the maximum amount of single pass enrichment. Overall production throughput will also be enhanced through the introduction of a high throughput gas centrifuge capability at ORNL to produce pre-enriched EMIS feedstock.

NUCL 94

Development of NCA radiometals for imaging and therapy

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Michael J. Welch was a key driver in developing methods to produce NCA radiometals for imaging and therapy, including novel targetry, separation, purification, quality control, and target recycling techniques. His impact is seen in the production of NCA radiometals at numerous sites and in the development of new “theranostic agents.” A brief overview will be presented highlighting Michael Welch's work and his impact on NCA radiometal development at MURR, including the NCA radiolanthanide Lu-177, which is currently used in clinical applications. Lutetium-177 attached to small molecules, peptides and antibodies has seen increased use for therapeutic and diagnostic applications due to its favorable nuclear properties (7 d half-life, ~0.5 MeV β^- , 208 keV γ (11%)). Indirect irradiation of Yb-176 yields a high specific activity Lu-177 (110 Ci/mg) that is easily incorporated into DOTA and DTPA chelates, and its long half-life allows for distribution to remote regions.

NUCL 95

Translation of NCA Lu-177 production scale from research to routine

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The demand for supply of NCA Lu-177 for clinical trials has increased due to its high deliverable dose and absence of the long-lived Lu-177m side product. The aim of this effort was to upgrade from research production of NCA Lu-177 at the University of Missouri Research Reactor Center (MURR) to routine and reliable Curie-scale production. Remote automation has been evaluated and developed to allow for hot cell and glove box manipulation of high amounts of activity. Quality control testing has been conducted to ensure the product is free of metal contaminants and meets the specifications required to label biomolecules in high radiochemical purity for receptor-targeted imaging and therapy, including samples evaluated by external users. Some of the challenges in translating from research to routine production, the results of quality control evaluations, and current production capabilities of NCA Lu-177 at MURR will be presented.

NUCL 96

Bredig transition and thermal expansion to melting of fluorite-type oxides

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There are common features in the coefficient of thermal expansion (CTE) of the fluorite-type compounds, culminating to Bredig transition hump and then melting. An empirical model CTE curve is presented, which reproduced the literature data of thermal expansion. Heat capacities were also analyzed by a Landau expansion method with a field term in order to support the general features of model CTE. Uniformity in volume expansion to melting point was found to be 1.13 ± 0.02 . Fractional volume change at melting is small, and it decreases with increasing molar volume of solid phase. This trend reflects structural characteristics of fused states. Existing data of actinide oxides are discussed in view of these findings.

NUCL 97

Low temperature specific heat: Providing insight into actinide elements Pa, Pu, Am, and many actinide compounds, e. g. PuGa₃, NpBe₁₃, NpIr₂, and PuAl₂

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The specific heat of the actinide elements and compounds reveals important information about the low temperature electronic properties. Several examples (including NpIr₂¹, Am², PuGa₃³, PuAl₂⁴) of such studies will be discussed. Work at Florida performed under the auspices of the US Department of Energy, Contract no. DE-FG02-86ER45268.

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NUCL 98

Recent developments in the pursuit of actinide electronic structure, from inverse photoemission to Pu cluster calculations

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Our long-term goal is the resolution of the plutonium (Pu) electronic structure problem. Here two important steps on that journey will be discussed. (1) One of the crucial questions of all actinide electronic structure determinations is the issue of 5f versus 6d character. Here, a break-through experiment is discussed, which has allowed the direct determination of the U5f and U6d contributions to the unoccupied density of states (UDOS) in Uranium Dioxide. [1] (2) A second novel avenue of attack upon the problem of Pu electronic structure is the utilization of reduced dimensionality. Calculations of the electronic structure of clusters of plutonium have been performed, within the framework of the Relativistic Discrete-Variational Method (RDV). [2] 1.J.G. Tobin and S.W. Yu, Phys. Rev. Lett **107** , 167406 (2011). 2. M.V. Ryzhkov, A. Mirmelstein, S.-W. Yu, B.W. Chung and J.G. Tobin," J. Physics Condensed Matter, submitted Sept 2012.

NUCL 99

Multiconfigurational nature of 5f orbitals in uranium and plutonium and some of their intermetallic compounds

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The first measurements of multiconfigurational ground states in a wide variety of uranium and plutonium intermetallic compounds are reported, including data on the alpha and delta phases of elemental plutonium. Multiconfigurational groundstates have been predicted previously, notably by the dynamical mean-field theory (DMFT) calculations of Kotliar and co-workers. We conclude such states exist in these actinide intermetallics by evaluating a combination of x-ray absorption near edge structure (XANES) and, most importantly, resonant x-ray emission spectroscopy (RXES) measurements. These results have direct implications for understanding the unique structural, electronic, and magnetic properties of these materials.

NUCL 100

Electron correlation and magnetism in f-electron metals under pressure

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Electron correlations play an important role for the electronic structure and phase stability in most rare-earth elements and the heavier actinide metals. The magnetic properties are linked to the presence of 4f (rare-earth) and 5f (actinides) electrons that

are also involved in chemical bonding and phase stability, particularly during compression. Therefore, it is not surprising to find that pressure-induced phase transitions can be associated with the *f*-electron character in terms of delocalization and magnetism. For instance, almost two decades ago, theory predicted that the rare-earth metal samarium is a 4*f*-delocalized ferromagnet at high pressure. In this case could not the tetragonal phase at about 1 Mbar be properly described in a non-magnetic model. A much later example of an analogous scenario is that of the heavy actinide metal curium that undergoes several phase transitions during compression. Here, density-functional theory (DFT) is able to very well reproduce these phase transitions in a spin-polarized model while a spin-restricted, non-magnetic, assumption cannot. This paper also illuminates the fact that the balance between spin-orbit interaction and spin exchange varies through the series of actinides. Another interesting case is that of americium metal under compression. Recent experiments as well as DFT modeling have found that in spite of the pressure-induced delocalization and phase transitions in Am, the 5*f* valence is not changed significantly during compression. The recent discovery of a prevalent monoclinic phase (C2/m) in many rare-earths under compressions raises the question if this phase is driven by *f*-electron delocalization (participation in bonding). We discuss this at some length and also make use of the fact that the C2/m has also been identified in the 4*d*-transition metal yttrium when pressurized.

NUCL 101

Strong correlations and the electronic structure of the actinide dioxides

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The series of actinide dioxides (AnO₂, An=Pa, ... Cm) are difficult challenges for electronic structure theory. The early members of the series are Mott insulators, the band gap corresponding to *f*-*f* transitions, while the later members, beginning with PuO₂, are O2*p* → An5*f* charge transfer insulators. I will review recent experimental results (X-ray absorption, photoemission and optical band gaps) which now allow us to distinguish among several many-body approximations to their electronic structure, including the SIC, DFT+U, DMFT+U and hybrid DFT (HSE) approaches.

NUCL 102

Pressure induced phase transitions in Cm

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Curium lies at the center of the actinide series and has a half-filled shell with seven 5*f* electrons spatially residing inside its radon core. In an attempt to understand the stability of the unusual Cm III structure with its lower C2/c symmetry, we performed

calculations using the full potential linear muffin-tin orbital (FPLMTO) method based on Density functional theory. We confirmed Cm phase transitions follow the sequence: double hexagonal closed packed ($P6_3/mmc$, CmI) \rightarrow face-centered cubic ($Fm3m$, CmII) to monoclinic ($C2/c$, Cm III) \rightarrow face-centered orthorhombic ($Fddd$, CmIV) \rightarrow primitive orthorhombic ($Pnma$, CmV). We also show that the AFM configuration is always lower in energy compared to the FM configuration for all structures. Our results reveal that curium is one of a few elements that has a lattice structure stabilized by magnetism.

NUCL 103

Ab initio study of U-Zr metallic nuclear fuels for fast breeder reactors

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The U-Zr alloys proved to be very promising fuels for TRU-burning liquid metal fast breeder reactors. In the present study we perform density functional (KKR-ASA-CPA and EMT0-CPA) calculations of the ground state properties of γ -U-Zr alloys and compare their heats of formation with CALPHAD assessments. We also confirm the empirical hypothesis [1] of stabilization of the δ -UZr₂(C32) compound against the α -Zr (hcp) structure due to increase of Zr d-band occupancy by the addition of U to Zr. Analogy with stabilization of the ω -phase in Zr under compression is made. This work was performed under the auspices of the US Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Work at LLNL was funded by the Laboratory Directed Research and Development Program under project tracking code 12-SI-008.

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NUCL 104

Radiochemical analyses supporting closure of Savannah River Site (SRS) radioactive waste tanks 18 and 19

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After decades of use, SRS radioactive waste tanks 18 and 19 were operationally closed in September 2012 per agreement with DOE, SCDHEC, and EPA. Prerequisites for operational closure included bulk waste removal, solids heel removal, demonstration that the residual highly radioactive radionuclides were removed to the maximum extent practical, and subsequent isolation and stabilization of the tanks. Radiochemical

analyses of waste residue samples collected following solids heel removal provided the means for characterizing the inventories of the residual radionuclides.

Over fifty radionuclides were quantified using radioanalytical methods developed specifically for the highly radioactive, high metal content matrices inherent to the Tank 18 and 19 waste residues. Robotic sample handling, multiple solid-phase digestion techniques, extensive radiochemical separations yielding up to eight orders of constituent decontamination, and various hybrid measurement techniques were necessary to effectively characterize the full suite of radionuclides.

A summary of the radioanalytical methods and results will be presented, along with a discussion of some of the more challenging analytical approaches that were utilized.

NUCL 105

Tank closure for radiochemical analyses-developing functional relationships and creating a roadmap for success

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Savannah River Site (SRS) high activity waste tanks are currently being characterized at an accelerated rate to support tank closure. Radiochemical analyses of waste residue samples collected following solids heel removal provide the means for characterizing the inventories of the residual radionuclides. These characterization campaigns consist of extremely complex, one-of-a-kind analyses performed in concert with method development for matrix-specific challenges. Regardless of the schedule and analytical challenges, the characterization must be carried out in a manner yielding analytical data of known and adequate quality.

In an effort to develop an acceptable plan to provide data with a sufficient pedigree, members of the radiochemistry team worked closely with Savannah River Remediation, EPA, SCDHEC, and DOE to determine the most efficient process of providing data of sufficient quality to support tank closure.

The results of this concerted effort will be reviewed.

NUCL 106

Application of quantum cascade lasers to IR spectroscopy

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This work investigates the applicability of quantum cascade lasers (QCL) for high resolution infrared spectroscopy of gases and compared their capabilities to FTIR spectroscopy. We chose to use carbon monoxide gas as a baseline analyte because it has a strong absorbance in the range of one of our QCL's. The primary features of interest in our experiments that will be discussed are spectral resolution, baseline noise, wavelength stability, and wavelength reproducibility.

NUCL 107

Derivatization of DWPF alternative reductants for analysis by GCMS at the Savannah River Site

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The Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) has recently explored alternative processing strategies for use in the Chemical Process Cell (CPC) portion of DWPF. Cesium containing nuclear waste is prepared for vitrification in the CPC by chemical adjustment and the addition of glass formers prior to heating in a melter. The current chemical treatment employs formic acid/nitric acid during the DWPF process to accomplish a number of different processing objectives: acidify the sludge, reduce mercury during the Sludge Receipt and Adjustment Tank (SRAT) cycle, and control melter REDuction / OXidation potential (REDOX). An alternative strategy is the use of glycolic acid in place of formic acid to lower flammable hydrogen generation. Analytical techniques must also follow to analyze for the glycolic acid as a process control. Current Ion Chromatography (IC) analytical techniques in use at the Savannah River National Laboratory for the analysis of glycolic acid will be discussed, as well as, the exploration into an alternative or confirmatory method by Gas Chromatography - Mass Spectrometry (GCMS). SRAT samples containing formic, acetic, glycolic and oxalic acids were derivatized using BF₃-butanol to prepare the corresponding n-butyl esters of the mono and dicarboxylic acids. Initial GCMS analysis of the esters showed good chromatography and recoveries for all derivatives but butyl glycolate.

NUCL 108

Examining the analysis of sulfur in Defense Waste Processing Facility feed and product materials: Importance and challenges

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The Defense Waste Processing Facility (DWPF) at the DOE Savannah River Site must control the amount of sulfur reaching the high level waste glass melter in order to prevent the formation of a sulfate salt layer on the glass melt pool which could cause a

safety concern resulting from the trapping of melter off-gas. Our work has demonstrated that initial non-sulfate sulfur species exist in the feed stream to the facility and persist through initial processing steps in the Slurry Receipt and Adjustment Tank (SRAT) thought to convert all sulfur species to sulfate. Analytical measurement of sulfate in the SRAT product by ion chromatography appears to be insufficient to quantify the total sulfur reaching the glass melter. Challenges in quantifying low levels of sulfur in the complex matrix, results of a round-robin analytical exercise, and methods for identifying the non-sulfate species will be addressed in this paper.

NUCL 109

Applications of inductively coupled plasma-mass spectrometry for high-level nuclear waste characterizations at the Savannah River National Laboratory

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The Savannah River National Laboratory (SRNL) uses Inductively Coupled Plasma Mass Spectrometry (ICP-MS) techniques to support numerous programs at the Savannah River Site. The most common application of ICP-MS techniques at SRNL is for characterizations of high-level nuclear waste required for the Defense Waste Processing Facility (the high-level waste vitrification plant) and for permanent closure of waste tanks. ICP-MS determinations of trace nuclear waste elements and radionuclides complement those from other techniques such as separation chemistry and nuclear counting methods. SRNL recently upgraded its ICP-MS instrumentation and is developing methods to increase sensitivity and applications of ICP-MS to high-level waste characterizations. The discussion details the development of ICP-MS techniques and applications to SRS high-level waste management programs.

NUCL 110

Analytical development support for the Defense Waste Processing Facility

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The Defense Waste Processing Facility (DWPF) is currently processing sludge batch 7b (SB7b). A sludge batch is defined as a single tank of sludge slurry or a combination of sludge slurries from different tanks that has been or will be qualified before being transferred to DWPF. Sludge batches consist of a mixture of sludge slurries from several F-area tanks (PUREX waste) and sludge slurries from H-area tanks that hold modified-PUREX process waste. Savannah River National Laboratory has been tasked with characterizing DWPF feed material, developing additional analytical characterization techniques if needed, and evaluating the current process analytical

methods used by the DWPF. Analytical methods developed and used to characterize DWPF sludge matrices will be discussed.

NUCL 111

Installation and performance of Isolok samplers for high-level radioactive sludge process tanks in the Defense Waste Processing Facility

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The Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) is used to immobilize high-level radioactive waste by mixing it with glass-forming chemicals and heating the mixture at 1050 °C to form borosilicate glass logs. An Isolok Sampler and supporting equipment to control the sampling of the Sludge Receipt and Adjustment Tank (SRAT) sampling within the DWPF sample cells has been installed in the facility and operating successfully for approximately 24 months. An Isolok Sampler for the Slurry Mix Evaporator (SME) is scheduled for installation in November 2012. This sampling technology is a replacement for the existing Hydragard sampler and is providing significant cost savings due to reduced in-cell contamination, improved equipment reliability, lower equipment fabrication costs and improved ergonomics. Details of the qualification testing program, shielded cell installation, and operation of the Isolok sampler will be discussed.

NUCL 112

NIST Standard Reference Material 1648a contains fallout radionuclides from atmospheric nuclear testing

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NIST offers several environmental standard reference materials (SRM) that were collected at or near known contaminated industrial sites and are certified for radioactivity. However, a SRM that represents typical global fallout concentrations or isotopic ratios is not currently available. NIST SRM 1648a is atmospheric urban particulate matter collected during the mid-1970s and is certified for inorganic elements. This material was investigated as a possible source of globally-dispersed fallout radionuclides derived from atmospheric nuclear testing conducted during the sample collection timeframe. This paper reports radiometric measurements (alpha spectrometry) of ^{238}Pu , $^{239,240}\text{Pu}$, and ^{241}Am as well as Pu isotopic composition (ICP-MS) for 1648a. The physical form and sample activity (e.g. $^{239,240}\text{Pu} = 6.6 \text{ mBq/g}$) suggests this material as a convenient matrix standard to validate analytical methods in environmental monitoring programs.

NUCL 113

Pu, Am, and Cs contamination in soils from Idaho National Laboratory

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At the Idaho National Laboratory (INL), solid low-level radioactive waste was disposed of via shallow land burial for many years; one such disposal site is called the Subsurface Disposal Area (SDA). This practice ceased in 1984, and remediation approaches are being considered. Remediation decisions depend, in part, on identification of the contaminant source. Previous studies of soils from this area revealed elevated Pu and ²⁴¹Am activities in both 0-4 and 4-8cm soil depths.¹ Reanalysis of the two highest activity soils more than 30 years later showed greater quantities of ²⁴¹Am than could be accounted for purely by in-growth from ²⁴¹Pu, suggesting the existence an additional ²⁴¹Am source term.² In this work, activities of Am, Pu, and Cs have been determined using radiometric and mass spectrometric methods. Measured activities and isotopic ratios as a function of location and depth will be discussed, along with their implications for source term identification.

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NUCL 114

TIMS vs. ICP-MS measurements for age dating ⁹⁰Sr

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The date on which a radioactive source material was last separated from its decay daughters is a useful parameter in deducing the material's origins and history for nuclear forensics investigations. Age dating a ⁹⁰Sr source requires accurate determination of the ⁹⁰Zr daughter and the residual ⁹⁰Sr parent in a sample of the source material so a time of decay can be calculated using the isotope's half-life. Because the target nuclides are isobaric, chemical separation of zirconium from strontium is required for mass spectrometric determination of the isotope amounts. Adding known amounts of low-abundance Sr and Zr isotopes prior to processing a sample and using the technique of isotope dilution (ID) permits accurate measurement of the ⁹⁰Sr and ⁹⁰Zr isotopes irrespective of chemical recovery. This presentation describes our application of an isotope-dilution method for determining ⁹⁰Zr and ⁹⁰Sr in a

^{90}Sr source material spiked with ^{86}Sr and ^{92}Zr . A miniature gas pressurized extraction chromatography (GPEC) system with a column containing Eichrom Sr ResinTM was used for the separation. Zirconium was rinsed through the column with 3M HNO_3 /trace HF and strontium was eluted with 1% acetic acid. Two mass spectrometric techniques, inductively coupled plasma mass spectrometry (ICP-MS) and thermal ionization mass spectrometry (TIMS), were used for measuring isotope ratios. Data were obtained with carefully prepared mixtures of non-radioactive strontium and zirconium and with ^{90}Sr from a blood-irradiator source dissolved by Idaho National Laboratory. Measured $^{90}\text{Zr}/^{90}\text{Sr}$ ratios and corresponding ages determined by ID-ICP-MS and ID-TIMS are presented.

NUCL 115

Identification and attribution of Ir-192 sources via ICP-MS

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Radioactive Iridium-192 sources are used in a variety of fields from medical brachytherapy to well-logging. It is the wide use and relatively low security surrounding these activated sources that could make them a target for use in radiological dispersal devices (RDD). Source attribution of these radioactive materials can be accomplished through their minor and trace element composition as well as their isotope ratio signatures. A major analytical challenge for attribution studies is the ability of iridium to resist dissolution by the strongest of acids. A method for the electrochemical dissolution of iridium for dissolution of both stable metal and activated iridium-192 sources has been developed. Results of the ICP-MS analysis of commercial iridium samples for source attribution will be presented.

NUCL 116

Development and validation of a methodology for uranium radiochronometry reference material preparation

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The development of a methodology for the preparation of a uranium-based radiochronometry reference material is presented, which can be applied as a reliable standard for age measurements based on the $^{230}\text{Th}/^{234}\text{U}$ chronometer. The material was prepared from high-purity uranium materials of various enrichments followed by the complete separation of thorium decay products. By this means, the age is exactly

known and well-defined, and the ^{230}Th presence in the material after purification will solely depend on the ingrowth from ^{234}U . The verification of the material was accomplished by comparing the measured ages with the known values as well as with the theoretical values deriving from the radioactivity decay equations. Based on the methodology, a new uranium age dating certified reference material is prepared at the EC JRC ITU jointly with the EC JRC IRMM, which will be available for the national nuclear forensic laboratories from the mid-2013.

NUCL 117

High precision determination of trace element impurities in a uranium matrix using high pressure liquid chromatography and isotope dilution mass spectrometry

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The accurate analysis of trace element impurities in uranium materials has been identified as a high priority in the nuclear forensic community. Uranium impurity analyses are being conducted on a routine basis worldwide, however, the current methodologies lack precision. These methods typically employ matrix matched external calibration standards, which yield relative uncertainties of +/-10% or greater. In addition, the methods suffer from matrix effects, isobaric interferences and the lack of matrix specific reference standards certified for the comprehensive list of analytes being measured. By using high pressure liquid chromatography (HPLC) combined with isotope dilution mass spectrometry, the influence of the matrix and isobaric interferences can be significantly reduced while providing an accurate and precise concentration determination. The HPLC technique, together with ICPMS instrumentation allows for trace element analysis with low relative uncertainties, <1% for single detector mass spectrometers to as low as 0.1% for multi-detector mass spectrometers.

NUCL 118

Radiological chronometry of nuclear forensic uranium metal samples

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Radiological chronometry (i.e. "Age Dating") is an important signature in nuclear forensics and involves determining the uranium and thorium isotopic content from the

fractional ingrowth of ^{230}Th from the decay of ^{234}U to estimate the time elapsed since the material was last purified or fabricated. A variety of uranium metal samples went through different etching procedures prior to sample dissolution and analyzed to determine the effects on radiological age determination. Results demonstrate that surface material should rigorously be removed to avoid introducing a systematic bias in determining radiological age. Samples with a less rigorous process were found to be 15 years too old. Unetched samples appeared several hundred years too old. These results may be the effect of the etching procedures used or from ^{230}Th contamination present at the time the uranium metals were fabricated. This is an important topic to address when developing standard reference materials for radiological chronometry.

NUCL 119

Thorium: The first 5f element in the actinide series

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It is standard practice to consider thorium as a traditional tetravalent *d* transition metal, belonging to the same group of elements as Ti, Zr, and Hf. However, we demonstrate that the experimentally observed fcc crystal structure for thorium is in complete disagreement with this picture. Instead we show that it is itinerant *5f* electrons which stabilize the fcc phase. Thereby we have established a close connection between thorium and the heavier actinide metals (Pa-Pu), which has previously been overlooked. Accordingly, thorium is the first 5f element in the Periodic Table.

NUCL 120

Structural and spectroscopic characterization of actinide coordination polymers

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The polymeric compounds between the man-made elements americium or curium and the dicyanometallates, dicyanoaurate or dicyanoargentate are discussed. Single-crystal X-ray diffraction studies reveal that this series of four isostructural compounds are all hexagonal. The actinide and transition metal ions are interconnected through cyanide bridging to form three-dimensional coordination polymeric structures. Raman spectroscopy of the ν_{CN} stretching frequencies reveal a blue-shift due to bridging of the dicyanometallate ions with the f-element ions and the subsequent electron density removal from the cyanide center. The strong red emission corresponding to the $^6\text{D}_{7/2} \rightarrow ^8\text{S}_{7/2}$ transition of the Cm^{3+} ions in these coordination polymers are compared with the emission observed in curium formate, another hexagonal system. Comparisons

with some lanthanide cyanometallate systems currently under investigation will also be discussed.

NUCL 121

Ab initio modeling of actinide containing materials

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In this lecture I will present our latest computational achievements on actinide chemistry. I will describe our ongoing studies on uranyl peroxide nanoclusters, with the aim of understanding the basic principles responsible for self-assembly of such systems and side-on neptunyl cation-cation interactions, occurring in Np-based materials.

NUCL 122

Evaluating actinyl orbital mixing (UO_2^{2+} , NpO_2^{2+} , PuO_2^{2+}) using O K-edge XAS and TDDFT

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The actinyl ions, AnO_2^{x+} ($\text{An} = \text{U}, \text{Np}, \text{Pu}, \text{Am}$; $x = 1, 2$), dominate the chemistry of light actinides in higher oxidation states and represent the key high-valent component in virtually every area of 5f element molecular chemistry. Hence, many studies have focused on advancing our understanding of actinyl electronic structure and covalent bonding. Presented here are our efforts to quantify An–O orbital mixing, and identify bonding trends as the actinide series is traversed from left to right. The experimental approach involves using synchrotron-generated radiation to probe O 1s→2p bound state transition intensities in AnO_2^{2+} ($\text{An} = \text{U}, \text{Np}, \text{Pu}$) via O K-edge X-ray absorption. Additionally we make use of time-dependent density functional theory (TDDFT) to guide the interpretation of the obtained spectra. The overall results will be presented in context of improving contemporary descriptions of covalency, electronic structure, and bonding in actinyls.

NUCL 123

Investigating the σ - and π -interactions between U(V) and halide, alkoxide, amide, and ketimide ligands

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The octahedral U(V) complexes recently reported by Hayton and co-workers represent a unique opportunity to directly probe the strengths of π and σ interactions between the uranium f-orbitals and a variety of ligands. These octahedral complexes, $[\text{UX}_6]$, consist of pentavalent uranium coordinated by a variety of ligands including alkyl ($X = \text{CH}_2\text{SiMe}_3$), alkoxide ($X = \text{O}^t\text{Bu}$), amide ($X = \text{NC}_5\text{H}_{10}$), and ketimide ($X = \text{N}=\text{C}^t\text{BuPh}$). This family of complexes is ideal for studying f-orbital bonding it spans a range of commonly used ligands in organouranium chemistry, and the spectroscopic data necessary to investigate the bonding is available. The bonding in these compounds may be compared to that in the well-known halide complexes ($[\text{UX}_6]^-$, $X = \text{F}, \text{Cl}, \text{Br}$; PaCl_6^{2-} ; NpF_6), which have been extensively investigated. In this study, we develop an MO model based on earlier work by Thornley, but reduced, orbital-specific spin-orbit coupling constants are used rather than a single spin-orbit coupling constant. This model is used to fit the optical and EPR spectra for the octahedral f^1 complexes, and is in excellent agreement with the experimental results. The new model is compared to the venerable Crystal Field model and the Thornley MO model using a single spin-orbit coupling constant. The new model involves much less covalency than the original MO model, yet this covalency plays a large role in determining the strength of the interaction between the f-orbitals and the ligand orbitals.

NUCL 124

Synthesis, structure, and reactivity of new classes of organoactinides: The metallocene allyl complexes, $(\text{C}_5\text{Me}_5)_2\text{U}(\text{CH}_2\text{CRCH}_2)_x$ ($R = \text{H}, \text{Me}$; $x = 1, 2$), and the U^{2+} complex, $[(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{U}][\text{K}(2,2,2\text{-cryptand})]$

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Synthetic efforts in organoactinide chemistry have led to two new classes of organouranium complexes. Although uranium metallocenes have been heavily investigated, examples of metallocene allyl complexes have not been previously reported. The synthesis and structure of both U^{4+} and U^{3+} complexes, including $(\text{C}_5\text{Me}_5)_2\text{U}[\text{CH}_2\text{C}(\text{R})\text{CH}_2]\text{Cl}$, $(\text{C}_5\text{Me}_5)_2\text{U}[\text{CH}_2\text{C}(\text{R})\text{CH}_2]_2$, and $(\text{C}_5\text{Me}_5)_2\text{U}[\text{CH}_2\text{C}(\text{R})\text{CH}_2]$ ($R = \text{H}, \text{Me}$) will be presented, as well as the reactivity of the latter complexes to make the nanometer-sized metallocene carbonate, $[(\text{C}_5\text{Me}_5)_2\text{U}(\text{CO}_3)]_6$. The conversion of the U^{3+} tris(cyclopentadienyl) complex, $(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{U}$, to a crystallographically characterizable U^{2+} complex, $[(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{U}][\text{K}(2,2,2\text{-cryptand})]$, will also be described.

NUCL 125

Comparing Th and Cm speciation in aqueous solution

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Despite its slightly smaller ionic radius, the homoleptic aqua ion coordination number of Th⁴⁺ [1] is greater than that of Cm³⁺ [2], both in solution and in the solid state. High-energy x-ray scattering (HEXS) has determined that Th in bromide solutions has 10 coordinating waters in the first coordination sphere with the bromide coordinating solely as an outer sphere ligand. In contrast, using the same structural probe, Cm is found to have nine coordinating waters in perchlorate solutions, again with the anion absent in the first coordination sphere. Combining both new experimental and theoretical information, this presentation will focus on the potential influence of dissolved anions on the metal ion's inner-sphere coordination in solution. This work and the Advanced Photon Source are supported by the U.S. DOE, OBES, Chemical Sciences, Geosciences, and Biosciences Division under Contract No. DE-AC02-06CH11357

[1] R.E. Wilson, S. Skanthakumar, P.C. Burns, L. Soderholm; *Angew. Chemi* 46 (2007) 8043

[2] S. Skanthakumar, M.R. Antonio, R.E. Wilson, L. Soderholm; *Inorg. Chem.* 46 (2007) 3485

NUCL 126

Recent results in actinide organometallic chemistry

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Non-aqueous chemistry of the actinides has proved invaluable for gaining insight into the behavior and properties of these elements in a variety of chemical environments. These range from inert atmosphere syntheses of well-defined actinide materials for nuclear fuel applications and materials science to addressing purely fundamental questions such as the involvement of 5f-orbitals in bonding and reactivity. Using metallocene platforms, and more recently the PNP pincer ligand, we have discovered a variety of unusual reactivity patterns unique to the actinides. We couple our synthetic efforts with spectroscopic and theoretical studies to gain insight into the role that f-orbitals and electrons play in the reaction chemistry, electronic structure and bonding of actinide complexes. This talk will describe recent advances in this area and their implications in actinide chemistry.

NUCL 127

USDA roles and capabilities in radiation emergencies contrasted with events following the Fukushima Dai-ichi radiation release

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Mr. Cleveland's presentation will provide information on USDA's responsibilities during a radiological emergency and how development of an appropriate response position at the Veterinary Service's National Center for Animal Health Emergency Management has helped identify and mitigate challenges to our response capabilities for the agriculture sector, and develop programs, technologies, and human resources to address those challenges. Radiological emergency preparedness in the U.S. in general, will be contrasted with the events that unfolded during the Fukushima Dai-ichi nuclear power plant disaster in Japan.

NUCL 128

Radionuclides in food - an update on FDA's on-going programs and emergency response activities

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The Food and Drug Administration (FDA) has supported a radionuclide in food effort since the 1950's. This has included emergency response planning, policy development, food monitoring programs, and special assignments. FDA also participates in radiological exercises and organizes the radiological component of the Food Emergency Response Network (FERN). This presentation details FDA's current radionuclide in food activities and shows how they contribute to a comprehensive approach to food safety both nationally and globally.

FDA has radionuclide monitoring and surveillance components in two long-standing food monitoring programs titled "Total Diet Study" and "Toxic Elements in Foods and Foodware, and Radionuclides in Food - Import and Domestic". These activities provide monitoring of the general domestic food supply and target areas such as nuclear power plants and import products. Special assignments are issued to address unique situations such as in FDA's response to the Fukushima Nuclear Power Plant accident in Japan.

NUCL 129

Contamination of food imports to the United States in the early days after the Fukushima accident

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Significant airborne releases of radioactive materials from the stricken Fukushima Daiichi units occurred between March 13 to 19, 2011. Contaminated food imports into the US from Japan were first observed in our laboratory on March 30, 2011, with several products exceeding the FDA Derived Intervention Level (DIL) for Cesium and Iodine isotopes. Some samples of fresh fish products imported for Sushi restaurants were found to have been inadvertently contaminated by tainted service water in a Fukushima food processing plant. In April, 2011, samples of Koji powder (precursor for soy sauce) were observed to be contaminated followed by green tea and seaweed samples in subsequent months. All contaminated food imports were destroyed by the importers, frequently at levels well below the FDA DIL limits.

NUCL 130

Preparation of certified reference materials for determination of radioactivity in foods and soils

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After the Fukushima disaster, various types of instruments for determination of radioactive contaminants in foods were installed in whole areas of Japan. This requires development of the standard reference materials certified with the proper procedure for quality control.

Our group started a short-term project supported by Japan Science and Technology Agency for development of the certified standard materials of foods and soils. The candidate materials were contaminated with radioactivity from the Fukushima incident. Preparation of the certified reference material of brown rice grain was completed in late August before the harvest season in Far East. Concentration of radiocesium was controlled as close to 100 Bq/kg which is the 'threshold' for distribution of rice in local market. The standard has been distributed by Japan Society for Analytical Chemistry which authorizes the certification procedure. Preparation of the reference standards of soybean and beef are now in progress.

NUCL 131

SOP for food sample preparation - application for radiological screening analyses

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A screening-analysis sample preparation standard operating procedure (SOP) will be presented. It provides a means for converting a quantitative analytical method into a screening method with increased sample throughput. It is available as an add-on to methods that are already used in the laboratory. It will likely be most useful for determining beta- and alpha-emitting radionuclides, which require extensive analysis time.

Multiple samples are combined into a composite, the composite is analyzed, and results are evaluated according to a screening level based on a regulatory level. Using this SOP, quantitative levels are not obtained for individual samples but a result below the screening level will show that all samples in the composite are below regulatory limits. Should a result be above the screening level, findings would be considered inconclusive. In this case, reserve test portions for each sample in the composite would be analyzed using the original quantitative method.

NUCL 132

Microwave assisted sample preparation of organic materials for gross alpha activity analysis

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In support of the Food Emergency Response Network's MENU 2010 exercise, the IEMA Radiochemistry Laboratory developed, tested and successfully demonstrated a rapid, cost-effective method for preparing liquid food samples. We will discuss the development and the results against the MENU 2010 samples.

NUCL 133

Screening of alpha emitting radionuclides of concern in food matrix by alpha spectrometry

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A fast and cost effective method to detect the presence of any alpha emitting radionuclide's of plutonium, americium, curium, thorium, and uranium that may be present in food matrix has been studied at the Wadsworth Center using DGA resin (normal, 50-100 µm size), and alpha spectroscopy. The isotopes of concern studied

were $^{239,242}\text{Pu}$, ^{241}Am , ^{244}Cm , $^{230,232}\text{Th}$, and $^{234,235,238}\text{U}$. The food samples studied included meat, dairy, vegetable, grain and composite meal. The method involves digestion of 50 to 100 grams of food sample with concentrated nitric acid and hydrogen peroxide, filtration, adsorption of actinides onto DGA resin, elution of actinides by HCl-oxalic acid solution, removal of organic material using a muffle furnace and finally electroplating and alpha spectroscopy to screen for actinides. To distinguish isotopes of similar alpha energies or overlapping alpha peaks, sequential elution using HNO_3 , HCl and HCl-oxalic acid solution was also studied to elute (a) uranium, (b) americium and curium, and (c) plutonium and thorium isotopes separately. This helped to distinguish isotopes with overlapping alpha energies in the alpha spectra. ^{232}U , ^{243}Am , $^{236,242}\text{Pu}$, and ^{230}Th were used as tracers to determine the activities of the radionuclides. This method can be used in the event of a radiological emergency resulting from a radiological incident.

NUCL 134

Sorbents for removal of radionuclides from water and foodstuffs

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Foodstuffs and their ingredients can be contaminated with radionuclides from both natural and anthropogenic sources. For example plants will concentrate uranium that occurs naturally in soil or is present due to the use of uranium-containing armor-piercing weapons. Nuclear fallout due to reactor accidents or atomic bombs can lead to milk contaminated with radioactive strontium isotopes. Calcium tungstate, tungstic acid, and tungsten oxide were discovered to react selectively with heavy metals and actinides, allowing their separation from beneficial metal ions. Reactions using bulk materials tend to be slow but can be accelerated by supporting the sorbents as nanoparticles on high-surface area support. In the case of calcium tungstate, this was accomplished by developing a single-source precursor. The tungsten oxide-based sorbents can be used to remove strontium from milk or calcium-containing food additives, can be used to purify water for drinking and agricultural purposes, and can prevent uptake of actinides by crops. Similarly, heavy metals can also be removed from foodstuffs and juices.

NUCL 135

Investigation into pre-concentration and separation of ^{241}Am from trivalent lanthanides in aqueous solution utilizing a carbon fiber microelectrode

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Previous work showed that a mercury film microelectrode was successful in pre-concentrating 10^9 atoms of an individual trivalent lanthanide or multi-element mixture via a monolayer sorption mechanism. This work focuses on applying the previously established pre-concentration technique to separate and pre-concentrate a mixture of trivalent lanthanides and ^{241}Am in an acidic aqueous solution.

NUCL 136

Effects of elemental interferences on radioanalytical analysis of urban rubble

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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. Of particular interest to nuclear forensics are methods that can be applied to the analysis of concrete, asphalt, glass, and steel. Chromatographic resins have been used for nuclear forensic separations for several years now, and a large amount of data has been published on the retention capabilities of these resins for a variety of elements that can be found in environmental samples. Little can be found, however, on the effects that complex matrices from debris samples can have on analyte uptake. The research presented aims at obtaining this information by examining common urban materials' compositions and investigating their effects on radioanalytical separations.

NUCL 137

Uranium age dating (U-234 to Th-230) using natural thorium as a yield monitor

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Typically, the measurements of Th-230 are accomplished using NIST standard Th-229 (SRM 4328C). This standard has proven to work well as the alpha peaks are easily resolved from other isotopes. The problem with this standard is that there is a relatively high uncertainty. NIST claims approximately 2% uncertainty based on measurements conducted in 1950 from the decay of U-233. Since then, a study has been made investigating this measurement¹ and determined the half-life of Th-229 to be 7% greater than the accepted value. If natural thorium is used instead for the uranium age date monitor, the uncertainty in the half-life is less than 1%. This will make a large difference in the precision and accuracy in the measured age of the sample. Data will be shown to compare the two isotopes as tracers.

1 Half-life of ^{229}Th . S.J. Goldstein, M.T. Murrell, R.W. Williams, Phys. Rev. C **40** (6), 1989

NUCL 138

Investigation of a modified carbon paste electrode utilizing Diethylenetriaminepentaacetic acid (DTPA) as a complexing ligand in aqueous media

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In nuclear forensic analyses, identification and quantification of trivalent f-element isotopic signatures in samples can provide valuable clues about the origin and history of the samples. Rapid separations are needed to prepare samples for actinide isotopic analysis by mass spectrometry, and these separations can be accomplished by automated approaches such as ion chromatography or capillary electrophoresis. However, these methods require relatively small volumes of dissolved samples, typically achieved via a pre-separation chromatographic clean-up of the sample using an ion-exchange or solid phase extraction column. Electroanalytical methods offer a small volume, fast and robust alternative to a pre-separation clean-up column. Modified carbon paste electrodes containing complexing ligands offers significant promise as a method for pre-concentrating trivalent f-elements in aqueous media. Our results to date will be presented and discussed in the context of the overall process of nuclear forensic analysis of environmental samples.

NUCL 139

Automation of column-based radiochemical separations for actinide analysis

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The isotopic analysis of actinides from complex matrixes such as environmental samples entails bringing the actinides into solution, separating them from the sample matrix, separating actinide elements from one another, and concentrating them for presentation as a source to a detector. We have developed a sequence of automated methods to both accelerate the processes of radiochemical sample preparation, and to reduce the labor using automation. Matrix separations may be performed using column-based extraction chromatography methods rather than classical precipitation methods. Actinides are separated by anion exchange, also a column-based method. We have developed an automated workstation for column-based separations to process several

samples in parallel, reducing labor and operator attention compared to gravity feed or vacuum box approaches. It has been designed with rigorous prevention of cross contamination. Examples and performance data using radiometric methods and mass spectrometry will be described for plutonium isotope determinations.

NUCL 140

Selective actinide coordination: Imine soft-donor ligands for sensors and sensing applications

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An increase in the use of nuclear fuels for electrical power production is one proposal to limit global dependence on fossil fuels; however, the environmental and health concerns that surround the use of nuclear fuels limit the acceptance of nuclear power by the public. Because of this, new ligands are required that can coordinate, sense, and purify actinides for use in sensors or decontamination applications. In an effort to develop inexpensive ligands for colorimetric selective sensing of actinides, we have developed ligands incorporating quinoxalines or imine aza-donors into a salen-like backbone. Complexes with early transition metals were also prepared for comparison and found to be useful in ligand supported catalysis. The spectroscopic results indicate potential for new colorimetric sensors for actinide metal ions. Expanding our fundamental knowledge of actinide coordination chemistry will allow for the development of improved actinide sensors, new separations methods, or new means of radioactive waste remediation.

NUCL 141

Quantitative separation of lanthanoids in nuclear fuel using a two stage separation technique

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We face challenges in predicting accurately and precisely the fission spectra produced by research reactors. To this end, we are analyzing spent nuclear fuels and comparing the lanthanoid isotopic spectrum to Origen and comparable predictive models. The fissionogenic isotopic spectra of Nd through Gd reveal the reactor's operational history and can be precisely measured using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), given high efficiency chromatographic separation methods. This work details a two-step cation exchange separation method of a surrogate nuclear fuel for the precise isotopic analysis of Nd, Sm, and Gd using MC-ICP-MS. Results

emphasize the significance of early separation of high activity contaminants from the lanthanoids. Refined cuts of individual lanthanoids show contamination from adjacent elements below 1 part in 10,000 with picogram blank levels. Presently, three nuclear fuel samples at SRNL have undergone the first stage separation and are being prepared for the lanthanoid separation.

NUCL 142

Characterization of actinide and lanthanide-N-donor ligand complexes by various kinds of spectroscopic methods

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The elucidation of chemical bond and structural properties of actinides and lanthanides with neutral N-donor molecules is key information for design for a new ion recognition reagent between trivalent actinides and lanthanides. Especially, it is important to note participation of generally-localized 5f electron into chemical bond across the filled 6s and 6p orbitals. The possibility that the covalent interaction is contributed by the 5f electrons was suggested by the DFT calculation methods while the studies dealing with this phenomenon based on the experiment are not still necessarily sufficient. On these backgrounds, we studied the electronic structural features of N-donor complexes with actinides: U, Pu, Am, Cm, Cf and lanthanides through the excitation and emission spectroscopies, and furthermore performed structural studies of uranium and lanthanide-N-donor complexes based on the X-ray crystallography and EXAFS methods. The N-donor ligands used in this study were pyridine amide (PDA), benzimidazole (BIZ), 1,10-phenanthroline (Phen), benzimidazole amide, and phenanthroline amide (PTA). In this talk, we will discuss about the relationship between spectroscopic features and coordination properties, e.g., coordination polyhedron, chemical bond properties, bond distances.

NUCL 143

Cation-cation interaction between Np(V) and U(VI) and its effect on the behavior of Np(V) in solvent extraction and disproportionation

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Cation-cation interactions between NpO_2^+ and UO_2^{2+} were studied at different temperatures (283.15 K to 358.15 K) and different ionic strengths (3 – 4.5 mol dm⁻³). The complex between NpO_2^+ and UO_2^{2+} was weak and became stronger as the temperature was increased. The molar enthalpy of complexation was directly determined for the first time by microcalorimetry to be (4.2 ± 1.6) kJ mol⁻¹ at 298.15K, in good agreement with the trend in the stability constant at different temperatures. The

small and positive enthalpy and entropy of complexation support the argument that the cation-cation complex between NpO_2^+ and UO_2^{2+} is of inner-sphere type, where the NpO_2^+ moiety enters the primary equatorial coordination sphere of UO_2^{2+} and coordinates to UO_2^{2+} with one axial oxygen of NpO_2^+ . At each temperature, the stability constants of the cation-cation complex were found to increase as the ionic strength was increased. In addition, the effect of the cation-cation interaction between NpO_2^+ and UO_2^{2+} on the behavior of neptunium in solvent extraction and disproportionation is investigated.

NUCL 144

Separation of americium from curium and trivalent lanthanides using pyridine-based receptors

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Spent nuclear fuel consists of four primary categories of waste: short-lived isotopes from neutron capture, short-lived fission products, long-lived actinides, and long-lived fission products. Of these, the long-lived actinides are particularly difficult to separate from the shorter-lived lanthanide fission products. Yet the isolation of the minor actinides from the lanthanides significantly reduces the radiotoxicity and heat-load of long-lived nuclear waste and also allows transmutation of the actinides to isotopes with shorter half-lives. Alternatives to the TALSPEAK process for the selective separation of minor actinides, particularly americium and curium, from lanthanides in actual spent fuel are being investigated. Separation of americium from curium is also of high interest for transmutation of americium and potential recovery of heavy curium. Compounds with selectivity for americium and curium under conditions relevant to the nuclear fuel cycle (i.e. nitric acid media containing light lanthanides through gadolinium in quantities about 10 times greater than those of minor actinides) are pyridine-based receptors. The nitrogen-based BTP/BTBP/BTPPhen ligands are desirable for both separation ability and for being incinerable, and can remove pH control and aqueous complexants from the extraction process requirements. The presentation will highlight several ligands in this class that were analyzed for their respective stability, solubility in Cs-7SB/Isopar L, and separation ability. Study of the impact of the addition of tetraethyl diglycolamide as an aqueous complexant showed that such a liquid/liquid system could lead to improvement in the observed americium/curium separation factor.

NUCL 145

Solution thermodynamics of actinide complexation by hydroxypyridinonate chelating agents and endogenous ligands

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Events of the last decade have called attention to the persistent possibilities of environmental and human contamination with radioisotopes such as lanthanide fission products and actinides. The challenge of limiting exposure to radionuclides and of establishing controlled industrial processes has given rise to unprecedented interest in developing specific lanthanide and actinide sequestering agents for separation and decontamination purposes. Our studies rely on several spectroscopic techniques to characterize the selective binding and recognition of *f*-elements by natural and synthetic ligands. The photophysics and solution thermodynamic properties of Ce(III), Cm(III), Ce(IV), Th(IV), Pu(IV), and U(VI) complexes formed with selected hydroxypyridinonate chelating agents and proteins were investigated. The specific interactions between the metal ions and these ligands were then correlated to the respective *in vivo* behavior of the resulting complexes and may be used in the development of general predictive thermodynamic models.

NUCL 146

Development and use of actinide specific sequestering agents

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A general review of the coordination chemistry of the actinides will be presented and specific aspects of ligand selectivity will be discussed. The development of actinide-specific sequestering agents at Berkeley began with the observation that the similar coordination features of Fe³⁺ and Pu⁴⁺ could be used to develop synthetic analogs of microbial iron transporters (siderophores) as potential therapeutic actinide chelators. Such agents have now been developed for applications in the removal of radioactive species in exposed individuals. While this chemistry has thus far been targeted toward decorporation, this technology can also be applied to the delivery of radioisotopes for diagnostic or therapeutic applications. A recent octadentate macrocyclic ligand has shown extremely high thermodynamic stability and fast metal complexation kinetics with Th(IV), and should be applicable in the chelation of many high-valent metal ions as components of radiopharmaceuticals.

NUCL 147

Understanding the chemistry of f-elements through systematic comparisons: A pathway toward effective fuel reprocessing strategies

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During a professional career spanning more than five decades, Dr. Richard G. Haire has had an opportunity very few scientists have enjoyed (or perhaps will ever again

enjoy): working “hands on” with “macroscopic” quantities of most of the actinides between Ac and Fm. A perusal of his publication list establishes an extraordinary breadth of studies of these most unique of elements, focusing primarily on very fundamental investigations of the physicochemical properties of actinide materials. That same philosophy (investigating the fundamental chemistry of f-elements) has the potential to provide important advances in the challenging technological task of partitioning of actinides from used nuclear fuels for recycle and transmutation. Building on PUREX chemistry, the more complex separations needed for transmutation and recycle of transplutonium actinides represent a fertile ground for fundamental science to have great impact. This talk will focus on selected fundamental studies of lanthanide-actinide separations challenges. Work supported by the U.S. Department of Energy, Office of Nuclear Energy, FCR&D Program

NUCL 148

Spectroscopic investigation of selected uranium compounds in ionic media

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Ionic systems consisting of salts that are liquid can act as solvents for a broad spectrum of actinide species. These melt systems consist only of ions and can be tailored for various pyrochemical processes. The unique solvation environment associated with these high-temperature media is the key to many of these application in potential advanced nuclear fuel cycles. High-temperature spectroscopic techniques have been used to probe the solvation environment and chemistry of actinides in molten salts. Challenges and opportunities in this research area will be discussed.

Acknowledgments : This work was conducted at the Oak Ridge National Laboratory and supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract No. DE-AC05-00OR22725 with UT-Battelle, LLC.

NUCL 149

Separations of berkelium from californium and other actinides using resin based columns

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Berkelium, a radioactive man-made element in the actinide series, was discovered in December of 1949. ²⁴⁹Bk is the most common isotope of berkelium having a 330 day half-life and nearly 100% low-energy electron emission via beta decay to ²⁴⁹Cf. Cf and

Cm isotopes present the greatest impurity issue to ²⁴⁹Bk processing since they are the nearest neighbors in the actinide series and are produced in large quantities during the target irradiation. The current separation and purification process utilizes solvent extraction methods that are both lengthy and complex. This report will discuss separation and purification of Bk using ion exchange resins and solvent extraction resins. Also investigated is the impact that the oxidation of Bk from +3 to +4 has on these resin separations

NUCL 150

Analysis of Plutonium-239 and Americium-241 in food samples by alpha spectrometry

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Plutonium-239 and Americium-241 are man-made isotopes which have entered the environment through the atmospheric testing of nuclear weapons during the 1950's and 1960's.

Six food matrices (flour, cinnamon, salmon, yogurt, baby food and lettuce) were selected for this study. Each matrix was analyzed at two spiking levels, 0.09 and 0.14 Bq with five to ten replicates for each level. Coefficient of variation was <10%.

Samples were digested in a microwave using nitric acid and hydrogen peroxide and passed through a resin column to chemically purify and separate plutonium and americium. Isotopes were eluted with hydrochloric acid, microprecipitated, mounted on 0.1 µm filters and counted on an alpha spectrometer for 1000 minutes.

This method is reliable with a 94 – 104% recovery. Validation results demonstrate this method is accurate, sensitive, rapid and suitable for monitoring food commodities suspected of exposure to radiation contamination.

NUCL 151

Rapid method for analysis of radiostrontium in milk

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Classical methods for the determination of radiostrontium in milk are labor intensive and relatively slow. This paper presents the results of method development work on a rapid radiostrontium analytic method that combines classical ion exchange and new SPE extraction chromatography.

NUCL 152

Marshall Islands dose assessment and radioecology program: An overview

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The United States conducted 67 atmospheric nuclear tests in the northern Marshall Islands between 1946 and 1958. Radiation doses calculated for radiological conditions on the main residence islands of Bikini Island at Bikini Atoll, Enewetak, Meden and Japtan Islands at Enewetak Atoll, Rongelap Island at Rongelap Atoll, and Utrök Island at Utrök Atoll show that cesium-137 accounts for up to 98% of the nuclear-test related dose for resettled and resettling populations. About 85 to 90% of the dose is derived from consumption of locally grown terrestrial foods containing cesium-137, and about 10 to 15% is due to external gamma exposure from residual cesium-137 in the soil. The other long-lived fallout radionuclides of potential concern include strontium-90, Pu isotopes and americium-241. Understanding of key radionuclides and their relative behaviors and exposure pathways in coral atoll ecosystems, updated assessments based on the effective half-life of cesium-137 in the environment, and introduction of appropriate remedial measures, where deemed applicable, show that the total predicted radiation dose (natural + anthropogenic) at Bikini, Enewetak, Rongelap and Utrök can be managed at each of these sites at levels that are less than the average natural background radiation dose in the U.S. and Europe.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

NUCL 153

Determination of the ingestion dose caused by natural and artificial radionuclides in various foodstuffs for the Austrian population

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Determinations of natural and artificial radionuclides in foodstuffs have been conducted in our laboratory for several years. The main focus of attention is the determination of ^{137}Cs and ^{90}Sr in several food stuffs and ^{238}U , ^{228}Ra , ^{226}Ra , ^{222}Rn , ^{210}Pb and ^{210}Po in water. In the year 2012 we started measurements of ^{90}Sr , ^{210}Pb , ^{210}Po , ^{137}Cs and ^{40}K in various foodstuffs. Measurements are performed with gamma spectrometry, liquid scintillation counting, ICP-MS and alpha spectrometry. For the sample preparation ion exchange columns, precipitations and extractive scintillation cocktails are used. The ingestion dose is assessed using the data of food consumption rates of the Austrian population and the committed effective dose per unit intake factors from the European

Commission Council Directive 96/29/Euratom of 13 May 1996. Short descriptions of the sample preparation, the results of our measurements and of the dose calculations are presented.

NUCL 154

Determination of Po-210 in groundwater for samples containing high dissolved solids

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An alpha spectroscopy method was developed for Po-210 analysis of groundwater samples. To obtain a LOQ of 1 pCi/L, a volume of 500 mL, or more, is often required. Typically, samples are acidified to 5% v/v with nitric acid to prevent Po-210 from precipitating or adhering to the container. Groundwater contains dissolved silica, often near its 14 ppm saturation level. During sample reduction, nitric acid concentrates and catalyzes the formation of silica gel, making quantitative Po-210 recovery unattainable. In this method, HF prevents silica gel formation; subsequently, boric acid dissolves insoluble fluoride salts. Po-210 was quantitatively recovered when 1 liter of Madison, WI tap water (treated groundwater with hardness 419 mg/L) was placed in polyethylene bottles, spiked with Po-210, and allowed to sit for up to 2 weeks before adding 5% v/v nitric acid and a Po-209 tracer. Thus, this method works on water of very high hardness.

NUCL 155

Rapid procedure for the analysis of radionuclides in liquid samples

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a multifaceted radiochemical testing procedure has been developed to analyze a large number of liquid samples and measure a wide range of radionuclides in a short period of time. This method involves a single unique and fast sample separation procedure in which the same prepared sample can be selectively analyzed by gross alpha counting, Gamma-ray spectroscopy, and alpha spectroscopy. This wide range of analytical capability allows for utilizing this method as a quick screening procedure or for identifying and quantifying most gamma- and alpha-emitting radionuclides. The main focus of this presentation will be the recent success of performing thick source alpha spectroscopy.

NUCL 156

Development of a sensitive on-line monitoring system for the analysis of radionuclides in water samples

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For the environmental analysis of radionuclides in water samples, off-line liquid scintillation counting (LSC), a mature radioactivity quantification technique, is often used for low-level measurements. However, the analysis is both time consuming and costly in terms of labour, consumables expenditure and waste production. In this work, we describe the development of a novel, portable on-line water monitoring system that undertakes automated sampling and measurement and can operate for long periods (weeks) unaided. The prototype system has been evaluated by the US EPA and has proven itself in terms of long-term reliability, low background levels (<5 cpm) and a detection limit in the nCi/L range, which is below the EPA and EU-imposed limits for tritium concentration. We also describe the research undertaken as a result of the evaluation, which has sought to optimise the instrument for a range of radionuclide analyses, to permit their discrimination and improve the sensitivity still further.

NUCL 157

Evaluation of gross alpha measurements for MCL compliance

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This two-part study quantified factors affecting the gross alpha activity (GAA) of groundwater samples analyzed by EPA Method 900.0. In part 1, a model was developed to estimate a sample's GAA range from its physical and radiological data; in part 2, 79 samples were analyzed, and model and experimental GAAs compared. Part 1 showed the GAA decreases as residue nonuniformity increases, the GAA increases as residue mass increases, and Ra-224 and its progeny and Ra-226 progeny contribute disproportionately to the GAA. Part 2 results showed the model and experimental GAAs agreed for most samples; however, the model GAA range increases significantly with residue mass. At low masses (≤ 5 mg), where the range is small, agreement between model and experimental GAAs was excellent. This study yielded guidance on identifying false-positive GAAs and showed that model GAAs are useful in determining whether a sample's alpha emitters have all been accounted for.

NUCL 158

Measurement of lanthanide isotope ratios in spent research reactor fuel by multi-collector inductively coupled plasma mass spectrometry

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Worldwide, research reactors are among the least secured nuclear material facilities, and they often contain high enriched Uranium materials. From a nuclear forensics perspective, research reactor fuels are also the least studied type of spent fuel. Nuclear power reactors are typically benchmarked by computer models, but it is uncertain if these models will accurately predict the spent fuel composition of a research reactor. Accurate modeling of this fuel is necessary, however, to provide reliable targets for a potential nuclear forensics investigation. In recent years, the Savannah River National Laboratory has undertaken a campaign to validate the predictions of these models for archived research reactor fuel. The focus of this talk will be on the efforts to measure rare earth element isotope ratios in samples of the archived fuel, via multi-collector inductively coupled plasma mass spectrometry.

NUCL 159

Carbon isotope signatures of TBP relative to nuclear reprocessing and disposal

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Tributyl phosphate (TBP) is predominately used in the PUREX process. After repeated use, TBP becomes inefficient and must be treated for disposal. A common disposal method is subjecting the spent solvent to alkaline hydrolysis. This work uses a Gas Chromatography Combustion Isotope Ratio Mass Spectrometer to determine whether there is a unique carbon isotope signature for TBP in nuclear reprocessing apart from disposal by studying fundamental characteristics of TBP in acidic and basic hydrolysis. The $\delta^{13}\text{C}$ value of our unreacted TBP is $-30.79 \pm 0.12\text{‰}$. This TBP reacted with 8M nitric acid for approximately one week is $-30.54 \pm 0.17\text{‰}$, and the TBP after reaction with 19M sodium hydroxide over the same period of time is $-30.54 \pm 0.24\text{‰}$ indicating no fractionation. However, the hydrolysis reactions were not complete and continuing experiments will show complete hydrolysis and carbon stable isotope analysis of TBP degradation products, dibutyl phosphate (DBP), monobutyl phosphate (MBP) and butanol.

NUCL 160

Production of protactinium-233 for age dating highly enriched uranium materials

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Age dating highly enriched uranium (HEU) materials for nuclear forensics is an important measurement to aid in the safeguarding and non-proliferation of this very sensitive man-made material. The two most prominent uranium based parent/daughter ratios used for age dating unirradiated HEU are $^{234}\text{U}/^{230}\text{Th}$ and $^{235}\text{U}/^{231}\text{Pa}$. It has been documented in the literature that the $^{234}\text{U}/^{230}\text{Th}$ clock can be measured with high precision using isotope dilution (ID) combined with multi-collector mass spectrometry techniques. However, due to the lack of a long-lived protactinium isotope age dating measurements have been limited to the use of alpha count techniques which have a higher degree of uncertainty than methods based on isotope ratios using mass spectrometry. Using the High Flux Isotope Reactor to produce protactinium-233 from neutron activation of thorium-232 for use as an ID spike, ORNL has measured the $^{235}\text{U}/^{231}\text{Pa}$ clock in HEU with a high degree of precision using ID techniques. Presented will be ORNL's effort to produce protactinium-233 for use as an analytical forensic tool for age dating HEU in support of nuclear safeguards and non-proliferation.

NUCL 161

Measurement of U and Pu isotope ratios in hair and nail samples using multi-collector inductively coupled plasma mass spectrometry and extraction chromatography

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Monitoring the production of weapons grade U and Pu in nations suspected of pursuing nuclear weapons is a national security interest. A bioassay of personnel suspected of involvement in nuclear activities could be included as part of an IAEA inspection process. Hair and Nail samples are a convenient, non-invasive biological monitor that could reflect occupational exposure to U and Pu. We will report on a method to measure $^{235}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$ and $^{239}\text{Pu}/^{240}\text{Pu}$ in hair and nail samples using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) with a desolvating nebulizer. The method employs a microwave digestion procedure followed by a separation with TEVA, UTEVA and DGA resins to isolate ^{239}Pu from U and other potential mass interferences for measurement of $^{239}\text{Pu}/^{240}\text{Pu}$. We will report spike recovery, instrumental detection limits, and isotope ratios of U and Pu measured in scrap hair and nail samples and reference materials.

NUCL 162

Organic fingerprinting of uranium ore concentrates using sorptive extraction

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A sorptive extraction method utilizing Gerstel Twister™ stir bars, in combination with GC-MS, has been successfully used for organic fingerprinting of uranium ore concentrate (UOC). This method was used to identify organic compounds characteristic of the purification process by which uranium was separated from ores obtained from two mining and milling sites. The polydimethylsiloxane coating on the Twister™ stir bars was used to extract organic components from UOC suspended in an aqueous media of 20% methanol/80% water. Following extraction of organics, the stir bar was analyzed directly in the inlet of a gas chromatograph fitted with a quadrupole mass spectrometric detector. Results showed excellent recoveries of internal standards, with the average being 97.5%, and qualitative differences between the two sources of UOC. Presented will be ORNL's effort to develop and validate this technology for use as an analytical tool for sourcing unknown UOC in support of nuclear safeguards and non-proliferation.

NUCL 163

Radionuclide plant uptake studies in support of nuclear forensics

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In this work, the influence of Fe(III) competition on Pu(IV) uptake in corn (*Zea Mays*) has been examined. Knowledge of the extent and mechanisms of radionuclide uptake in plants can be used to support nuclear forensics efforts wherein the plants serve as in situ collection and monitoring devices. To effectively apply this concept; the extent of radionuclide uptake into plants must be known in order to identify plant types capable of accumulating sufficient activities of radionuclides for subsequent detection. Radionuclide uptake can be influenced by complexation with natural organic matter or through competition with major cations such as Fe(II) or Fe(III). ²³⁸Pu and ⁵⁵Fe uptake was monitored in hydroponic systems and both the roots and the plant shoot were monitored separately. The results indicate that 1.8% ± 2.3% and 8.6% ± 3.8% of the total iron and plutonium, respectively, was taken into the root system and that 0.19% ± 0.17% and 0.06% ± 0.05% of the total iron and plutonium, respectively was taken all the way into the shoots (n=8). The difference in the extent of Fe(III) and Pu(IV) transfer to

the shoots is likely attributable to differences in Fe(III) and Pu(IV) binding with plant derived organic ligands and can be explained using thermochemical speciation modeling. Similar fractions of Pu(IV) are accumulated in the plant across a wide range (10^1 - 10^5) of Fe:Pu molar ratios. Therefore, there is little apparent competition between Fe(III) and Pu(IV) and the potential for an alternative pathway for Pu(IV) uptake exists. Ongoing experiments using mutant strains of corn with limited iron uptake ability will examine the potential for this alternative pathway.

NUCL 164

Living under pressure: Experimental studies of actinide metals at ITU and ORNL

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In contrast with other metals, actinide elements from protactinium through plutonium exhibit, at atmospheric pressure, low-symmetry crystal structures and small compressibility, as an effect of the *5f*-electron character in their bonding. Americium and heavier actinides have fully localized *5f* electrons and more symmetrical close-packed crystal structures, similar to those observed in lanthanides. However, upon compression, changes in the *5f* occupancy and the hybridization with *spd* states destabilize the crystal structure and give rise to a rich polymorphism not observed elsewhere in the Periodic Table. Here, I will present some of the most significant results obtained at the Institute for Transuranium Elements in the framework of a collaboration with Dick Haire, which has been ongoing for more than three decades, including high-pressure x-ray diffraction characterization of allotropic phases in Pa, Am, Cm, Bk, Cf, and Es, studies of electronic spectra in Am and Cm, superconductivity in Am, and magnetism in Cm.

NUCL 165

Transuranium elements: Impact on geologic disposal

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Transuranium elements, particularly Pu and Np, have a substantial impact on strategies for the geologic disposal of nuclear fuel. During the past decade, researchers, including Richard Haire, have investigated chemically durable, radiation-resistant materials, such as actinide-bearing pyrochlore, $A_2B_2O_7$ (A = rare earths; B = Ti, Zr, Sn, Hf), for the immobilization and disposal of actinides. Systematic studies of rare-earth pyrochlores have led to the discovery that certain compositions (B = Zr, Hf) are stable to very high doses of alpha-decay event damage. The radiation stability of these compositions is related to the structural distortions that occur for specific pyrochlore compositions and the electronic structure of the B-site cation. The observed trends in radiation resistance have been extended to understanding order-disorder transformations and radiation-

induced amorphization under very extreme conditions of high pressure (up to 100 GPa) and high-energy (GeV) irradiations.

NUCL 166

Production and recovery of transplutonium elements at ORNL

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The Radiochemical Engineering Development Center (REDC) and the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL) have produced transplutonium elements since 1965. With the exception of ^{252}Cf , all of these elements have been used for research and development. All of the feed material for the production of the transplutonium elements was produced at the Savannah River Site (SRS). With the shutdown of the reactors at SRS and the loss of feed material due to decay and production of transplutonium elements at ORNL, the preservation and efficient use of the remaining feed materials is critical to a continuing supply of transplutonium elements for research and development.

Efforts to maintain and supplement the existing supply of feed material are currently underway and/or being studied. In addition, specific transplutonium isotope production and recovery scenarios are being analyzed that should offer higher yields and/or a more flexible availability than in the past.

NUCL 167

Non-aqueous synthesis and crystal growth of rare-earth metal organics for radiation detection applications with implications for actinide chemistry

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We have shown that new scintillating materials can be developed based on the non-aqueous synthesis and crystal growth of rare-earth metal-organic compounds. The first scintillator of this type consisted of single crystals of $\text{CeCl}_3(\text{CH}_3\text{OH})_4$ that were grown by reacting CeCl_3 in methanol. These crystals were applicable to both gamma ray and fast neutron detection. We have now extended this class of scintillating materials by reacting CeCl_3 or CeBr_3 with different isomers of propanol and butanol – including 1-propanol, isobutanol, n-butanol, and tert-butanol. These reactions form new and relatively complex molecular crystals whose structures were determined using single-crystal X-ray diffraction. These scintillator materials were grown in single crystal form from solution, and their scintillation characteristics were investigated using X-ray-excited luminescence and pulse height spectra obtained with gamma ray and alpha particle sources. If the reactions between the inorganic and organic components are not carried

out under dry conditions, molecular structures can be formed that incorporate waters of hydration. The observation of scintillation in hydrated rare-earth metal-organic compounds is apparently an original finding, since we are not aware of previous reports of scintillation for any material that incorporates waters of hydration. We believe that these results also have implications for the non-aqueous synthesis of potentially new actinide molecules.

NUCL 168

Recovery and target production of Cf-251 for super heavy element research

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A californium product that is enriched in ^{251}Cf has been recovered for use in establishment of a new route for super-heavy element (SHE) research. This neutron rich isotope provides feed material for SHE research that has sufficiently low radioactivity to enable safe target production and handling for experiments to access elements $Z=118$ and above. The focus of this work was the processing of old ^{252}Cf neutron sources in storage at ORNL. These sources have decayed for over 30 years thus providing material with a very high ^{251}Cf to ^{252}Cf ratio. After the capsules were opened, the Cf was purified and electrodeposited onto thin titanium foils for use in the accelerator at Dubna, Russia. Presented will be the processing and chemical steps involved in the capsules recovery, sample dissolution, chemical separation, and electrodeposition.

NUCL 169

Superheavy element discovery and chemistry program at LLNL

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The heavy element program at Lawrence Livermore National Laboratory has a long tradition of nuclear and radiochemistry dating back to the 1950's. Some of the most exciting work has been in collaboration with the Flerov Laboratory of Nuclear Reactions in Dubna, Russia with the discovery of elements 113, 114, 115, 116, 117, and 118. By pushing the boundaries of the periodic table, we can address the possibility of an "Island of Stability" where nuclides would have lifetimes longer than those currently observed. We have seen evidence of extra-stability in the heaviest nuclides, with half-lives long enough for us to perform chemistry on these isotopes. Work is underway on developing automated chemistry that will be used for studying the transactinides. These experiments will provide the ground work for performing aqueous chemistry on even heavier elements. In this overview the discovery of these elements and chemical experiments in progress will be discussed

NUCL 170

Great discoveries in the new millenium: Physics and chemistry of the heaviest elements

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Since the dawn of the new millenium, a Dubna-LLNL collaboration has been reporting production of superheavy element (SHE) isotopes in reactions of ^{48}Ca beams with actinide targets. To date, these experiments have netted 52 new isotopes of six new elements. Despite attempts at other laboratories, these results went unconfirmed for over eight years. Finally, the production and decay of ^{283}Cn was reproduced both with the SHIP separator at GSI and in radiochemical experiments by the PSI group working at Dubna. Early in 2009, we used the $^{48}\text{Ca} + ^{242}\text{Pu}$ reaction in the Berkeley Gas-filled Separator at the LBNL 88-Inch Cyclotron to independently verify the production and decay of two isotopes of element 114 ($^{286}114$ and $^{287}114$). Later in 2009, we also participated in a further SHE confirmation experiment with the TASCA gas-filled separator group at GSI. In these experiments the production and decay of two more neutron-rich isotopes of element 114 ($^{288}114$ and $^{289}114$) was observed in the $^{48}\text{Ca} + ^{244}\text{Pu}$ reaction. In all $^{283}112$ and $^{286-289}114$ confirmation experiments, the production cross sections, half-lives, decay modes, and decay energies agree with the present Dubna claims. These confirmations led to the recent naming of Flerovium, Fl, and Livermorium, Lv, for elements 114 and 116, respectively.

First chemical characterization gas phase experiments of Fl and Cn will be discussed. Liquid-liquid extraction studies on Fl and Cn homologues will be reported.

NUCL 171

Electrodeposition of actinide compounds from an aqueous ammonium acetate matrix: Experimental development and optimization

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Electrodeposition is an experimental technique routinely employed in nuclear research for the preparation of thin solid films (e.g. actinide films) that can be used in accelerator beam bombardments, irradiation studies, or as radioactive sources. The present study investigates the deposition of both lanthanides and actinides (lanthanides serve as nonradioactive actinide surrogates) from an aqueous ammonium acetate electrolyte matrix. Electrodepositions were performed on platinum disks, stainless steel disks, and titanium foil, with yield analysis evaluated using both UV/VIS spectrophotometry and gamma spectroscopy. Experimental parameters (run time, current density, and voltage) were studied and modified in order to optimize the deposition and maximize the yield. Initial development utilized samarium as the plating material, with and without a

radioactive tracer. Surface morphology studies are performed by scanning electron microscopy.

NUCL 172

Rapid screening of $^{243+244}\text{Cm}$ in foods by solid phase extraction: Liquid scintillation counting

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This paper presents a rapid screening method for the detection of $^{243+244}\text{Cm}$ alpha radioactivity in foods. The method uses DGA resin (*N,N,N',N'*-tetra-*n*-octyldiglycolamide), which has strong affinity for curium (Cm) in nitric acid media, to extract Cm isotopes from foods that were wet ashed in 8M nitric acid. The extracted Cm isotopes were reclaimed from the resin using 0.1M HCl–0.1M $\text{H}_2\text{C}_2\text{O}_4$ and total alpha radioactivity was then quantified by alpha/beta discriminative liquid scintillation counting. The method was developed and validated using meat, grain, vegetable, dairy, and composite food samples spiked with known amounts of ^{243}Cm and ^{244}Cm . The study results showed that matrix and natural radiometric interferences were adequately removed while greater than 95% of ^{243}Cm and ^{244}Cm were recovered from 15-min batch extraction using 1 g of DGA resin. The experimental results, instrument optimization, and estimate of minimum detection limit with consideration of alpha/beta crossover interference will be discussed.

NUCL 173

Applying self-attenuation and coincidence-summing corrections for gamma-ray spectrometric analysis of foods using GESPECOR and LabSOCS

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This paper presents a practical application of Monte Carlo simulation packages, i.e., GESPECOR and LabSOCS, for computing self-attenuation and coincidence-summing correction factors in gamma-ray spectrometry analysis of foods. Analysis of gamma emitters in foods is routinely performed in large-sample volume and close-to-detector geometry, where the counting efficiency subjects to significant self-attenuation and coincidence summing due to density variations and complex decay scheme. The required corrections are difficult to derive experimentally without appropriate physical standards which are expensive and not commonly available. To overcome such

limitation, a computational technique with the knowledge of detector characteristics, matrix composition, decay scheme, shielding material, and counting geometry is first applied to identify the key variables that dominate self-attenuation and coincidence-summing effects. Then, the values of self-attenuation and coincidence-summing correction factors relating to the identified key variables are computed. The results from a validation study comparing computational technique with physical standards method will be discussed.

NUCL 174

Monitoring food items for radioactivity content

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The nuclear accident at the Fukushima Daiichi Nuclear Power Plants led to a release of material from the reactor containment into the surrounding area and into the food chain. In response to this threat to public health, there was increased activity in the monitoring of food items for radioactive contamination in Japan, surrounding regions and by importers around the world.

Many food monitoring solutions are now available to provide assurance that the levels of radioactivity in foods are below safe levels (as defined by government health organizations). The challenge for the designers of these systems is that they are used by a range of operators who are not experts in radiation measurement. There need is for rapid deployment, ease of use and ease of interpretation of results.

This paper describes how this and other measurement challenges were addressed in the design of the Canberra Industries FoodScreen system. This shielded system encapsulates several innovative technologies such as the LabSOCS mathematical modeling package in order to pre-calibrate the system for a range of food containers (the operator is not required to calibrate the system and there is no need for radioactive sources). The patented LED detector stabilization technology means that the energy calibration remains stable for a broad range of environmental conditions, deeming re-calibration unnecessary.

The result is an innovative, simple to use system with very low maintenance needs. The system provides a go/no go determination based on I-131, Cs-134, and Cs-137 content. The sensitivity of the system is such that it meets the international regulatory limits for Minimum Detectable Concentrations (MDC) for these nuclides, including stringent new limits imposed by the Japanese regulator in April 2012.

The operational and performance characteristics of the system will be discussed in detail.

NUCL 175

Gamma-ray spectrometry of food and environment

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We describe two applications of low-background gamma spectrometry: measuring Cs-137 in milk and aerosol transport from 2011 Fukushima accident, as well as discuss density and coincidence corrections in samples of food. Following the FERN 2012 Political Surveillance Assignment, we measured Cs-137 in 20 samples of milk from Tampa region of Florida. It is recognized that in the 1960s milk from Florida had one of the nation's highest concentration of Cs-137 resulting from radioactive fallout due to atmospheric nuclear weapons testing. One reason for this is the natural deficiency of Florida soils in potassium, resulting in plants compensating by increased uptake of cesium; another is a particularly high uptake of cesium by Pangola grass, which was used as cattle feed. Using low-background gamma-ray spectrometry, we were able observe the remnants of this effect by detecting Cs-137 in 9 of these samples, with concentrations ranging from 0.061 to 0.22 Bq/kg. Following the Fukushima March 11, 2011 nuclear disaster, low-background gamma spectrometry was used to detect radioactive plume in New York State. Due to atmospheric transport and deposition, only very small levels of radioactivity could be detected. In spite of this, Te-129, Te-132, I-131, I-132, Cs-134,136,137, and La-140 were identified on air particulate filters. It was possible to determine as low as 0.65 micro-Bq/m³ of La-140 on air filter, and 1.8 mBq/L of I-131 in reservoir water. Measuring gamma radiations from voluminous food samples creates challenges due to density, which can vary from 0.3 to 1.5 g/cm³ depending on the food type and the level of blending. In addition, coincidence-summing is a significant effect in large Ge detectors. We have calculated the density and coincidence-summing corrections for different geometries and radionuclides in a tabular format. These corrections are then applied automatically as a last sequence in commercial gamma-analysis software.

NUCL 176

Study on diffusion process of radioisotope materials by destroyed Nuclear Power Plant for ecosystem in offshore FUKUSHIMA-KEN (Prefecture), Japan

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As of 09-OCT-2012 I was employed as a doctoral research fellow for following investigation by Tokyo University of Marine Science&Technology(TUMST) funding by

Ministry of Environment. However it is not easy research because majority of related researchers is feared by something pressures and they have lack of freedom atmosphere for the investigation.

Tokyo Electric Power Fukushima Dai-Ichi Nuclear Power Plant in Fukushima-Ken(Prefecture) was destroyed on 11-MAR2011 due to huge earthquake(Magnitude=9) in Offshore Northeast of Japan with historical Tsunami on 11-MAR-2011. Due to nuclear meltdown, ect. and contamination of cooling water from the reactor, it has been emitted huge amounts of radioisotope to not only atmosphere but also marine water. Currently it is prohibition of fishery in offshore FUKUSHIMA-KEN because majority of fishery product has still contained exceeding Japanese Standard Value of radioisotopes by intermittent investigations until now. Fukushima Prefectural Government and TUMST have measured amounts of radioisotope of fisheries organisms at offshore IWAKI-SHI(City),FUKUSHIMA-KEN(Prefecture)(Located at South of destroyed Nuclear Power Plant) and have continued to discussion on variation of amounts of radioisotope of fisheries organisms based on prediction of diffusion of radioisotope on 11-MAR-2011. However it has never had sufficient data at offshore North of destroyed Nuclear Power Plant and coastal region. It had detected radioisotope Cesium Mass Number 134 and 137 at nearest coastal region in IWAKI-SHI,FUKUSHIMA-KEN, Japan by previous research. Hence it will be very important to monitor diffusion process of radioisotope by fisheries organisms continuously toward the future. We set the two observation lines at IWAKI-SHI,FUKUSHIMA-KEN(Located at 55 km South of the plant) and SOMA-SHI, FUKUSHIMA-KEN(Located at 50 km North of destroyed the plant)for this investigation.We have collected inorganic particles, micro alga, phytoplankton, seaweed, invertebrate and fish at reef ecosystem and sand beach ecosystem to unveil distribution of radioisotope materials and process of diffusion of radioisotope materials.

NUCL 177

¹²⁹I assessment on kelp, oyster, and sea water reveals the influence of Fukushima Incident and local nuclear power plant in Daya Bay, China

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In order to assess the radioactive impact of Daya Bay Nuclear Power Base on the environment of Daya Bay, Guangdong, we combined accelerator mass spectrometry (AMS) with epithermal neutron activation analysis (ENAA) and measured the level of long-lived radionuclide ¹²⁹I in surface sea water, collected from Dapeng Peninsula area in the October of 2010. After the Fukushima incident in March of 2011, we collected surface sea water, oyster and kelp, i.e. *Sargassum henslowianum*, in June of 2011 and April of 2012 to assess the influence of the incident through bioindicators. According to results, ¹²⁹I level showed no significant change in surface sea water caused by

Fukushima incident or Daya Bay Power Plant, but rose significantly by 163% in oyster ($p < 0.001$) and by 101% in kelp ($p < 0.05$) from June of 2011 to April of 2012. This is likely due to bio-magnification from sea water to organisms. Because sea current along the east coast of Japan flows northeast, away from Guangdong area, atmospheric transmission should be the major channel for ^{129}I from Fukushima. This conclusion concurs with the detections of ^{131}I in Novosibirsk and Shanghai after the incident, respectively. According to the standard of Codex Alimentarius Commission, the ^{129}I levels in kelp and oyster are far below the maximum accepted amount in diets, causing no harm to the health of local citizens, but considering the constant release of ^{129}I at the accident site, long term monitor for radioactive nuclides along Guangdong coastal area is necessary and important. Besides, ENAA showed that average ^{127}I level was $5.83\mu\text{g/g}$ in oyster and $461.11\mu\text{g/g}$ in kelp, with concentration coefficients at 217 and 17119, respectively, indicating that oyster and kelp possess high capability of iodine enrichment and are suitable bioindicators for ^{129}I .

NUCL 178

Long-term monitoring of radioactivity in seafood from New York waters

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As part of an environmental surveillance program operated by the New York State (NYS) Department of Health, measurements of various radionuclides in seafood from waterways in NYS have occurred for decades. An investigation was undertaken to gain a better understanding of the sources, activity levels, and extent of radionuclide variations in seafood obtained from local waterways in relation to concentrations reported in seafood from sites outside NYS. For comparison, levels of radionuclides in vegetables, fruits, water, milk, and meat, measured as part of the surveillance program and laboratory participation in the Food Emergency Response Network (FERN), are provided. Estimates of the effective dose resulting from eating seafood were calculated for the observed radionuclides.

NUCL 179

Measurements of natural radioactivity in food crops locally grown in the neighbourhood of Minjingu phosphate mine

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Studies of radioactivity in food crops are important in estimating the radiological hazards and dose exposure to the public. In this study, natural radioactivity levels of ^{40}K , ^{232}Th

and ^{238}U were determined in two staple foods (maize and mung beans) locally grown at Minjingu village where the Tanzania biggest phosphate mine resides. The analysis was carried out using gamma spectrometry of Tanzania Atomic Energy Commission (TAEC) in Arusha. Results from this study will provide information that can verify the extent and the nature of the level of pollution in Minjingu Village associated with phosphate mining. The result will also be used by the authorities for proper intervention to the problem. One of the aims of this study is to determine the safe distance from the mine for crop cultivation. Further studies which will identify the type of crop grown in the area with least uptake of radionuclide are proposed.

NUCL 180

Chemical speciation for forensic science

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We present the application of chemical speciation for forensic science. Many signatures arising from production, conversion, and aging processes are chemical in nature, and spectroscopic measurements performed at LANL reveal the potential to detect persistent molecular signatures characteristic of material origin. The scientific challenge is to identify, measure and understand those aspects of chemical speciation that carry information about material origin and history most relevant to forensics. Research at Los Alamos National Laboratory is making contributions in these areas, from research directed at new materials for radiation detection, to the development of new tools to correlate materials characteristics with its technical history. Here, we describe our efforts in material synthesis and analytical methods development to provide the fundamental science required to correlate chemical and materials properties with its technical history. LA-UR 12-26003

NUCL 181

Coupling radioelement speciation with forensics signatures

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There is a clear desire to improve signature identification for nuclear forensics. A useful approach involves the incorporation of radioelement and radionuclide speciation. Identifying the radionuclide chemical form can be used in different aspects of nuclear forensics. Exploiting the speciation of targeted radionuclides in samples can aid in separations, decreasing time needed for isotope evaluation. For analysis, molecular forensics science has been shown to provide useful information on material of interest. Both these improvement leverage radionuclide speciation in improving forensic analysis.

For separations, an example is provided for volatility separation techniques for nuclear forensics applications. The described volatility separations focus on direct treatment of oxide samples, with actinide and lanthanide oxides treated with hexafluoroacetylacetonate. Through an understanding of the radionuclide speciation in the sample, conditions can be tuned to selectively form actinide or lanthanide species. This can provide a rapid, volatility based analysis yielding isotopic ratios for forensics signatures.

Molecular forensics science provides signatures based on chemical speciation, structure, morphology, and trace composition. As actinide materials are processed for nuclear applications, potential signatures exist that can provide data on origin, separation dates, and chemical treatment. An example is provided for uranium oxides. The use of spectroscopy and microscopy analysis is used to demonstrate the utility of molecular forensics science in identifying signatures. Microscopy analysis revealed origin of uranium oxides. Morphological features provided insight into process conditions for uranium oxide species. Synchrotron spectroscopy gave information on speciation and element correlation.

NUCL 182

Evaluation of the effects of environmental stress on uranium particulates produced using ultrasonic atomization

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Although the majority of studies focus on the environmental transport of dissolved uranium species into the subsurface, airborne particulates formed from industrial processes have the ability to transport long distances. The chemical species of uranium can be altered by interactions with light, humidity, internal chemical species within the particle, or external chemical species on surfaces that come in contact with the particle. Surrogate particulate materials were produced using an ultrasonic atomization process, allowing particulates to be deposited either actively or passively on a variety of substrates that were then stored under static relative humidity environments ranging from 17-95% at room temperature. This work has shown that atomization of uranyl nitrate rapidly and unexpectedly produces material identified as metastudtite ($\text{UO}_4 \cdot 2\text{H}_2\text{O}$). A transition from the dehydrate UO_4 species to a more hydrated studtite ($\text{UO}_4 \cdot 4\text{H}_2\text{O}$) occurs over the course of days to months depending on environmental storage conditions.

NUCL 183

Characterization of humidity induced structural changes in uranium salts monitored by powder X-ray diffraction

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Uranium particulate species generated from commercial reprocessing of nuclear fuel are of interest for nuclear safeguards and security for monitoring activities. Various particulate uranyl species have been produced by ultrasonic atomization of different uranyl salt solutions (nitrate, chloride, oxalate) and exposed to humidity to characterize the induced structural changes. These transitions have been carefully monitored *in situ* by powder X-ray diffraction in a sample holder capable of controlled temperature and relative humidity. Preliminary characterization shows that metastudtite ($\text{UO}_4 \cdot 2\text{H}_2\text{O}$) can be produced from uranyl nitrate solutions and upon exposure to humidity, this mineral transitions to more highly hydrated studtite ($\text{UO}_4 \cdot 4\text{H}_2\text{O}$) over the course of days to months. Rietveld refinement of diffraction scans shows good agreement with recently published structures for both metastudite and studtite and indication of a complete structural transformation. Additional X-ray diffraction characterization of uranium bearing particulates, including uranyl chlorides and oxalates, will be presented as available.

NUCL 184

Feasibility of a uniquely fabricated SERS-SEIRA substrate for uranyl detection

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We have combined two popular nanofabrication methods, physical vapor deposition (PVD) and electroless deposition (ED), to create an optimized SERS-SEIRA substrate. For this approach, a 5 nm Au cap layer is deposited by PVD on top of the Ag-Ge substrate formed by ED. The ED Ag surface serves as the nano-template for Au layer. The Au layer improved the quality of the SEIRA spectra and increased the SEIRA enhancement factor from 20 to 63 without affecting the overall morphology of the underlying nanoparticles. The long term stability, durability, and reproducibility (62% RSD without Au to 17% RSD with Au layer) of the substrate also improved. This substrate is also SERS active using four different wavelengths: 488, 514, 633, and 785 nm. With 785 excitation, detection of trans-1,2-bis(4-pyridyl)-ethylene (BPE) in the femtogram (fg) range has been observed. Initial studies using these substrates for uranyl detection and differentiation will be discussed.

NUCL 185

Fluorescence spectroscopy investigation of the transformation of U(VI) speciation under environmental conditions

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Most uranyl species in both solid and solution phases display bright green-yellow fluorescence spectra with well resolved spectral progressions. The spectral position, vibronic peak spacing, and fluorescence lifetimes often vary as a function of the equatorial ligand coordination and its hydration status. These spectral characteristics allow the determination of uranyl speciation and its transformation under various environmental conditions and thus can be potentially exploited in nuclear forensic applications. This work describes the general spectral properties of uranyl nitrate in both solid state and aqueous solutions, as well as spectral changes occurring during ultrasonic atomization of the solution and subsequent aging processes. Multiple uranyl nitrate and oxyhydroxide complexes form depending on the solution composition and sample treatment. Through spectral comparison, the possible speciation transformation pathways and end states of aerosolized uranyl nitrate particles stored under a variety of environmental conditions are presented in this work.

NUCL 186

Evaluation of the effects of environmental stress on plutonium particulates produced using ultrasonic atomization

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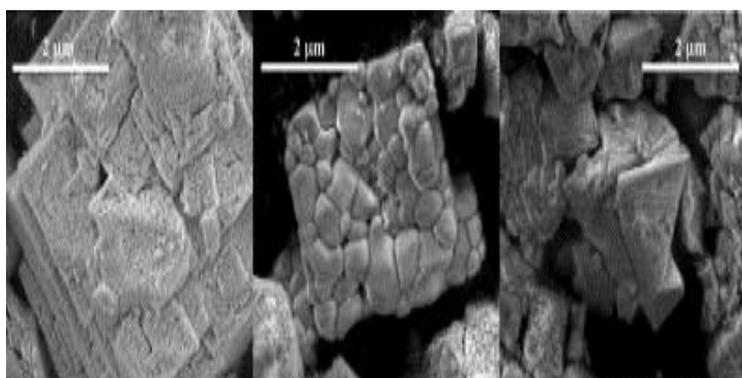
Although the majority of studies focus on the environmental transport of dissolved plutonium species into the subsurface, particulates formed in the environment from industrial processes have the ability to transport long distances. Limited information is available on formation of airborne plutonium particulates or their stability when interacting with light, humidity, internal chemical species within the particle, or external chemical species on surfaces that come in contact with the particle. Surrogate particulate materials were produced using an ultrasonic atomization process that allows for a variety of anions to be generated and characterized. These particulates can be deposited either actively or passively on a variety of substrates and were then stored under static relative humidity environments ranging from 33% to 95% at room temperature. Samples are analyzed to determine changes in morphology, structure and chemical species over several weeks.

NUCL 187

Morphological process signatures in PuO₂ produced by Pu(III) oxalate precipitation

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A set of PuO₂ samples subjected to different processing conditions was characterized by SEM/EDS to explore how variations in process conditions affect morphology. The samples display distinctive differences in morphology at a micrometer scale (Figure 1), correlated to changes in calcination temperature (300 and 800 °C) and the concentration of nitric acid used during precipitation. We discuss the potential for using morphological features as a nuclear forensics process signature for PuO₂ produced by Pu(III) oxalate precipitation.



LLNL-ABS-599017. This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

NUCL 188

Tribute to Richard G. Haire – mentor, collaborator, coauthor and colleague

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In celebrating the career and accomplishments of this year's Seaborg Award recipient it is fitting that I recount his impact on my career and pay tribute to his scientific legacy. I first met Dick in 1975 while I was attending the University of Tennessee, Knoxville, and performing my doctoral research at the Transuranium Research Laboratory (TRL), Oak Ridge National Laboratory. The TRL was a focal point of actinide science attracting notable researchers from around the world. Dick was a TRL staff scientist at the time and he took an interest in my work. I quickly learned that he was a valuable resource for all things actinide. He even took me under his wing when my thesis director took a one-year sabbatical leave in Europe. We performed the first synthesis and analysis of

americium through einsteinium phosphates and the electrochemistry of berkelium, curium and californium, to be presented.

NUCL 189

Characterization of anhydrous transcurium halides by absorption spectrophotometry

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The synthesis and characterization of anhydrous halides of einsteinium, berkelium, and californium was carried out in the late 1970's at the Transuranium Research Laboratory at Oak Ridge National Laboratory. Richard Haire was a critical member of the research team that prepared the 1 – 10 µg-sized samples of these compounds. This presentation will focus on the role that spectrophotometric analysis played in the identification of the oxidation states and coordination numbers of these metal ions. The sensitivity and interpretative abilities of this technique will be illustrated by its application to the study of californium and berkelium halides produced the decay of einsteinium halides.

NUCL 190

Electrodeposition and characterization of plutonium and uranium deposited onto thin carbon and titanium substrates

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Physics experiments aimed at deducing key parameters for use in a variety of programs critical to the mission of the National Laboratories require actinide targets placed onto various substrates. The target material quantity and the substrate desired depend upon the type of experiment being designed. The physicist(s) responsible for the experimental campaign will consult with the radiochemistry staff as to the feasibility of producing a desired target / substrate combination. In this report we discuss the production of U and Pu targets on very thin C (100 mg/cm²) and Ti (2 & 3 mm) substrates. The Ti targets are plated on both sides simultaneously. The techniques used, plating cells designed for, tips, and limits will be discussed.

A new apparatus for performing high-precision alpha spectrometry on the produced targets has been constructed using an alpha pinhole camera and a micropositioning X-Y stage. Results for the assay of large area targets (4-cm diameter) will be discussed.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

NUCL 191

Computational modeling of actinide species in the natural environment

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Actinides are of environmental and health concern due to their introduction into ground water and the natural environment via nuclear activities. The complicated electronic structure of actinide complexes leads to their versatility of chemical binding, reactivity, and spectral and magnetic properties. It is critical to have a fundamental understanding of the electronic structures of actinides in homogeneous and heterogeneous environments. In this talk, we will show that, complimentary to modern experimental spectroscopic techniques, computational chemistry modeling has become an effective tool in providing a first-principle description yielding insight into actinides-ligand bonding interactions. Relativistic density functional theory (DFT) and time-dependent DFT have been applied to study the thermodynamic and spectroscopic properties of actinide complexes. Furthermore, we study the dynamical behavior of actinide species interacting at a heterogeneous interface using *ab initio* molecular dynamics. Our calculations provide insights into the physico-chemical properties of actinide complexes in the natural environment, a step towards rational design of therapies for removing toxic actinyl cations and remediation technologies for environmental contaminants.

NUCL 192

Oxidative ammonolysis of actinide fluorides to actinide nitrides

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Actinide nitrides, in particular uranium(III) nitride (UN), are being considered as fuel types for advanced nuclear reactor systems. In this talk, we describe a novel, low-temperature synthesis route that could be developed into a commercial fabrication process for UN and other actinide nitride fuels. Uranium(III) nitride was prepared in 3 steps starting from UO₂. UO₂ is first treated with NH₄HF₂ in a ball mill at 20 °C to form tetravalent ammonium uranium fluorides. Subsequent reaction with gaseous ammonia at 800 °C oxidizes these tetravalent uranium fluorides to hexavalent UN₂. The final product, UN, is obtained by decomposing UN₂ at 1100 °C under argon to produce UN through an intermediate U₂N₃ phase. Characterization of intermediates and extension of this approach to other actinide nitrides will be discussed.

NUCL 193

Theoretical heavy element chemistry

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The author will present an overview of results on theoretical and computational studies of actinide and transactinide chemistry as a tribute to Dr. Richard Haire, the recipient of the 2013 ACS Glenn T. Seaborg Award for Nuclear Chemistry.

NUCL 194

Actinide chemistry in the gas phase: From thorium to einsteinium

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Reactions of actinide ions with neutral molecules in the gas phase offer opportunities to probe 5f-element chemistry absent secondary perturbations present in solids and liquids. Our gas-phase studies spanning two decades and the actinides from Th to Es have focused on a variety of reactions, molecules and complexes, including elementary oxides and organometallics. Examples of seminal endeavors inspired and enabled by the extraordinary insights and expertise of Richard Haire will be presented.

NUCL 195

Assessment of anthropogenic isotopic concentration in sediments collected from a lake located in the vicinity of a nuclear power plant

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Lake and River sediments have a tendency of accumulating and preserving environmental pollutants, analysis of sediments provides us with definite information related to local and global pollution events. In this perspective, a radiological assessment is performed on sediment samples collected from a lake located near a nuclear power plant. A set of 15 samples are collected at arbitrarily chosen locations within the Port Lake for the analysis of isotopes of interest. To justify obtained radiation measurement values in the area of interest, sediments are collected from a different lake located 17 miles away from the GGNS. The samples collected from both the lakes are analyzed using gamma spectroscopic techniques. The presented data include comparison of radioactivity values of measured/identified isotopes in both sample sets (<5 and 17 miles). Finally, the obtained radionuclide concentration levels are compared with the average worldwide concentration values of identified isotopes available in the documented literature.

NUCL 196

Radioactive iodine in precipitation and river water from Germany

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The natural abundance of ^{129}I has been changed through anthropogenic activities. It is emitted in gaseous and liquid form by the nuclear reprocessing facilities in Western Europe, with most of it as liquid waste which flows into the North Sea [1]. From there it is reemitted to and distributed in the atmosphere, and precipitates as wet deposition [2].

We analyse precipitation and river water samples from several sampling locations in Germany.

Iodine is extracted from the water using ion exchange resin. ^{127}I is analysed by ICP-MS and the isotopic ratio is determined via AMS.

Isotopic ratios range between $14 \cdot 10^{-9}$ and $2000 \cdot 10^{-9}$ (precipitation) and between $3 \cdot 10^{-9}$ and $40 \cdot 10^{-9}$ (river water), and are at least 3 orders of magnitude higher than the natural isotopic ratio of $1.5 \cdot 10^{-12}$ [2].

[1] J.M. Gómez-Guzmán et al. (2012) *Atmospheric Environment* **56**, 26-32. [2] R. Michel et al. (2012) *Science of the Total Environment* **419**, 151-169.

NUCL 197

Radioactivity in soil, vegetation, and vegetable of some area of KPK, Pakistan using γ -ray spectrometry

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The analysis of gamma emitters natural radionuclides i.e. ^{226}Ra , ^{232}Th and ^{40}K has been carried out in soil, vegetation, vegetable and water samples collected from some Northern area of Pakistan, using gamma spectrometry. The gamma spectrometry was carried out using high purity Germanium (HPGe) detector coupled with a computer based high resolution multi channel analyzer. The specific activity in soil ranges from 24.7 to 78.5 Bq/kg, 21.7 to 75.3 Bq/kg and 298.5 to 570.8 Bq/kg for ^{226}Ra , ^{232}Th and ^{40}K with the mean value of 42.1, 43.3, 9.5 and 418.3 Bq/kg, respectively. In the present analysis, potassium-40 was the major radionuclide present in soil, vegetation, fruit and vegetable samples. The concentration of ^{40}K in vegetation sample varied from 646.6 Bq/kg to 869.6 Bq/kg on dry weight basis. However, the concentration of ^{40}K in fruit and

vegetable samples varied from 34.0 Bq/kg to 123.3 Bq/kg on fresh weight basis. In vegetation samples, along with ^{40}K , radium-226 and thorium-232 were also present in small amount. The transfer factors of these radionuclides from soil to vegetation and vegetable were also studied. The mean transfer factors of ^{40}K , ^{226}Ra and ^{232}Th from soil to vegetation were estimated to be about 1.91, 0.06 and 0.06, respectively. The analysis of water samples showed specific activities values for all radionuclides below detection limit. The specific activities of radionuclides found in all samples during the current investigation were nominal. Therefore they are not associated with any potential source of health hazard to the general public.

NUCL 198

Overview of ^{226}Ra and ^{228}Ra in drinking water in several counties in Texas, USA

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In 1979 the United States Environmental Protection Agency (EPA) set the current rules and guidelines for different radionuclides in drinking water. These guidelines were set so that all water systems could meet health standards without creating much financial burden to the towns and counties with the potentially contaminated water arising from naturally occurring radioactive material (NORM) or technology enhanced NORM known as TENORM (Hess et al., 1985). The Texas Commission on Environmental Quality (TCEQ, 2012) is in charge of monitoring the drinking water systems throughout the state. Both water testing and enforcement of any violations that may occur fall under their mandate. The radionuclides found most commonly in the Texas drinking water are ^{226}Ra and ^{228}Ra which emit alpha and beta particles along with gamma-ray emissions, respectively. Elevated concentrations of ^{226}Ra and ^{228}Ra are deleterious to humans because they are members of group II alkaline earth metals, which also include calcium and thus compete for the same biological sites with the body. A detailed literature search was undertaken to assess the levels of ^{226}Ra and ^{228}Ra in all of the Texas counties.

NUCL 199

MENU2010: a FDA/USDA radiological capability and capacity inter-laboratory comparison exercise

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MENU2010 was a FDA/USDA Food Emergency Response Network (FERN) exercise designed to assess some of the analytical capabilities of 38 participant laboratories

following a radiological emergency. MENU2010 had two parts: a one-week part simulating the immediate aftermath of an emergency; a three-week part simulating the latter stages of an emergency. Participants could analyze any or all of 10 food-radionuclide combinations using methods of their choice; some developed methods specifically for MENU2010. Of the 10 data sets, 9 were non-normally distributed, 7 had a significant high or low bias, and 9 had standard deviations in excess of any reasonable experimental error. Results of those who analyzed multiple samples of a given combination were significantly more accurate than those who analyzed just one. MENU2010 was valuable in establishing a baseline method accuracy of the FERN laboratories. A future exercise would be valuable in determining the progress of the FERN laboratories.

NUCL 200

Method development and interlaboratory study for screening alpha and beta radioactivity in foods

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Concerns over radioactive food contamination from nuclear and radiological activities rise considerably with aging nuclear power plants, continuing nuclear proliferation, and potential breach in safeguarding nuclear materials. To ensure food safety in the event of an accidental or intentional release of radioactive materials, a solid-phase extraction liquid scintillation counting technique is developed and validated to simultaneously detect foodborne alpha/beta radionuclides that are mostly concerned and difficult to detect. An inter-laboratory study, participated by 11 food emergency response network laboratories, is conducted with wide range of foods spiked with alpha/beta radioactivity. This paper presents insights on experimental approach, method performance characteristics, and current network capability. The study results show that the method is robust and suitable for high-throughput sample analysis. The developed method allows an adequate assessment of alpha/beta radioactivity in foods in the first 24-hrs after the incident which significantly enhances the FDA's ability in ensuring food safety and protecting public health.

NUCL 201

Incident command decisions in a FERN radiological contamination exercise

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Releases from Chernobyl and Fukushima showed that a radiological event can happen anywhere, anytime, and affect conditions thousands of miles from the source. State

radiation laboratories in the United States are at the ready to produce exacting data during these events. However, does public health incident command have the resources to ask for, receive, and interpret the data in order to make sound decisions to mitigate the event? An exercise simulating a reactor release into a farming area was conducted with five state radiation laboratories by the FERN FSIS and the reports received were reviewed from the perspective of Incident Command, highlighting useful information for decision making and possible pitfalls hidden in the data. The purpose of this part of the exercise was to help IC determine important questions during a radiological contamination event, how to pose those questions, and what results do and do not say about radiological contamination.

NUCL 202

Nuclear Forensics International Technical Working Group: A global community of nuclear and radiochemists combatting nuclear terrorism

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The Nuclear Forensics International Technical Working Group (ITWG) is an informal association of nuclear forensic practitioners, created in 1996 following a G-8 Summit in Ottawa, Canada and a subsequent International Conference on Nuclear Smuggling Forensic Analysis held in the United States in 1995. Today, with the participation of international experts representing more than 40 countries, the ITWG has become the clearing house for developing and promoting nuclear forensic “best practices” worldwide. Much of these “best practices” are developed through the execution of international exercises requiring the analysis of special nuclear materials under realistic seizure scenarios. Past exercises have involved the nuclear forensic analysis of plutonium oxide, and high-enriched uranium oxides and metals, at times incorporating “traditional” forensic evidence (e.g., fingerprints, tool markings, fibers) comingled with radiological materials. A summary of past exercises will be provided along with a discussion on the successes and challenges of these exercises over the 17-year history of the ITWG.

NUCL 203

Neutron activation analysis of uranium for safeguards applications

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The measurement of the $^{235}\text{U}/^{238}\text{U}$ ratio may be made by the use of Instrumental Neutron Activation Analysis. The ^{235}U is quantified nondestructively using the comparator method and measuring the delayed neutrons emitted by the various precursor isotopes while ^{238}U is measured by gamma-ray spectrometry after neutron

activation to ^{239}Np . Such measurements may be made with little effort and great speed and are useful for the screening of materials for nuclear nonproliferation applications. Detection limits as low as 15 picograms for ^{235}U and 1 nanogram ^{238}U have been achieved. The method is particularly well suited for larger sample sets resulting from nuclear event or accident recovery efforts and routine facility monitoring. The technique may be applied to the analysis of vegetation, soils, textiles, plastics, paint, and wood. This work details the results, sources of uncertainty, interferences, figures of merit, and recommended analytical procedures for the routine neutron activation analysis of cellulose swipes.

*This work was sponsored by the Department of Energy, National Nuclear Security Administration, Office of Nonproliferation and International Security (NA-24) under contract DE-AC05-00OR22725 in conjunction with Oak Ridge National Laboratory managed and operated by UT-Battelle, LLC.

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NUCL 204

Simultaneous quantification of fissile U and Pu nuclides using delayed neutron activation analysis

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The ability to quickly and accurately quantify fissile constituents in bulk materials remains essential to many aspects of nuclear forensics and for safeguarding nuclear materials and operations. This often entails the analysis of trace quantities of nuclear debris or effluents, and typically requires bulk sample digestion followed by actinide separation and mass spectrometry. Because destructive methods are time and labor intensive, efforts have been made to develop alternative nondestructive methods for this type of analysis. This work, performed at Oak Ridge National Laboratory at the High Flux Isotope Reactor (HFIR), seeks to utilize delayed neutron activation analysis on samples of interest containing multiple fissile constituents. Based on the variances in the fission product yields of individual fissile nuclides, this work utilizes methods of linear regression to derive a technique that allows for such analysis, forgoing chemical separation and using only a single irradiation and counting step.

NUCL 205

Nuclear forensics support at a commercial licensed laboratory

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The Materials and Chemistry Laboratory (MCLinc) in Oak Ridge, Tennessee is now a fully commercial facility that had its origins as an applied research center for the U.S. Department of Energy (DOE) uranium enrichment enterprise. As such, MCLinc applies its expertise in uranium chemistry and material identification to samples originating from both Federal facilities (e.g., DOE, COE and their subcontractors) and commercial clients (e.g., nuclear engineering firms and NRC-licensed clients). The commercial client side frequently focuses on industrial forensic issues as applied to nuclear materials, such as resolution of material incompatibilities or failures and chemical process upsets, but support also includes treatability studies for recalcitrant radioactive wastes, as well as more routine, but highly specialized, analyses that are required to qualify low enrichment nuclear fuel. Support to federal contractors, including DOE National Laboratories, frequently involves application of micro-analytical techniques such as scanning electron microscopy to identify morphological and chemical signatures, and impurities, associated with highly enriched uranium from various process origins and from legacy wastes. Some representative illustrative examples will be presented for each of these categories.

NUCL 206

Individual hot particle characterization methods by autoradiography, nuclear counting and microanalysis

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Analytical methods based on the combination of microscopy, nuclear counting, micro X-ray fluorescence mapping (μ -XRF) and image processing of autoradiographs for the high throughput analysis of individual radioactive "hot" particles are described. This approach provides a means to rapidly evaluate particle size distributions, while also providing chemical and isotopic identification soon thereafter. The applicability of this new approach is evaluated with various test samples including cesium aerosols, and thoriated tungsten, uranium and plutonium particles. The relative merits and limitations of each measurement approach are described along with the potential development of particle standards.

NUCL 207

Determination of isotopic ratios of uranium samples using passive gamma spectroscopy with multiple detectors

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Uranium samples of various enrichments have been passively counted on the University of Texas detector system consisting of two HPGe detectors and a NaI(Tl) active shield. By observing ratios between gamma rays emitted from U-235 and its daughters compared to gamma rays emitted by U-238 daughters and comparing these ratios between standards of known enrichments, the ratio of U-235 to U-238 can be determined in an unknown sample. Because the gamma rays from U-235 are generally in the low-energy regime, there is a strong susceptibility to background interferences. To overcome this, we have produced two-dimensional gamma-gamma coincidence spectra. By gating on the low energies, the low energy interferences are reduced, and the U-235 gamma rays can be analyzed with a high degree of precision. The self-attenuation effects have been determined using MCNP and incorporated into the analysis.

NUCL 208

Release of ^3He from tritium aged $\text{LaNi}_{4.25}\text{Al}_{0.75}$ hydride

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The demand for ^3He has increased dramatically recently due to widespread use in neutron detectors for Homeland Security, cryogenic applications, and medical applications. Essentially all of the world's supply of ^3He is created by the radiolytic decay of tritium. The Savannah River Site Tritium Facilities utilizes LANA.75 in the tritium process to store hydrogen isotopes. The vast majority of ^3He "born" from tritium stored in LANA.75 is trapped in the hydride metal matrix. The SRS-TF has multiple LANA.75 tritium storage beds that have been retired from service with significant quantities of ^3He trapped in the metal. The Savannah River National Laboratory (SRNL) conducted thermogravimetric analysis coupled with mass spectrometry (TGA/MS) on a LANA.75 sample with more than 20 years of tritium exposure. Prior to testing, the sample was isotopically exchanged to minimize residual tritium and passivated with air to allow handling outside of an inert glovebox. This work examines the quantities and species of gases that evolved from the solid as the sample was heated in an argon environment.

NUCL 209

Spectroscopic and energetic properties of thorium(IV) molecular clusters

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There is substantial interest in understanding the hydrolysis reactions of actinides which control their aqueous chemistry. The tetravalent actinides exhibit extensive hydrolysis and condensation behavior due to their high charge density and acidity and polynuclear species are known to play a significant role in their overall chemistry. Electronic structure calculations of the $\text{Th}_6\text{O}_8^{8+}$ and $\text{Th}_8\text{O}_{12}^{8+}$ core clusters with carboxylate, sulfate and selenate ligands provide new insights into their stability, reactivity, and role as nucleation site precursors. DFT was used to calculate the geometries, vibrational frequencies, acidities, $^1\text{H-NMR}$ chemical shifts, and relative energies of different structures. The results are in good agreement with experiment and were used to assign the experimental spectra. When these clusters are protonated, they are medium to strong gas phase acids but are weak acid in aqueous solution. This work is supported by the U.S. DOE Office of Science (BES) under the SISGR Program.

NUCL 210

X-Ray crystallographic and first-principles theoretical studies of K_2TcOCl_5

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Technetium ($Z = 43$) is a transition metal element of particular interest, primarily due to the synergy of its radiolytic properties and rich coordination chemistry, which has been widely utilized in the field of radiopharmaceuticals. In particular, Tc(V) compounds exhibiting the $(\text{TcO})^{3+}$ core are important precursors to low-valent Tc complexes utilized for diagnostic imaging. The pentachloro-oxotechnetate(V) $[\text{TcOCl}_5]^{2-}$ has previously been reported, but the crystal structure was unknown. In this work, the dipotassium oxopentachlorotechnetate, K_2TcOCl_5 , was isolated as single crystals from the dissolution of $(\text{NH}_4)\text{TcO}_4$ in 0°C 12M HCl and careful precipitation with KCl. The structure of this compound was determined using single-crystal X-ray diffraction and compared with the corresponding molybdenum and rhenium analogues. The K_2TcOCl_5 structure was also investigated using density functional calculations, which agreed with the crystallographic data. Oscillator strengths for the electronic transitions in the C_{4v} -symmetry $[\text{TcOCl}_5]^{2-}$ and $[\text{TcOCl}_4]^-$ complexes were also calculated using time-dependent density functional theory and compared with the experimental UV-Vis spectrum.

NUCL 211

Preparation and characterization of the Tc_6Br_{12} cluster

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Transition metal binary halides exhibit catalytic, photochemical and redox properties that are of interest for industrial and medical applications. One transition metal whose halide chemistry is relatively unexplored is technetium, the lowest atomic number radioelement. Currently, nine technetium binary halides phases are known (TcF_6 , TcF_5 , $TcBr_4$, $TcBr_3$, $TcCl_4$, α/β - $TcCl_3$, α/β - $TcCl_2$). Technetium dichloride is the most recent phase to be discovered; it can be prepared by reaction of Tc metal with Cl_2 in a sealed tube, or by thermal decomposition of $TcCl_4$ under vacuum. Technetium dibromide is still unknown and the methods used to prepare $TcCl_2$ have heretofore not been tested on the bromide system. During decomposition of $TcBr_4$, $TcBr_3$ and ultimately the Tc_6Br_{12} cluster are produced. The latter compound has been characterized by single crystal XRD and theoretical methods. In this talk, we will describe the molecular and electronic structure of the Tc_6Br_{12} cluster.

NUCL 212

National Analytical Management Program (NAMP) radiochemistry webinars: A useful resource for all radiochemists

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A number of reports have indicated that a sizable percentage of the nation's experts in radiochemistry is nearing retirement age. This reality has been a concern since the 1970s, when declining numbers of radiochemists worldwide was first observed. To bolster interest and increase awareness in radiochemistry, NAMP is offering webinars developed by experts on different topics relevant to radiochemistry. The first series of radiochemistry webinars focusing on actinides was launched in April 2012 under the auspices of the Department of Energy and the Department of Homeland Security. Several organizations and universities participate in their development from initial concept to full realization. Each webinar is unique and provides a basic understanding of fundamental chemical and physical properties of different actinides. This paper assesses the current webinar series, describes webinars currently in development, and explains how to participate in the live webcasts and how to access archived webinars from the NAMP website.

NUCL 213

Geochemical association of uranium in contaminated sediments

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This study is based on South Terras abandoned uranium mine, Cornwall, UK, where the effect of open-system on natural uranium geochemistry was explored. In total, 20 stream sediments were collected. The uranium content, excluding two samples with elevated uranium, ranges from 3.0– 19.0 ppm. The two samples (S3 and S7) are organic-rich sediments (organic matter 37 % and 21 %) with the uranium concentrations around 95.0 and 270.0 ppm respectively. Sequential extraction results for S3 and S7 show that about 60 % of uranium for both sediments associates with the carbonate fraction, while organic phase holds 37 % of uranium in S3 and only 10 % of uranium in S7. These two fractions are U-enriched compared to the Fe/Mn oxide and residual fractions, particularly for S3. The resistant fraction of S7 holds 25 % of the uranium, suggesting occurrence of primary U-source. The exchangeable fraction in both sediments contains negligible uranium.

NUCL 214

Lowering background in gamma-ray spectrometry

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Low-background gamma spectrometry is an important tool for basic and applied projects requiring gamma-ray measurements. Lowering of the spectrometer background involves science of the detector and pure materials, radiation (including muon and neutron) interactions, and it also requires long-term commitment. We operate a 140 % efficient Model GX13023 germanium detector with a carbon composite window, sensitive down to 10-keV (XtRa configuration). The detector is inserted into a 3-layer lead shield consisting of Boliden- and Plombum-grade lead, 3-inch thick each, as well as 2-cm thick Alpha-lo grade lead insert. The lead shield is surrounded from the top and the sides by a plastic-scintillator muon shield. The spectrometer is placed in a 6-inch-thick steel-walled room made of pre-World War II steel, which is located under a 47-story building providing 33 m of water equivalent shielding. We have achieved an overall background reduction by a factor of 9436 relative to the ambient. The integrated background rate in the energy range of 50-2700 keV was measured as 15 counts/ks/kg Ge. This is second best to the IAEA MEL Monaco laboratory, which achieved the value of 10, among ground-level or shallow-underground located laboratories that reported their results. The residual background consists of natural series radionuclides present in

the detector holder, end cap, and shielding lead. Additional background originates from neutron capture and activation by neutrons from muon capture. In measuring voluminous samples containing hydrogen, such as water, the background is increased due to neutron capture in hydrogen. Noise at low energies has two components: electronic-exponential and signal baseline restoration. The latter can be eliminated with pole-zero adjustment. However, the resulting pole zero setting is not optimal for gamma resolution at high energies, which is thereby compromised.

NUCL 215

Iodine isotopes (^{127}I and ^{129}I) in aerosol from Germany

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Iodine is an essential trace element. Anthropogenic ^{129}I ($T_{1/2}=15.7$ Ma) is of concern due to its high mobility and increase inventory in the environment, potential toxicity due to bioaccumulation through the food chain and in the thyroid gland. The determination of the $^{129}\text{I}/^{127}\text{I}$ isotope ratio gives important information about the source of radioiodine and its distribution in the environment.

The atmosphere is a very important compartment for transport of iodine from the ocean to the terrestrial ecosystems. Iodine from the atmosphere is removed via aerosols by dry and wet fallout. It is interesting to measure ^{127}I and ^{129}I in atmospheric aerosols, because there is studies about ^{129}I in aerosols is scarce.

Iodine was separated from the sample matrix by solvent extraction, and was analysed for ^{129}I by AMS at ETH Zurich and for ^{127}I by ICPMS. Concentrations of ^{127}I , ^{129}I , and the $^{129}\text{I}/^{127}\text{I}$ ratio in aerosol samples in Germany will be presented in the talk.

NUCL 216

DTRA basic research for combating weapons of mass destruction

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The Defense Threat Reduction Agency safeguards the United States and its allies from weapons of mass destruction (WMD) by providing capabilities to reduce, eliminate, and counter the threat and mitigate its effects. DTRA accomplishes its mission by investing in basic research efforts at universities, national labs and DoD service labs to better counter threats posed by WMD. We also facilitate productive relationships with other scientific organizations and seek to identify promising research efforts overseas. Through the Basic Research program, DTRA recruits and trains scientists and engineers to develop a talented workforce for the future.

Basic research is directed towards greater knowledge or understanding of phenomena without regard to specific applications. The DTRA Basic Research Program pursues efforts within and across disciplines such as chemical science, computer/network science, materials science, mathematics, nuclear science, and physics. The presentation will describe the DTRA Basic Research Broad Agency Announcements, research “Thrust Areas,” proposal solicitation processes, and technical areas or subjects of interest.

NUCL 217

FERN 101

Michael A McLaughlin, *Michael.McLaughlin@fda.hhs.gov*. Food Emergency Response Network, US Food and Drug Administration, Rockville, MD 20857, United States

An overview of the Food Emergency Response Network (FERN). This presentation will review of the principles of FERN with an emphasis on Radiological activities.

NUCL 218

FERN response to Fukushima

Michael A McLaughlin, *Michael.McLaughlin@fda.hhs.gov*, **Susanne M Brooks**. Food Emergency Response Network, US Food and Drug Administration, Rockville, MD 20857, United States

Review FERN's response to Fukushima, ICS structure, and FERN Incident Response SOP. Discuss reporting in eLEXNET and interpreting results, including DIL.

NUCL 219

Description of FERN Radiological Cooperative Agreement Program activities

Susanne M Brooks, *susanne.brooks@fda.hhs.gov*. Food Emergency Response Network, US Food and Drug Administration, Rockville, MD 20857, United States

An overview of FERN exercises and assignments, including Menu2010, RadEx2011, Political Assignment 2012. Discuss challenges and successes, how to improve future activities, and possible proficiency tests to illustrate capability and capacity.

NUCL 220

Standardizing of the FERN sampling protocols and forms

Susanne M Brooks, *Susanne.Brooks@fda.hhs.gov. Food Emergency Response Network, US Food and Drug Administration, Rockville, MD 20857, United States*

Proposal for how to improve the FERN sampling protocols, forms, and how laboratories interpret them. Compare to Microbiology CAP standardized worksheets and practices.

NUCL 221

Future directions and funding for food radiochemistry

Susanne Brooks, *susanne.brooks@fda.hhs.gov. Food Emergency Response Network, US Food and Drug Administration, Rockville, Maryland 20857, United States*

Preparation and sharing of split samples and standard reference materials for food radiochemistry. Discuss equipment, funding future projects, and method development.

NUCL 222

Thermoluminescence of commercial borosilicate glass for intrinsic dosimetry

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Intrinsic dosimetry is the method of measuring total absorbed dose received by the walls of a container holding radioactive material. By considering this dose in tandem with the physical characteristics of the radioactive material housed within that container, this method can provide enhanced pathway information for interdicted radioactive samples. Thermoluminescence dosimetry was used to measure ionizing radiation dose effects on raw stock borosilicate container glass. The corresponding TL glow curves were separated into five peaks. Differences in TL glow curve shape and intensity were observed for glasses from different geographical origins. Electron paramagnetic resonance and multi-elemental analysis were used to relate the differences in TL intensities and peaks to electron/hole traps and compositional variations.

NUCL 223

Direct solid analysis for trace elements in actinide oxide by DC arc spectrometry

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DC Arc technology has been used for decades in trace elemental analysis. It is a special tool for samples that are difficult or impossible to dissolve or digest into aqueous

form. A fast and quantitative analytical method has been developed to determine trace elemental compositions in both uranium oxides and plutonium oxides. The instrument, a Prodigy DC Arc spectrometer, is a prototype DC Arc spectrometer developed by Teledyne Leeman Labs. It represented a new era in the DC arc technology because of the state-of-the-art solid state detector equipped with the L-PAD detection system. Calibration curves can be established for more than two orders of magnitude of trace element concentration. Sample analysis time is 1 to 2 minutes with only 100 to 500 mg sample required. The wavelength range spans from 195 to 700 nm, which covers a great suite of elements. The Prodigy DC Arc spectrometer stands outside the glove box and interfaced to a SPEX arc chamber located inside a radioactive contaminated enclosure. The Prodigy replaces an old photographic plate spectrograph instrumentation that had been used for more than half a century in routine solid sample analysis. It is a technological advance for Los Alamos National Laboratory in direct solid determination for trace elemental constituents in actinide oxides. LA-UR-12-25869.

NUCL 224

First-principles prediction of solid-state NMR parameters in fluorine-containing inorganic actinide complexes

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NMR crystallography, or the use of solid-state NMR to elucidate the crystal structure of inorganic compounds, has become a very useful tool for understanding fine details of complex structures. Coupling NMR measurements with first-principles calculations allows for spectroscopic identification of crystalline metal fluorides, particularly those that have multiple crystallographic fluorine sites. Recently, first-principles calculations have been extended into the area of actinide complexes, but the work so far has only focused on simple octahedral complexes. In this work, we will discuss our efforts of using NMR chemical shift calculations in the framework of density functional theory (DFT) to identify the fluorine sites in uranium-containing solid state compounds. Results show quantitative agreement is made between calculated and experimental NMR parameters to allow assignment of the ¹⁹F signals.

NUCL 225

Design of sensors of uranium and plutonium using ab initio methods

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We will show calculations to design arrays of self-assembled electronic molecular devices as sensors for traces of Pu and U using precise ab initio computational calculations. The idea is to use the plasmonic features of graphene molecules in order

to transfer the electrical, magnetic, vibrational, and optical characteristics into the graphene plasmons, which produce an enhancement (amplification) of observable quantities. Theoretical simulations have shown the possibility to use sensors to identify single molecules with modes in the terahertz region. On the other hand, molecular potentials have become the type of signal suitable at the nanoscale for detection of atoms and small molecules. Plots of the molecular potentials around complexes of U and Pu would allow us to distinguish the main differences similar to those observed in biological systems where receptors are able to distinguish its transmitters or when a donor of electrons is able to match with an acceptor.

NUCL 226

Problem of unaccounted nuclear material in processing facilities: Detecting nuclear material holdup

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It is important to monitor the amount of nuclear material that is held up in facilities for safeguards, criticality, waste management, worker safety, and facility operations purposes. Measurements of holdup require rugged detector systems and a technique that can determine both the isotopic distribution and mass of the special nuclear material (SNM) despite various geometries, material properties, shielding materials, and contaminants. The current methods of measuring holdup could be improved upon with an update in equipment, software, and technique. The current practices for measuring holdup are reviewed, followed by the existing difficulties in holdup measurements, and then a sampling of newer technologies and techniques that could be useful to this field.

NUCL 227

Developing a model national nuclear forensics database: Report on the pilot project in Ukraine

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It is widely recognized that building information capabilities on the national level and establishing protocols for international cooperation in information exchange are vitally important in nuclear forensics and nuclear security. Nuclear forensic libraries and databases enable effective and timely attribution of seized nuclear materials, as well as ensure the access to and transfer of knowledge in a nuclear security event. In 2011, the US Government initiated a pilot project in Ukraine to create a model national nuclear forensic library and database from initiation and data discovery, through algorithm

development, querying, and statistical and spatial analysis. The model library and database are being created in accordance with international guidance, and a series of development, training and oversight documents will be published at the conclusion of the project, enabling the international community to assess and scale this model according to their individual government's needs. We will report on progress on this pilot project, including lessons learned and challenges to date.

NUCL 228

Nuclear forensics signature analysis of fast and thermal reactor produced weapons-grade plutonium

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The objective of this project is to use computational and experimental methods for reliably predicting and measuring a unique intrinsic signature in separated weapons-grade plutonium produced by certain reactors, specifically fast breeder reactors and CANDU-type thermal reactors. These reactor fuels burned to low burn-ups produce weapons-grade plutonium; however the neutron energy spectrum differences shall result in variations in the plutonium isotopes produced. The computational part of the project utilizes MCNPX-2.7 radiation transport code to perform burn-up cycles for both reactors for estimating the resulting isotopics of actinides and trace elements in the discharged fuel. The simulations gave the material composition of the fuel after standard burn and decay cycles. Specific plutonium isotopes and fission products retrieved from the simulation results were investigated for correlations and will be compared with the experimental data when they become available in the latter half of this investigation.