NUCL

Development of reactive membranes for the rapid quantification of radionuclides in water

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Traditional approaches for the detection of trace-level alpha-emitting radioisotopes in water require lengthy offsite sample preparations and do not lend themselves to rapid quantification. Therefore, a novel platform is needed that combines onsite purification, concentration, and isotopic screening with a fieldable detection system. In this presentation, we will describe the development of reactive membranes for isolation and concentration of uranium from various aqueous matrices, including high-salinity seawater. The aim was to develop a field portable screening method for the rapid quantification of isotopic distribution by alpha spectroscopy. The reactive membranes were prepared from ultrafiltration membranes by modifying their surfaces to add uranium-selective functional groups. The membrane surfaces were characterized with scanning electron microscopy to gain insight on pore size and atomic force microscopy to analyze surface roughness. Pressure-assisted filtration of uranium solutions was used to load uranium onto the reactive membranes, which subsequently were used as substrates for alpha spectroscopy. Flowthrough uptake experiments were conducted to evaluate the effects of flow rate, membrane support, and modification conditions on sample preparation time and peak energy resolution. The experimental breakthrough data were fitted to a theoretical model to determine the maximum binding capacities and sorption rate constants. Alpha spectroscopy pulse height spectra were analyzed, and excellent resolution with full width at half-maximum values from 30 to 49 keV were recorded, comparable to the results obtained from electrodeposited standard which range from 31 to 36 keV. This membrane-based purification and quantification method enables the rapid, fieldable screening analysis of radionuclides in water for environmental monitoring studies and nuclear forensics investigations.

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3D printed microfluidic supported liquid membrane modules for actinide separations

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Supported liquid membrane (SLM) separations use the high selectivity of an organic phase extractant immobilized in a hydrophobic porous polymer membrane to combine

liquid-liquid extraction and stripping in a single unit operation. Since the concept was first proposed over fifty years ago, fundamental and applied studies of SLMs for industrial-scale applications, including nuclear fuel cycle separations, have been extensively reported in the literature. However, the application of SLMs to microfluidic actinide separations has not been explored. In this work, we report the design, fabrication, testing, and mass transport modeling of 3D printed microfluidic SLM modules. Experimental tributyl phosphate (TBP) SLM uranium extraction trends are consistent with a mass transport mechanism combining advection and diffusion, with no mass transport resistance at the liquid-liquid interfaces. The modules are demonstrated to be effective for the purification of uranium, with preliminary separations following the well-known trends in TBP selectivity.

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Spectrophotometry and multivariate analysis for monitoring plutonium-238 anion exchange column runs

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The Plutonium-238 Supply Program at Oak Ridge National Laboratory (ORNL) is establishing an online monitoring capability to advance the timeliness of analytical measurements and support radiochemical separations taking place in heavily shielded hot cells. After bulk separation of Pu by solvent extraction, anion exchange column runs are used for purification of the Pu, removing phosphorus-containing contaminants from solvent degradation, remaining fission products, Th, and most of the remaining Np. To monitor this process, multivariate models (e.g., partial least squares regression) were built from historical UV-Vis absorption data. The training sets included spectral signatures corresponding to Pu(III), Pu(IV), Pu(VI), Np(IV), and Np(V) spanning the anticipated conditions expected in the column effluent streams. The models were specifically developed to identify Pu(VI) during the high acid wash and when to redirect column effluent to collection tanks and identify the appropriate time to collect ^{238}Pu product in collection bottles. A commercially available process monitoring software, Process Pulse by Camo Analytics, was used to convert convoluted absorbance spectra to process data, viewable in real time, to help make process decisions in multiple Pu anion exchange column runs. The prediction performance for the Pu product was suitable for this application since the predictions were in good agreement with alpha spectroscopy and inductively coupled plasma mass spectrometry analytical results. Future development may include incorporating spectral signatures for the quantification of nitric acid profiles.

NUCL

Quantification of iodine gas using Raman and fluorescence spectroscopy

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In the nuclear field, molten salts are a growing area of interest to support molten salt reactors as well as pyroprocessing. Monitoring the production of potentially toxic or hazardous gases in these systems is important in preventing the release of such gases into the environment. Iodine is of particular interest, as radioactive I-129 has a long half-life and its toxicity and persistence in the environment make it a great safety concern. Spectroscopic online monitoring tools are well suited to interrogate the harsh environment of molten salt reactors and are ideal for the quantification of iodine in the gas phase due to molecular iodine's distinct Raman and fluorescence signature. Ultimately, on-line monitoring tools can support a range of work including efficient design of off-gas treatment systems to enabling operator control in deployed systems. Here, we discuss our work pairing Raman and fluorescence spectroscopy with chemometric analysis for the quantification of molecular iodine as a function of pressure and temperature using two laser excitation sources.

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Investigation of gas-phase acetate exchange of tetravalent thorium and plutonium complexes

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Fundamental gas-phase reactions of actinide complexes elucidate their chemistry. Gas-phase studies provide uniquely detailed information on underlying chemical properties that influence bond dissociation and activation. Ligand exchange for actinide-acetate complexes $An^{IV}L_x(OCOCH_3)_{5-x}^-$ (An = Th, Pu; L = Cl, NO_3), as shown by reaction (1) probes the effect of the metal center and its ligand environment on reactivity. Using deuterated acetic acid, $DOCOCD_3$, as the exchange reagent allows determination of kinetics for this thermoneutral reaction.
$AnL_x(OCOCH_3)_{5-x}^- + DOCOCD_3 \text{-->} AnL_x(OCOCH_3)_{4-x}(OCOCD_3)^- + DOCOCH_3$ (1)
By comparing reaction (1) for different actinide metals, as well as for different ligands (L), systematic variations in bonding and reactivity are assessed. Experimental results show that reaction (1) is more efficient for $Th(NO_3)(OCOCH_3)_4^-$ versus $Pu(NO_3)(OCOCH_3)_4^-$. Density functional theory computations of the reaction potential energy profiles are in accord with the observed kinetics. Analysis of the reaction mechanism using a Distortion/Interaction-Activation Strain (DIAS) model suggest a less favorable Pu-ligand interaction energy as the underlying cause for diminished reactivity. The results and analysis reveal and elucidate different characteristic chemistry of Th(IV) and Pu(IV).

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An experimental and computational investigation of pseudohalogen-oxo interactions in bimetallic UO_2^{2+}/Co^{2+} thiocyanates

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The uranyl cation (UO_2^{2+}) remains of interest due to its relevance to the nuclear fuel cycle and the potential environmental impact of uranyl-containing materials. Presented is a family of UO_2^{2+}/Co^{2+} isothiocyanate materials containing $[UO_2(NCS)_5]^{3-}$ and/or $[Co(NCS)_4]^{2-}$ building units charged balanced by tetramethylammonium cations and assembled *via* S···S or S···O_{yl} non-covalent interactions (NCIs). Materials were structurally characterized *via* single crystal X-ray diffraction and interrogated using diffuse reflectance and Raman spectroscopy. In the bimetallic phase, assembly proceeds *via* rare -NCS···O=U interactions, which is accompanied by an unexpected *blue shift* in the UO_2^{2+} symmetric stretch frequency. As a consequence, a combined experimental and computational (density functional theory and natural bond order analyses) approach was utilized revealing vibronic coupling, as opposed to bond strengthening, as the origin of the atypical stretch frequencies. As typical discussion of the uranyl relies heavily on comparing stretching frequencies as a measure of relative U=O bond strength, our work reveals an unexpected limitation when using this correlation alone when evaluating uranyl bonding.

NUCL

Curies: Compendium of uranium Raman and infrared experimental spectra

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Optical vibrational spectra are powerful indicators of solid phase U(VI) coordination chemistry. In addition, U(VI) minerals exhibit extreme chemical and structural diversity as artifacts of geochemical processes leading to ore formation. To determine the extent to which spectroscopic data permits identification of U solids with respect to chemistry and structural attributes, the Compendium of Uranium Raman and Infrared Experimental Spectra (CURIES) is being developed. CURIES is being compiled via exhaustive survey of peer-reviewed literature and databases and new spectral collection from undercharacterized materials. Through review of literature and databases, mineral species that lack spectra will be identified and obtained from museum and academic collections for analysis. Mineral samples that cannot be obtained from other sources will be synthesized, leveraging synthesis capabilities at Oak Ridge National Laboratory. Subsequently, characteristic spectroscopic features for subgroups of uranyl minerals within CURIES will be determined using multivariate statistical analyses on the basis of the underlying crystal chemistry.

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Photoinduced charge transfer of solid-state uranyl-viologen-bearing materials: A structural, optical, and kinetic study

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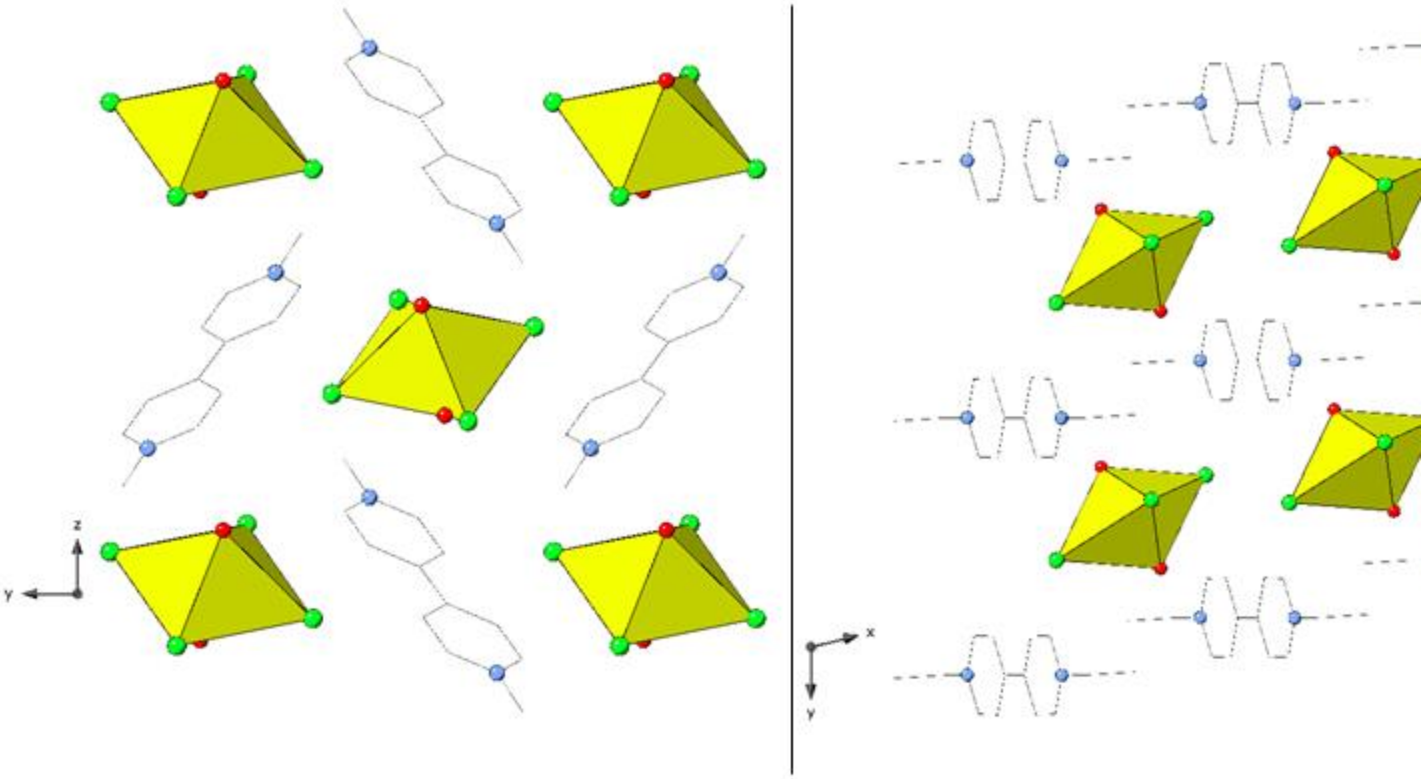
The synthesis and characterization of three new uranyl compounds featuring the uranyl-tetrachloride $[UO_2Cl_4]^{2-}$ dianion paired with various 1,1’-dialkyl-4,4’-bipyridinum dications (i.e. viologens) is reported. A simple uranyl species paired with the redox-active cation may support charge transfer in the solid state providing a unique perspective when probing the photochemistry of uranyl-bearing materials. Irradiation with UV light causes a marked reduction of uranyl emission intensity over time, which can be partially recovered by placing the sample in the dark. Kinetic treatment of the time-dependent data reveals a quenching efficiency and rate constant dependence on viologen identity. We propose a photoinduced electron transfer mechanism for this reaction which is support by experimental and computational data. Density functional theory (DFT) based calculations are utilized to (i) map the band structure of these materials, (ii) determine electronic structure of photochemical products, and (iii) identify the donor and acceptor orbitals involved in charge transfer. Our findings support the formation of a notable oxidized $[UO_2Cl_4]^{1-}$ species bearing a U(VI) bound to a radicalized chloride ligand. These efforts will inform studies of uranyl as a photocatalyst or in radiation detection, yet perhaps more importantly, may contribute to our fundamental understanding of energy transfer within actinide bearing hybrid materials.



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Characterization and first principles modeling of tritium trapping in γ-LiAlO$_2$ nanovoids

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The essential components for tritium production in TPBARs are the γ-$LiAlO_2$ pellets, which contain about 25% of the total lithium as ^{6}Li. Despite a total Li burnup of about 12% (i.e. ~50% of total ^{6}Li), the $LiAlO_2$ pellets can survive very well neutron irradiation during the 18 months of in-reactor operation. In order to improve the fundamental understanding of physical phenomena occurring in TPBARs during irradiation, a series of post-irradiation examinations were conducted for the various components of the TPBAR. In the specific case of the pellets, transmission electron microscopy (TEM) and atom probe tomography (APT) identified irradiation induced microstructures at the nanoscale level. Both techniques reveal the clear the presence of nanovoids in γ-$LiAlO_2$ pellets. While those nanovoids can affect the diffusion of tritium in pellets, first principles simulations have been conducted to evaluate the potential for tritium trapping by single and double cation and anion vacancies. It was found that tritium trapping allows recovery of a significant amount of the formation energy cost of cation vacancy, while the trapping of tritium by anion vacancies further increase the energy cost of forming a vacancy. The simulations also indicated the potential for tritium to be trapped in various forms by forming bonds such as Al—T, O—T or T_2. These results raise further questions regarding the speciation and dynamics of tritium trapped in nanovoids.

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Colorimetric detection of actinides (CoDeAc)

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The Colorimetric Detection of Actinides (CoDeAc) uses a novel system of color changing agents to produce a color change in the presence of actinides. Imagine a Handi-Wipe that turns a different color when it picks up uranium (U) or plutonium (Pu) and you've got the basic idea of CoDeAc. When responding to anything from a "dirty bomb" attack to condensation on a surface at a nuclear power plant, first responders, military personnel, forensic investigators and radiological control technicians need simple, rapid and reliable field equipment to detect actinide contamination. Hand-held radiation detectors may provide adequate screening for beta, gamma and neutron-emitting sources, but they may lack the field sensitivity and adaptability for detecting alpha particle emitters in the presence of certain environmental interferences. A new selective colorimetric technology has been developed for response personnel to characterize actinides, such as U and Pu, contamination for both field contamination events and everyday maintenance testing at nuclear facilities. Results have shown success in both selectivity and sensitivity for low level concentrations of U and Pu at parts-per-billion (ppb, pCi/L) and parts-per-million (ppm, nCi/L) levels, respectively.

CoDeAc uses a selective color change method which renders a go/no go detection of U and Pu at low levels in under a minute and on scene of a radiological event. This novel chemical detection method will allow civilian and military first responders to more effectively assess a radiological event’s magnitude, dimensions, and severity early, thereby helping on-scene coordinators to make crucial decisions quickly.

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Synchrotron X-ray techniques for nuclear forensics and safeguards particle analysis

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The field of nuclear forensics and safeguards has seen increased importance in recent years. In particular, particle analysis has been an increasingly important component of these fields. In nuclear forensics, a specimen can be analyzed using a number of different techniques to narrow down its possible origin. The development of new, non-destructive analysis tools are an important part of refining this process to yield more accurate results. X-ray probes are a promising non-destructive method of providing additional information about specimens, particularly chemical speciation, which is not typically currently examined. To this end, prior work done using a Scanning Transmission X-ray Microscope (STXM) has shown that soft X-ray Absorption Spectroscopy (XAS) has demonstrated the ability to distinguish between many different uranium species, offering an opportunity to provide important information on a sample's origin. Current efforts are focused on improving a particle identification method by providing additional elemental and chemical information through x-ray fluorescence, as well as improving throughput to analyze particles more quickly.

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Harvesting ^{62}Zn from an aqueous cocktail at the NSCL

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From the accelerated heavy ions at the NSCL (National Superconducting Cyclotron Laboratory) only a small fraction is used for the production of secondary beams. Replacing a conventional solid beam blocker with a flowing water target creates a possibility to collect a variety of exotic radionuclides in a synergistic manner with other experiments. The radioisotopes ^{77}Kr and ^{76}Kr represent the main reaction products of a

^{78}Kr beam stopped in water, however, in a side reaction the formation of ^{62}Zn ($t_{1/2}$= 9.2 h) occurs at a production rate of 9.08(30)*10^{-5} atoms per incoming ^{78}Kr. The positron emitting ^{62}Zn decays to the short-lived ^{62}Cu ($t_{1/2}$= 9.7 min, $I_{\beta+}$= 100%) and currently both find collective application in nuclear medicine for the ^{62}Zn/^{62}Cu PET generator. Additionally, zinc functions as essential nutrient in many biological systems which makes this heavy metal also interesting for plant uptake studies.
In this work we present the feasibility of collecting 7.6 (29)–11.1 (41) µCi ^{62}Zn in the background of a ^{76,77}Kr collection, both created by an impinging ^{78}Kr beam (150 MeV/u, max. 2.2–3.7 pnA, 14.9–25.1 W) on an aqueous matrix. The produced radionuclides were captured on a set of cation and anion columns, whereby ^{62}Zn exclusively exists as cation under the prevailing neutral pH conditions. A kinetic model was used to describe the column adsorption behavior of the generated radioactive species and additionally allowed estimation of the formation rates of twenty other radionuclides. With the subsequent purification method, based on anion exchange, ^{62}Zn was separated from accompanying radioactive and stable nuclides. The radiogenerator principle was demonstrated by the successful isolation of pure ^{62}Cu. Secondly, the obtained ^{62}Zn was utilized in a proof-of-principle uptake and imaging experiment in a hydroponic garden cress culture.

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Influence of *Z* and *N* on the synthesis of heavy elements in fusion-evaporation reactions

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Several experiments worldwide have attempted to discover the currently unknown elements 119 and 120. Although the experimenters have a deep understanding of the problem and have very sensitive equipment, no widely accepted reports of decay chains attributable to these elements have been published. These reactions utilized projectiles heavier than ^{48}Ca bombarding targets of actinide elements with the goal of creating fusion-evaporation products. The lack of success in these experiments has stimulated interest in the influence of the projectile on fusion-evaporation reactions. In the current research, projectiles of ^{44,48}Ca, ^{45}Sc, ^{50}Ti, and ^{54}Cr bombarded lanthanide targets, and a large number of *xn* and *pxn* excitations functions were measured using the MARS spectrometer at Texas A&M University. The projectile and target were systematically varied, and the resulting cross sections were compared against model calculations. The data suggest that the properties of the compound nucleus play a dominant role in the fusion-evaporation cross section. This talk will discuss the experiments, the theoretical model, and the implications for the formation of new superheavy elements.

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Nuclear structure, stability, and nucleon pairing are served by alternating up and down quark sequences

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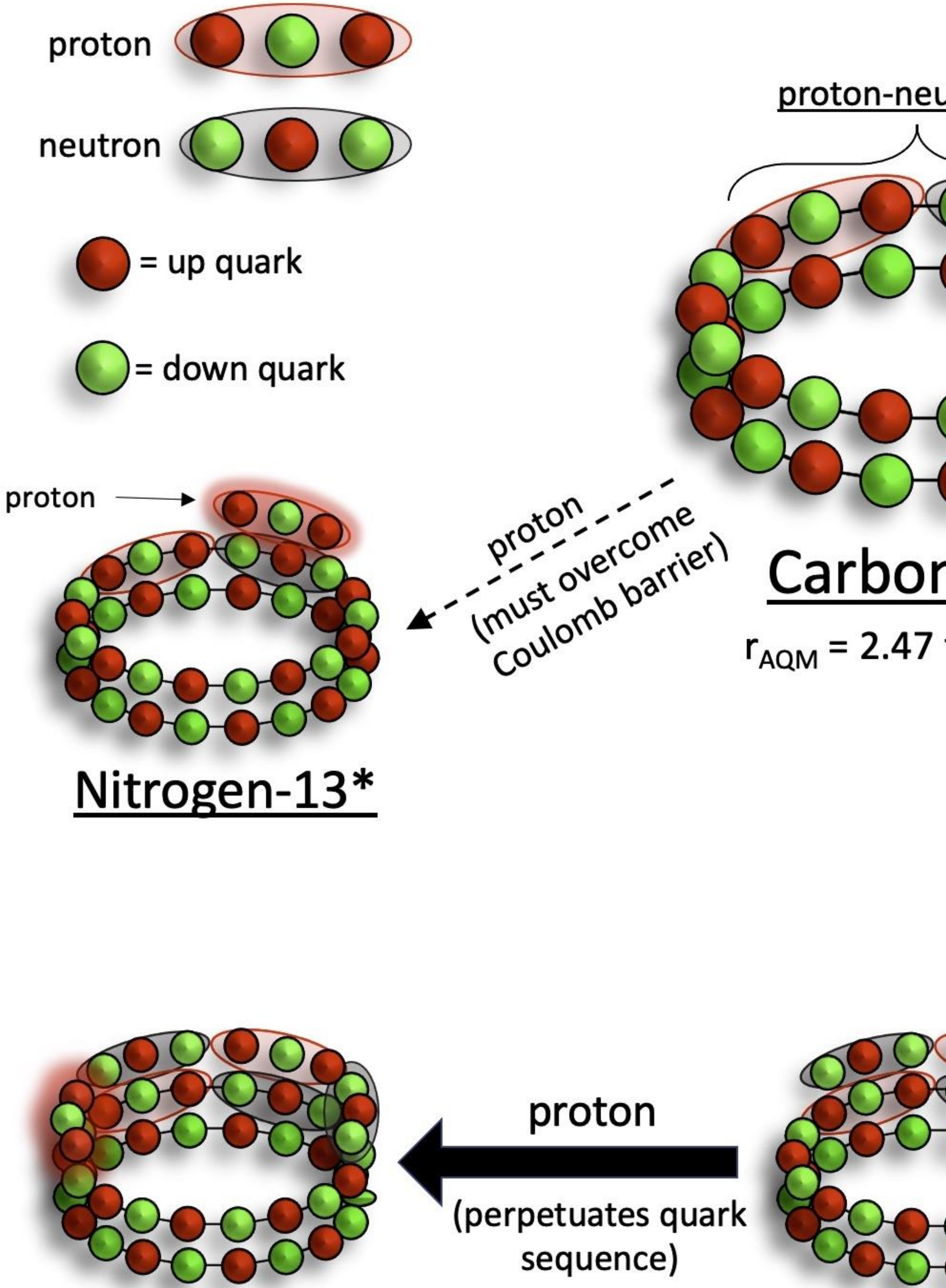
Nucleosynthesis is the creation of naturally occurring elements and their isotopes from protons and neutrons. Primordial nucleosynthesis created H and He, cosmic ray nucleosynthesis creates Li, Be, and B, while stellar nucleosynthesis created carbon and heavier elements. Regardless of nucleosynthetic pathway, questions remain as to why some combinations of protons and neutrons are stable while others are not, why protons and neutrons tend to pair within the nucleus, and what role quarks might play in nuclear structure and stability. The Alternating Quark Model (AQM) proposes light nuclide structures based on average quark positions. The model predicts which type of nucleon added to a given light nuclide will form the next stable nuclide. AQM structural constraints accurately predict one stable isotope for F and Na, three stable isotopes for Ne and Mg, and two stable isotopes for the remainder of the light nuclei. Radius predictions arising from AQM structures demonstrate 98% agreement (SD 2%) and .99 (p=.001) correlation with accepted radii for the stable light nuclides through Mg-26. Close-proximity short-range correlated (SRC) nucleon pairs within the atomic nucleus are an inherent feature of AQM structures. Ringed sequences of alternating up and down quarks contain equal numbers of protons and neutrons. Individual quarks have never been observed, but the various constraints and parameters of AQM may provide further insight into the structure of up and down quarks. AQM may offer an additional set of tools to generate future nucleosynthetic pathways.


proton
neutron
= up quark
= down quark
proton-neu
Carbor
r_AQM = 2.47
proton
(must overcome
Coulomb barrier)
proton
Nitrogen-13*
proton
(perpetuates quark
sequence)

The double ring structure of carbon-12 (center) shows alternating up/down quarks sequences that inherently produce alternating proton/neutron sequences, and proton-neutron pairs. The alternating quark model predicted radius r_{AQM} is shown next to the experimental value in parenthesis. Solid arrows indicate the stable pathway (intermediary structures not shown) and whether an additional proton or neutron will produce a stable nuclide. The dashed arrows lead to unstable nuclides (designated by *).

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Evaluation of actinium-225 radiolabeled cyclized alpha-melanocyte stimulating hormone (CycMSH) peptide for targeted alpha therapy (TAT)

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With four alpha ($^4He^{2+}$) particles in its decay chain, actinium-225 (^{225}Ac, $t_{1/2}$ = 9.9 d) is ideal for incorporation into radiopharmaceuticals for targeted alpha therapy (TAT) of cancer. Tumour targeting biomolecules allow for site-specific delivery of radioactive emissions to the disease cell. Lactam-bridged cyclized α-melanocyte stimulating hormone (CycMSH) peptide has high affinity for over expressed surface receptors on most malignant melanomas, making it a promising target for melanoma therapy. Herein, ^{225}Ac-labeled CycMSH derivatives were evaluated as novel TATs for melanoma in a preclinical mouse model. DOTA- and macropa-CycMSH conjugates were radiolabelled with ^{225}Ac with radiochemical yields (RCY) of <10 and >99 %, respectively. Low % RCY of the DOTA-conjugate precluded in vivo evaluation. The biodistribution of ^{225}Ac-macropa-CycMSH (molar activity, S.A. = 1.38 kBq/pmol) in B16F10 tumour-bearing mice (n = 4) was evaluated for 2 different injected radioactivities (103.6 kBq and 51.8 kBq) 2 h post-injection and was found to be 2.50 and 0.67 % injected dose/gram in tumour. The moderate-to-low tumour uptake highlights the need for development of efficient and robust ^{225}Ac chelators that produce high S.A. radiopharmaceuticals with favourable biodistribution.

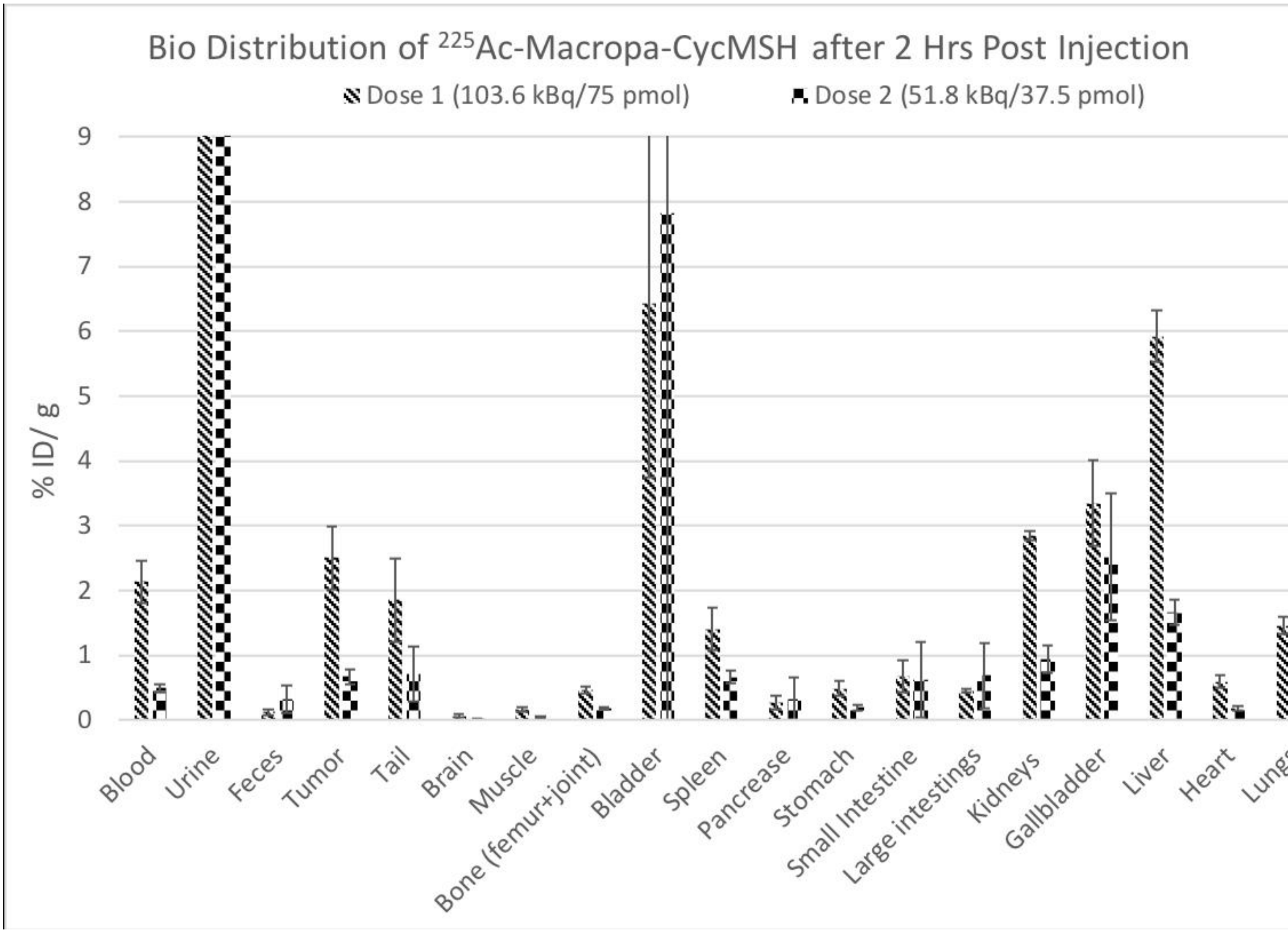

Figure 1: The biodistribution 2 hours post injection of ^{225}Ac-Macropa-CycMSH in B16F10 tumour-bearing mice (n = 4) for dose 1 (diagonal lines) and dose two (checkered).

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Potassium copper hexacyanoferrate impregnated on electrospun nanofibers for selective removal of cesium ions

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Due to the potential for an uncontrolled release of radionuclides with high levels of radioactivity, it is important to develop strategies for selective adsorption of cesium ions and minimizing the final waste volume. In this work, we demonstrate a novel strategy to fabricate a composite adsorbent immobilizing potassium copper hexacyanoferrate (KCuHCF) in electrospun nanofibers. Transition metal hexacyanoferrates (MHCF) have been extensively studied for removal of cesium, since it has a unique crystal structure for selective insertion of alkali-ions with high adsorption capacity. However, it is necessary to immobilize them to the support for practical application, due to their too small particle size and high water-dispersibility. Thus, we immobilized KCuHCF nanoparticles to the nanofiber membrane through in-situ crystallization to evenly distribute the nano-adsorbents and expose them to the support surface. The supporting nanofiber matrix was fabricated through an electrospinning technique with poly(vinyl alcohol) (PVA) and sodium alginate mixture, and the anionic carboxylate functionality on the alginate effectively coordinated with Cu^{2+} precursor ions for subsequent synthesis of KCuHCF. The amount of anionic functionality of alginate was controlled by varying the mixing ratio of PVA, and it affected the amount of the KCuHCF content and the uniformity of the composite. The textural characterization was conducted through electron microscopy and spectroscopic analyses, and as a result, well-dispersed KCuHCF particles on the surface of the nanofibrous membrane were confirmed with the optimal PVA/alginate ratio. The composite showed a high cesium adsorption capacity of 114 mg g^{-1}, and it exhibited superior selectivity for cesium with distribution coefficients on the order of 10^4-10^5 mL g^{-1} under seawater and groundwater conditions that containing large amounts of competitive coexisting cations. In addition, it showed rapid cesium uptake kinetics not only in a batch system, but also in the membrane filtration experiment. Under the pressure of 2 bar, efficient decontamination of cesium ions was achieved by removing 180 mg g cesium per 1 m^2 with a high flux of about 170 L m^{-2} h^{-1}. Thus, in-situ immobilization of KCuHCF on the surface of electrospun nanofibers could achieve rapid and selective removal of cesium ions. This immobilization strategy and adsorptive filtration method could be a practical alternative in the radionuclide treatment system.

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Production and recovery of targeted alpha therapy nuclide ^{230}U via ^{232}Th(p,3n)^{230}Pa at the Los Alamos isotope production facility

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Uranium 230 ($t_{1/2}$ = 20.8 d) is an alpha emitting radionuclide that has potential application in targeted alpha therapy (TAT) of cancer. Uranium 230 is also the parent of ^{226}Th, another potential TAT isotope with a much shorter half life (31 min). Uranium-230's parent isotope ^{230}Pa ($t_{1/2}$ = 17.4 d), in turn, can be produced by proton irradiation of thorium metal (monoisotopic primordial ^{232}Th) targets. Preliminary ^{230}Pa production runs were conducted at the Los Alamos National Laboratory Isotope Production Facility (LANL IPF) exposing thin Th metal disks to a proton beam of energies 15 to 30 MeV, followed by radiochemical separation of ^{230}Pa from the irradiated target matrix. The measured ^{230}Pa production yields were found to exceed the predicted values in most of

the experiments that were performed. This data will inform further production efforts for providing ^{230}Pa/^{230}U for clinical trials. Moreover, a dual generator system was designed and tested to provide a reliable supply of ^{226}Th: uranium 230 can be conveniently supplied from a ^{230}Pa/^{230}U generator. The ^{230}U/^{226}Th generator, in turn, provides thorium 226 in high radiochemical yield and purity and in a form that is amenable to direct labeling with chelates for use in targeted alpha therapy.

NUCL

Thermodynamic, heat, and radiolytic stability of LN and DGA resins for the production of ^{161}Tb

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^{161}Tb is an emitter of both low energy beta particles and Auger electrons, which makes it an ideal candidate for targeted radiotherapy. Reactor production of ^{161}Tb through irradiation of ^{160}Gd has proven successful, although the difficulty of lanthanide separation has provided a need for further ^{161}Tb yield optimization in order to achieve a higher specific activity product. Thus, in this study, it is proposed that an *in situ* Szilard-Chalmers method be utilized to improve separation of ^{161}Tb from reaction bi-products and target material. The Szilard-Chalmers method has proven effective at separating isotopes of the same element, thus it may prove a useful tool for the separation of neighboring lanthanides Tb and Gd due to their chemical similarity. Fruitful performance of an *in situ* Szilard-Chalmers process for ^{161}Tb production requires that separation resins be identified which can withstand the high temperatures and neutron flux of a reactor core. In this work, LN and DGA extraction chromatographic resins were evaluated for their thermodynamic, heat, and radiolytic stability using ^{160}Tb as a tracer. Three separate concentrations of nitric acid (0.01, 0.1, 1 M) were used to widen the scope of results, highlighting resin properties in varied solvents and hastening identification of an optimal acid concentration for an *in situ* Szilard-Chalmers. The enthalpy, entropy, and Gibb's free energy of binding was measured at temperatures of 30, 40, 50, and 60°C for both resins. Radiolytic stability of the resins was determined via thermodynamic evaluation of resins irradiated with various gamma doses utilizing a 6,000 Ci ^{137}Cs source. Additionally, resins were incubated at elevated temperatures for 7 days and binding thermodynamics were assessed to determine heat stability.

NUCL

Investigation of a new resin for development of ^{72}Se/^{72}As radioisotope generator

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Arsenic-77 ($t_{1/2}$ = 38.8 h; E_{β^-max} = 0.683 MeV) and ^{72}As ($t_{1/2}$ = 26.0 h; E_{β^+max} = 3.334 MeV) are radioisotopes that can be used as a theranostic matched pair. Arsenic-72 is the decay product of ^{72}Se ($t_{1/2}$ = 8.4 d; ε = 100%) and forms the basis of a potential ^{72}Se/^{72}As generator. The Dowex AG1-X8 (Bio-Rad) and Poros XQ (Thermo Fisher Scientific) anion exchange resins were compared for separating Se and As using the reactor-produced ^{75}Se and ^{76}As tracers. The distribution coefficients (K_d) of selenate (Se(VI)), selenite (Se(IV)) and arsenate (As(V)) were determined on the Poros XQ resin and compared with the previously-evaluated Dowex AG1-X8 resin. The ^{75}Se and ^{76}As were oxidized in 0.1 M NaOH with 30% H_2O_2 to ensure each was in its highest oxidation state. Several series of samples were then prepared by adding the Poros XQ or Dowex AG1-X8 resin (50 mg) to tubes, varying the solution pH from 0-8, and spiking with either ^{76}As or ^{75}Se. Each sample was vortexed for 1 min and then centrifuged for 2 min. Aliquots of the supernatant and original stock solutions were counted on an HPGe detector for calculation of the K_d values. Selenic acid (pKa_2 = 1.7) is a strong acid, while selenous (pKa_1 = 2.62) and arsenic (pKa_1 = 2.19) acids are weak. Results show greater retention of arsenic and selenous acids with the Poros XQ resin than with the Dowex AG1-X8 resin. The selenic acid K_d, which is expected to reach its maximum at a lower pH than that of arsenic acid, will be determined in ongoing studies. These results suggest the potential utility of the Poros XQ resin as the basis for a ^{72}Se/^{72}As generator to elute ^{72}As while retaining ^{72}Se with greater capacity than Dowex AG1-X8.

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Nuclear data for isotope production

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The future of nuclear medicine would appear to be the paradigm of personalized medicine — targeted radionuclide therapy to spare healthy tissue, and theranostic medicine, which pairs an imaging isotope with a therapeutic isotope to provide simultaneous, real-time dose delivery and verification, leading to reductions in prescribed patient dose.

Candidate isotopes to meet these needs have been identified based on their chemical and radioactive decay properties. However, there are significant uncertainties in both the reactions used to produce these radionuclides and/or the intensities and energies of

their decay radiation. The Bay Area Nuclear Data (BAND) Group is currently leading a series of campaigns to perform targeted, high-priority measurements of thin-target cross sections and thick-target integral yields, as part of a larger campaign to address deficiencies in nuclear data needs. These studies will serve to support the production of clinically-relevant quantities of radioactivity.

This campaign has two goals. Primarily, we have performed multiple measurements of thin-target cross sections for proton- (≤200 MeV), deuteron- (≤50 MeV), and alpha-induced (≤90 MeV) reactions. These measurements have focused on the production of high-priority emerging therapeutic radionuclides (^{58m}Co, ^{193m}Pt), as well as diagnostic radionuclides for use in theranostic pairs (^{44}Sc, ^{86}Y, ^{134}Ce). Additionally, we are developing improved monitor reactions for use at high-energy isotope production facilities.

The second goal has been the development of intense energetic neutron sources, for use as alternative production pathways for medical radionuclides. Both quasimonoenergetic (Li(p,n)) and broad-spectrum (deuteron breakup) sources are available to suit production needs. These have been used to demonstrate the production of high-profile radionuclides, including ^{47}Sc, the ^{64}Cu/^{67}Cu theranostic pair, and ^{225}Ac. Since the range of these energetic neutrons is far larger than for charged-particle beams, production yields may be trivially increased by scaling up target thickness. Notably, the primary deuteron beams used for producing these secondary neutrons offer the potential for “simultaneous production”, reacting the primary beam on a thin (<5 MeV) target to make a desired radionuclide via (d,xn) reactions. The unreacted beam emerges to undergo breakup, using the energetic secondary neutrons for production on a different target via (n,x) reactions.

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Beam characterization for safe ^{211}At production

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The properties of astatine-211 make it a great candidate for targeted alpha therapy for cancer due to its short half-life (7.2 h) and non-toxic decay pathway. However, its natural occurrence is miniscule, but can be produced in useful quantities via the ^{209}Bi(α,2n)^{211}At using a 28.5 MeV alpha beam. The Texas A&M Cyclotron Institute has recently joined the DOE University Isotope Network to produce astatine-211 in a location proximal to major cancer research centers. To optimize the production of astatine, the beam current and alpha projectile coverage of the bismuth target should be uniform. Non-uniform beams lead to increased temperature and possible melting in spots on the bismuth targets and can cause volatilization of the astatine. In order to combat these challenges, a custom, 3D-printed Faraday cup viewer in the exact size and position of the target, and an air monitoring system were developed. Before inserting the target into the beamline, the alpha beam is tuned onto the faraday cup viewer comprised of 37 individual Faraday cups. In addition to phosphorescing, the viewer provides a position dependent reading of the beam current. This Faraday cup viewer diagnoses hot spots in the beam providing valuable feedback during beam tuning for a greater overall current on the target. After the target irradiation, the air monitoring system confirms the air inside the chamber is safe for target removal. This combination of the Faraday cup viewer with the air monitoring system increases the safety of astatine production.

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Fast and efficient recovery of At-211 at Texas A&M University: From fundamental insights of At chemistry to an applied separation system

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Interest in α-emitting radionuclides for applications in Targeted Alpha Therapy (TAT) continues to grow. With its relatively short half-life (~7.2 h) and its rather simple decay scheme, At-211 is one of the most advantageous nuclides for this purpose. However, study of astatine chemistry has been limited due to the practical difficulties of having no long-lived isotopes to investigate. The K150 cyclotron at Texas A&M is capable of producing α-particle beams necessary to make At-211 via the Bi-209 (α,*2n*) reaction and is continuing an effort to establish the capability to routinely produce At-211. The availability of the short-lived species at Texas A&M provides an avenue to achieve systematic analysis of its chemical properties. The aim of this investigation is to perform a fast and efficient recovery of At-211 from a bombarded Bi target. Recent findings from At-211 extraction into a variety of solvents has resulted in new insights into the fundamental properties of At-211. From this enhanced understanding, the behavior of At-211 can be better controlled. This has led to the development of a separation system, based on extraction chromatography, which results in a high yield, high purity At-211 product. Details of the liquid-liquid extraction of At-211 and the separation system being developed will be discussed.

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Conventional and non-conventional solvents for astatine and bismuth separation

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Astatine is one of the least chemically studied elements. Its investigation is limited by absence of long-lived isotopes of this element along with only 29 cyclotrons worldwide capable of astatine production. However, investigators interested in Targeted Alpha Therapy consider ^{211}At to be one of the most promising radionuclides. The relatively short ~7.2 h half-life and convenient ~1 barn cross section of ^{209}Bi(α, 2n) reaction at ~29 MeV beam energy make this nuclide suitable for fundamental investigations. Any chemical experiment of this kind usually starts with dissolution of a metal Bi target in concentrated nitric acid with consequent conversion of this matrix to hydrochloric acid and, unfortunately, this delays the At recovery. The team at Texas A&M University has decided to improve and speed up the At separation by working directly with nitric acid solution. To reveal fundamental aspects of both At and Bi behavior under these conditions, a series of liquid-liquid extraction experiments has been performed and a set of conventional and non-conventional solvents has been tested. Based on mathematical analysis of observed data, corresponding thermodynamic parameters such as stability and extraction constants along with astatine speciation and reduction in the nitric acid media have been estimated. Details and results will be discussed.

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Harvesting ^{76}Br and ^{77}Br generators from a flowing-water target at the NSCL

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As a radiohalogen theranostic pair, ^{76}Br and ^{77}Br could become a valuable tool for systemic radiotherapy. The formation of generators from the shorter lived ^{76}Kr and ^{77}Kr parents (14.8 h, and 1.24 h respectively), makes it possible to isolate and use the radioactive daughters for different applications. The isotope harvesting program at the National Superconducting Cyclotron Laboratory (NSCL) provided access to these krypton parents from cooling-water off-gas, and the future Facility for Rare Isotope Beams (FRIB) will produce them in much higher quantities.

In this work, a flowing-water target was irradiated with up to 4 pnA of 150 MeV/nucleon ^{78}Kr over the course of 11 hours, with a total integrated beam current of 16 pnA*h. During the course of the end-of-beam-line experiment, a total of around 205 and 1115 μCi of ^{76}Kr and ^{77}Kr were collected, respectively. The experimental set up employed the use of cryogenic gas traps made of either stainless steel or molecular sieve-filled glass

for the collection of krypton. These traps were part of a larger gas-collection loop which was used to de-humidify the off-gas from the water collection system and remove unwanted gaseous radionuclide products through the use of boric acid and soda lime traps.

Following the beam-line collection, methods for generation and separation of both ^{76}Br and ^{77}Br from the respective parent radionuclides were established. This involved the timely transfer of krypton gas from one cold trap to another. In addition, methods for elution of radiobromide from the traps were tested.

Future experimentation will include utilizing metal organic frameworks (MOFs) for the selective capture of krypton gas. The structure and properties of MOFs can be tailored according to the desired function. Research is ongoing to determine the best architecture for the selectivity of krypton capture over other gaseous radionuclidic products in this system.

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Harnessing the coordination chemistry of scandium to develop radiopharmaceuticals

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Advancements in accelerator physics has enabled the production of radiometals with a broad range of half-lifes and emission properties, expanding the scope of potentially imageable disease targets. However, subsequent development into clinically applicable radiopharmaceuticals remains often impeded by a significant gap in knowledge of aqueous coordination chemistry of the corresponding metal ions. Scandium(III) aqueous chemistry represents a prime example of this conundrum. ^{43}Sc ($E\beta^{+}_{avg}$ = 476 keV, $t_{1/2}$= 3.9h), ^{44}Sc ($E\beta^{+}_{avg}$ = 632 keV, $t_{1/2}$= 4h) have ideal properties for prolonged positron emission tomography (PET) imaging up to 24h post injection. For therapy applications, the emission properties of ^{47}Sc ($E\beta^{-}_{avg}$ = 162 keV, $t_{1/2}$ = 80.4 h) are comparable to ^{177}Lu ($E\beta^{-}_{avg}$ = 134 keV, $t_{1/2}$ = 159.6h). The Sc(III) ion is a close chemical match to Lu(III); therefore ^{43}Sc/^{44}Sc represents an ideal diagnostic isotope partner to the ^{177}Lu therapy isotope, with the ^{43}Sc and ^{44}Sc isotopes accessible through low energy p,n reactions. However, a pronounced lack of studies on the aqueous coordination chemistry have impeded development of Sc-based radiopharmaceuticals.

Our lab has developed novel coordination chemistry approaches and spectroscopic and spectrometric characterization methods to fill this gap. Recently, we have successfully developed the chelator picaga, which radiolabels ^{44}Sc at room temperature. A proof-of-concept bifunctional conjugate targeting the prostate-specific membrane antigen (PSMA) to successfully image PSMA-expressing tumors in vivo. Radiotherapeutic intervention with a single dose of the ^{47}Sc and ^{177}Lu labeled analogue successfully slowed tumor growth in comparison with saline treated cohorts. Herein, we will discuss second-generation chelator designs based on picaga towards enabling radiochemistry with fluorine, scandium and lutetium isotopes under mild conditions.

NUCL

Ligand design strategies for the chelation of theranostic radiometals

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The use of radioactive metal ions for both therapeutic and diagnostic applications has led to significant advances in the field of nuclear medicine. A key requisite for their implementation in this area, however, is that they be stably attached to a biological targeting vector with an appropriate bifunctional chelating agent. Given the diverse chemical properties of radiometals that are useful for nuclear medicine, the design and optimization of bifunctional chelating agents is an important aspect for the development of novel radiopharmaceutical agents. In this presentation, we will discuss our efforts to synthesize and understand the coordination chemistry of new chelating agents for nuclear medicine. A particular emphasis is given on structural features that give rise to distinct selectivity patterns for different radiometal ions and how they might be applied in different contexts.

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Unveiling the elusive coordination chemistry of radium and actinium: Towards targeted separations and therapeutics

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High-energy alpha particles emitted by the decay of radioactive isotopes demonstrate great promise for the treatment of cancer. Among the few α-emitting isotopes that possess radiological properties suitable for therapeutic use, Ac-225 and Ra-223 have shown remarkable efficacy in clinical studies. For these isotopes to be widely implemented for the treatment of soft-tissue metastases, however, two key challenges must be addressed. The first challenge resides in the limited availability of these isotopes, most notably Ac-225. The second challenge is the lack of suitable chelators to

stably retain these isotopes in vivo. Both the production and therapeutic utility of these isotopes would benefit greatly from knowledge of the coordination chemistry of Ac^{3+} and Ra^{2+}, enabling the development of highly selective ligands that can efficiently separate Ac-225 and Ra-223 from complex mixtures generated during their production as well as stably deliver them to metastatic lesions. To date, however, the chemistry of these two ions remains unresolved. In this presentation, we report our efforts to probe the coordination chemistry of Ra-223 and Ac-225 using a toolkit of reverse size-selective macrocyclic chelators. Specifically, leveraging the unique radiological resources available at Oak Ridge National Laboratory, we describe our experiments to obtain the first ever stability constants of Ra^{2+} and Ac^{3+} with this class of ligands. These thermodynamic values, which are scarcely reported for radium and actinium, reveal important structure-stability trends that will facilitate and guide future ligand design efforts towards targeted Ra-223/Ac-225 separations and therapeutics.

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Evaluating poly(lactic-*co*-glycolic acid) nanoparticles for targeted radiotherapy

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Organic nanoparticles have shown promise as delivery platforms for a variety of anti-cancer agents. Here we evaluated poly(lactic-*co*-glycolic acid) (PLGA) nanoparticles a radioisotope delivery vehicle for targeted radiotherapy. PLGA nanoparticles offer the potential to encapsulate radioisotopes within a biodegradable and biocompatible delivery vehicle that could improve their administration and minimize their relocation from the tumor site. A double-emulsion method with D-α-Tocopherol polyethylene glycol 1000 succinate as emulsifier was used to synthesize PLGA nanoparticles with a mean hydrodynamic diameter < 300 nm. PLGA nanoparticles show high colloidal stability in biologically relevant media over time. Optimization of synthesis conditions was carried out by assessing the encapsulation of metal ions as surrogates of therapeutic radionuclides. The concentration of metal ions within PLGA nanoparticles was determined using inductively coupled plasma mass spectroscopy. Results indicate that the concentration of metal ions within PLGA nanoparticles depends on the element being evaluated and its initial concentration. Chelation of surrogate ions with different compounds increased the metal concentration within PLGA nanoparticles. The encapsulation of surrogate metal ions demonstrates the potential of PLGA nanoparticles for targeted radiotherapy. This low cytotoxicity vehicle offers further opportunities for developing combination of radio-chemotherapeutic and theranostic agents.

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Development of $^{134}Ce/^{134}La$ radiopharmaceuticals as positron emitting analogues of alpha emitting radionuclides

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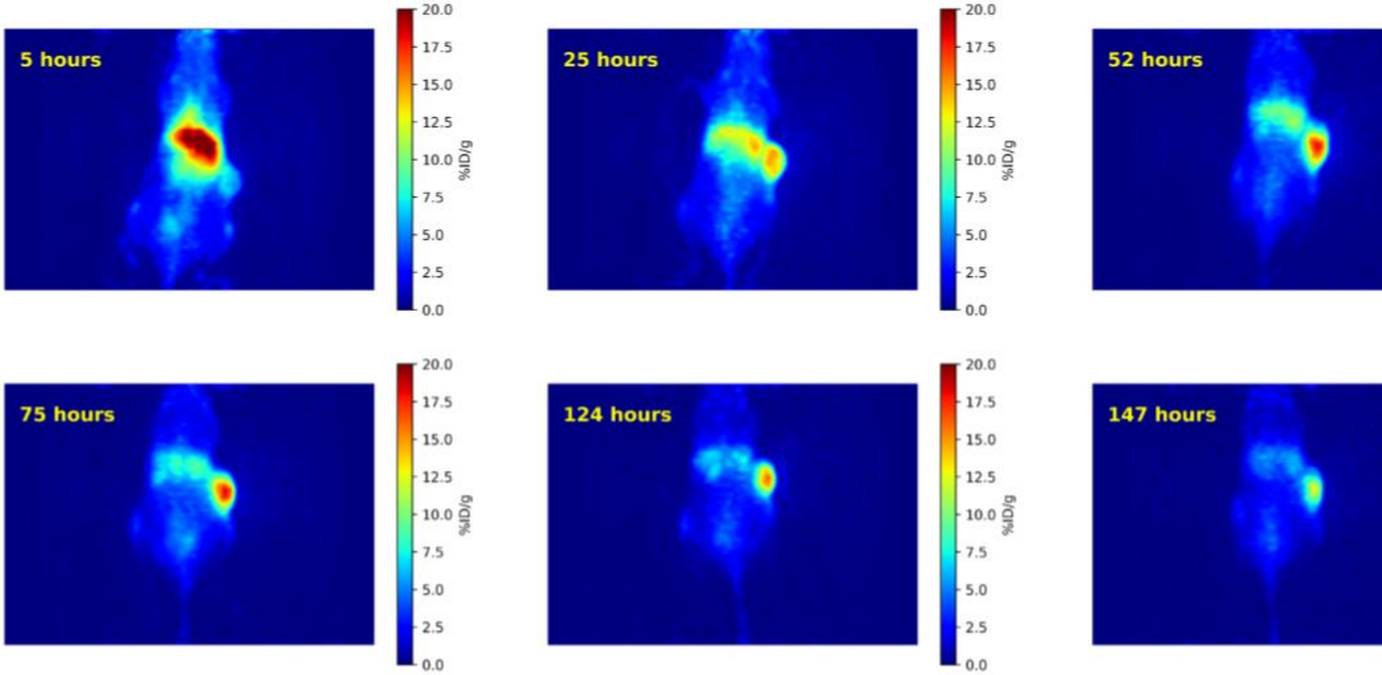
Actinium-225 ($t_{1/2}$ = 9.9 days) and thorium-227 ($t_{1/2}$ = 18.7 days) are the preeminent candidates for Targeted Alpha Therapy (TAT), where alpha-emitting radionuclides are chemically coupled to targeting vectors in order to deliver high linear energy transfer (LET) radiation to nearby tissue. Since ^{225}Ac and ^{227}Th do not produce a signal that can be detected by Positron Emission Tomography (PET), positron-emitting surrogate radionuclides will have to be developed to allow for patient-specificay efficacy and dosimetry of radiopharmaceuticals incorporating ^{225}Ac or ^{227}Th. The ^{134}Ce/^{134}La ($t_{1/2}$ = 3.16 days/6.45 minutes) *in vivo* generator system has been hypothesized to be a surrogate radionuclide for both of these alpha-emitters since its oxidation state can be stabilized to match the oxidation state of ^{225}Ac and ^{227}Th in physiological conditions and has a suitably long half-life, allowing for the tracing of large macromolecules' *in vivo* biodistribution and pharmacokinetics. This talk will discuss the incorporation of ^{134}Ce/^{134}La in antibody drug conjugates (Trastuzumab-DOTA-^{134}Ce(III)). The utility of this system will be displayed through *in vivo* MicroPET imaging of the candidate molecule in a SK-OV-3 tumor bearing NOD SCID mouse model.



Biodistribution of Trastuzumab-DOTA-^{134}Ce over 6 days after injection.

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Production of high specific activity rhenium radioisotopes for radiotherapeutic applications

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Therapeutic radioisotope demand has increased due to growing successes with therapeutic radiopharmaceuticals in the clinic. Since rhenium radioisotopes are considered matched therapeutic partners to ^{99m}Tc, the most widely used diagnostic radioisotope in nuclear medicine, their routine availability at high specific activity is of interest in theranostic radiopharmaceutical development. Three radioisotopes of rhenium have suitable nuclear properties for radiotherapy. High specific activity ^{188}Re (17.0 h half-life, 2.12 MeV β^-_{max}, 155 keV γ (15%)) is available from the ^{188}W/^{188}Re generator system. However, its high beta energy and short half-life limit its use to certain applications, for example treating larger-sized tumors and with targeting agents having relatively short biological half-lives. Rhenium-186 (89.3 h half-life, 1.07 MeV β^-_{max}, 137 keV γ (9%)) is potentially useful in a wider range of applications due to its longer half-life, with its lower beta energy finding utility in treating a range of tumor sizes while lowering toxicity to non-targeted tissues. Rhenium-189 (24.3 h half-life, 1.01 MeV β^-_{max}, 216 keV γ (5.5%)) is an alternative option with nuclear properties between those of ^{186}Re and ^{188}Re. Neither ^{186}Re nor ^{189}Re is routinely available in high specific activity. To address this, we established a quadrilateral collaboration of scientists and trainees at the University of Missouri (MU), University of Washington (UW), Brookhaven National Laboratory (BNL) and Argonne National Laboratory (ANL). This collective effort brings together various reactor and accelerator facilities, equipment, experience and resources to bear on radiorhenium isotope production, including a 10 MW light-water nuclear reactor and 16.5 MeV GE PETtrace cyclotron at the MU Research Reactor (MURR), a Scanditronix MC-50 compact cyclotron at UW, a 50 MeV/25-kW electron linear accelerator (linac) at ANL, and the 66-200 MeV incident energy Brookhaven LINAC Isotope Producer (BLIP) at BNL. Various high specific activity ^{186}Re and ^{189}Re production routes under investigation will be discussed.

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Production of high specific activity rhenium-186 via the ^{186}W(d,2n)^{186}Re nuclear reaction using pressed tungsten-186 metal targets and evaluation of separation methods

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Rhenium-186 ($t_{1/2}$ = 3.72 d) is a highly desirable radionuclide that emits therapeutic β^- particles with a β^-_{max} energy of 1.07 MeV, allowing for a targeted tissue range of up to 3.6 mm. In addition, its 137 keV (8.6%) gamma emission makes it suitable for theranostic applications. Currently, low specific activity ^{186}Re is produced in a reactor via the ^{185}Re(n,g)^{186}Re nuclear reaction, but demand for high specific activity ^{186}Re for targeted radiotherapy applications can potentially be met using charged-particle activation of ^{186}W targets via the ^{186}W(d,2n)^{186}Re nuclear reaction.

A graphite-encased ^{186}W metal target (99.9% enriched) was prepared by uniaxially pressing ^{186}W metal powder between two layers of graphite flakes with 13.8 MPa of hydraulic pressure. The target was bombarded with 22 MeV deuterons for a total of 27 μAh, with an estimated incident deuteron energy of 19.5 MeV on the ^{186}W metal layer. Following a cool-down period to allow co-produced W-187 to decay, the target was dissolved using 30% H_2O_2 and then divided into two aliquots. Separation of the ^{186}Re product in these aliquots was evaluated using an Analig Tc-02 resin column procedure and a methyl ethyl ketone (MEK) solvent extraction procedure. The isolated ^{186}Re product was evaluated by radiolabeling a 222-MAMA-*N*-propionate ligand. Further studies were performed to optimize separation yield conditions by varying resin type, loading solution, and target mass.

An EOB ^{186}Re yield of 0.611 GBq (16.5 mCi) was obtained after a 27 μAh deuteron bombardment. We report a method for the production and separation of high specific activity ^{186}Re from the deuteron bombardment of graphite-encased ^{186}W metal targets. Both separation methods resulted in high recovery yields of ^{186}Re, which was then successfully used to radiolabel a 222-MAMA-*N*-propionate ligand.

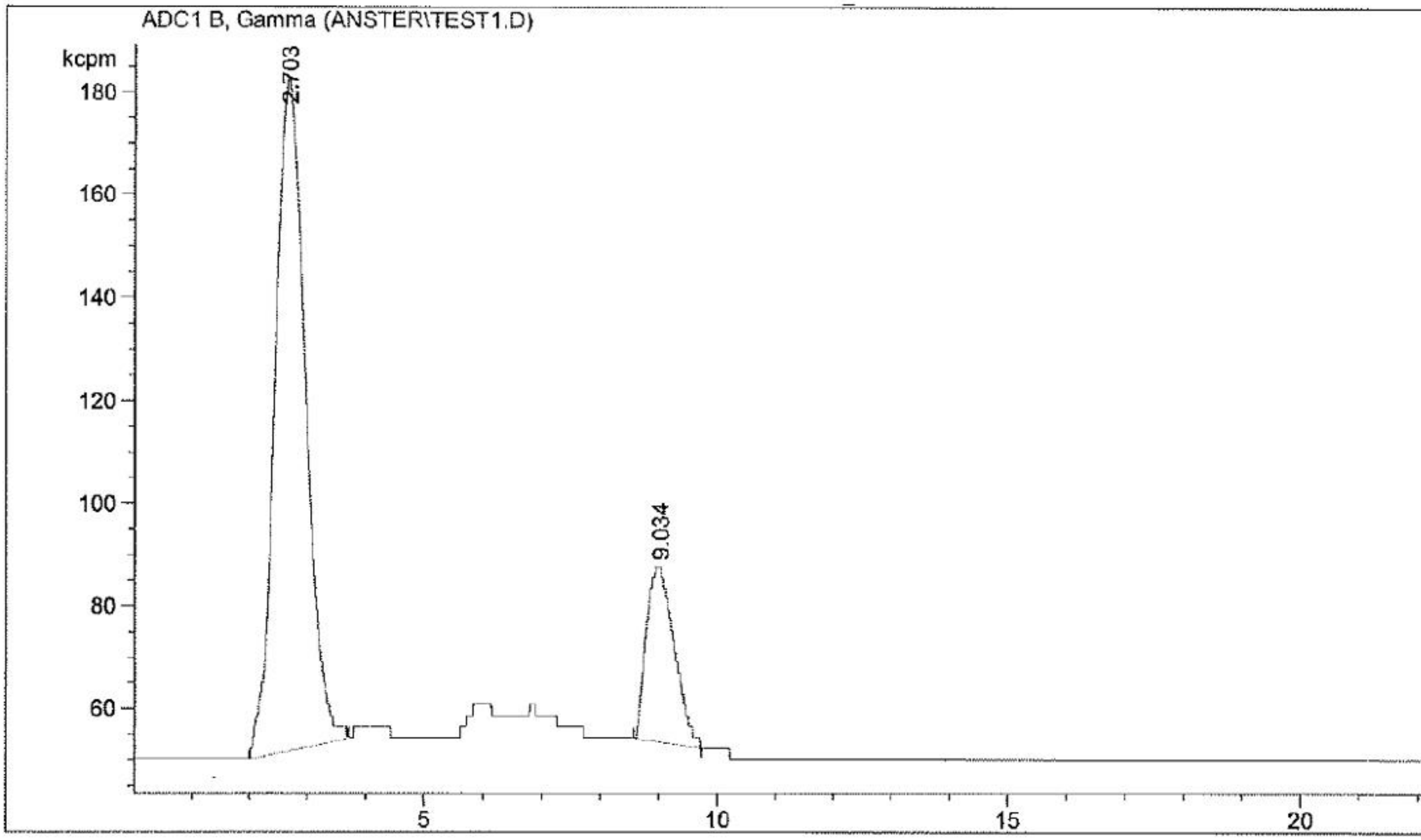

Figure 1: HPLC gamma chromatogram of radiolabeling reaction mixture showing radiolabeled ^{186}Re- MAMA at 9 minutes and $^{186}ReO_4^-$ at 2.7 minutes (20-80 % H2O/MeCN in 20 minutes.

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VPAC targeted Cu-67-TP3805 for prostate cancer therapy

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Treating oncologic diseases successfully, continues to be challenging. In recent years much attention has been drawn to the use of theranostic agents, consisting both alpha and beta emitting radionuclides. Although results are encouraging, several weaknesses persist. For example, Lutetium-177 PSMA-617 (Lu-177-PSMA-617), used widely in many countries, targets prostate specific membrane antigen (PSMA) expressed on prostate cancer (PCa) cell membrane, i) eliminates 10-15% of the PCa patients from treatment, ii) induces mild to severe xerostomia, requiring botulinum toxin treatment of salivary glands ,iii) risks renal impairment, iv) induces , a considerable myelotoxicity and v) creates , due to Lu-177m contaminant, a radioactive waste disposal problem particularly for patients who are incontinent and wear diapers.

We have developed a small radioactive molecule (Cu-64-TP3805) with a high affinity (Kd 3.1 x 10 $^{-9}$M) for genomic, VPAC receptors expressed in high density on cells of all PCa type, that detects, in humans, primary PCa, bone metastatic lesions and malignant lymph nodes with >95% sensitivity. The agent has no urinary excretion, has no salivary gland or bone marrow uptake and has only a small uptake in the renal cortex, not sensitive to radiation damage.
Beta emitting Copper-67, (t½= 2.6 d, γ-185 KeV (40%) ,βmax^{-} 580 KeV) can be easily used to synthesize Cu-67-TP3805. Since **i**) the tissue penetration range (0.6 mm) and the linear energy transfer for Cu-67 is the same as Lu-177,and ii) Cu-67-TP3805, will have, the same tissue distribution as that of Cu-64-TP-3805 with high uptake both in primary PCa and metastatic lesions, **iii**) no urinary excretion, **iv**) no salivary gland uptake, **v**) no bone marrow uptake, Cu-67-TP3805 treatment will be readily applicable to all PCa patients without having to perform patient suitability examination or any anti-toxicity treatment. The data will be discussed.

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Development and exploration of bifunctional chelating ligands for mercury-197m/g

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Theranostic radiometals such as mercury-197m/g ($^{197m/g}$Hg, $t_{1/2}$ = 23.8 h/64.1 h) continue to attract interest as the incorporation of these radionuclides in radiopharmaceuticals have profound potential to both image (diag*nostic* SPECT imaging via gamma-ray decay emissions) and treat diseases such as cancer (*thera*peutic radiation via Auger electrons) simultaneously, using the same drug construct. The literature surrounding $^{197m/g}$Hg radiopharmaceuticals is limited. Particularly, the underdevelopment of selective and stable bifunctional chelators (BFCs) for $^{197m/g}$Hg prevents its use in clinical radiopharmaceuticals. In this study, BFCs that efficiently coordinate to $^{197m/g}$Hg for incorporation into radiopharmaceuticals are identified by screening commercially available and novel sulfur-rich BFCs. This work includes novel ligand design and synthesis, followed by complex characterization and the determination of the radiochemical conversion for these ligands with $^{197m/g}$Hg.

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Single-dose of 212Pb-YS5 significantly inhibits tumor growth in prostate cancer xenograft mouse model

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Introduction: We have developed a new human monoclonal antibody that selectively targets CD46 in all subtypes of prostate cancer. The objective of this study is to test if this antibody can deliver 212Pb radionuclide for effective radioimmunotherapy in prostate cancer.

Methods: The human antibody YS5 was first conjugated with a chelator TCMC followed by radiolabeling with 212Pb. The 212Pb-YS5 was evaluated binding with tumor cells (PC3) in vitro to confirm the cell binding. For in vivo studies, five dosages of 212Pb-YS5 were administered in mice without tumors to identify the safe dose. Finally, the safe dose of 212Pb-YS5 was used to evaluate the therapeutic efficacy for 60 days post-injection in PC3 xenograft tumor mouse models with measures of tumor growth, body weight, survival, and health status.

Results: The labeling yield of 212Pb-YS5 was 65-75% and final products after purification was 99% in radiochemistry purity. The in vitro cell study confirmed the tumor cell binding with a binding affinity of 27-35Nm. Among the dose tested (5 µCi, 10 µCi, 20 µCi, and 50 µCi), 5-20 µCi were safe without any death while 50 µCi resulted in 80% death in one week. Compared with the control group with tumor growing and 80% within 3 weeks and 100% death within 40 days, the radiotherapy study group with a single dose of 20uCi showed significant tumor inhibition with no tumor growth for 40 days post-administration of 212Pb-YS5 and 0% death even after 60 days.

Conclusion: This initial radiotherapeutic study demonstrated that 212Pb-YS5 exhibited excellent therapeutic efficacy and warrant further extensive investigation.

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At-211 labeled small molecule based on the flutemetamol scaffold: Potential theranostic for Alzheimer’s disease

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Recently, targeted alpha-particle therapy (TAT) has garnered recognition for the treatment of various cancer types. The high linear energy transfer of emitted alpha-particles enables targeted cleavage of chemical bonds at proximal distances (micrometer range), leaving neighboring healthy tissues unharmed. We propose this strategy can be applied for the treatment of Alzheimer's disease using astatine-211 (At-211) as a covalently bound alpha-emitting radionuclide. Flutemetamol (X = F-18) is an FDA-approved radiopharmaceutical for positron-emission tomography (PET) imaging of beta-amyloid deposition, a diagnostic tool for Alzheimer's disease. The incorporation of astatine-211 onto the derivative thioflavin scaffold (X = At-211) could result in a novel theranostic agent (1) for the targeted obliteration of amyloid aggregates. Here, we report on the synthesis and characterization of flutemetamol I-127 and At-211 derivatives. (This abstract was updated from a previous submission to a 2020 symposium canceled due to the COVID-19 pandemic.)

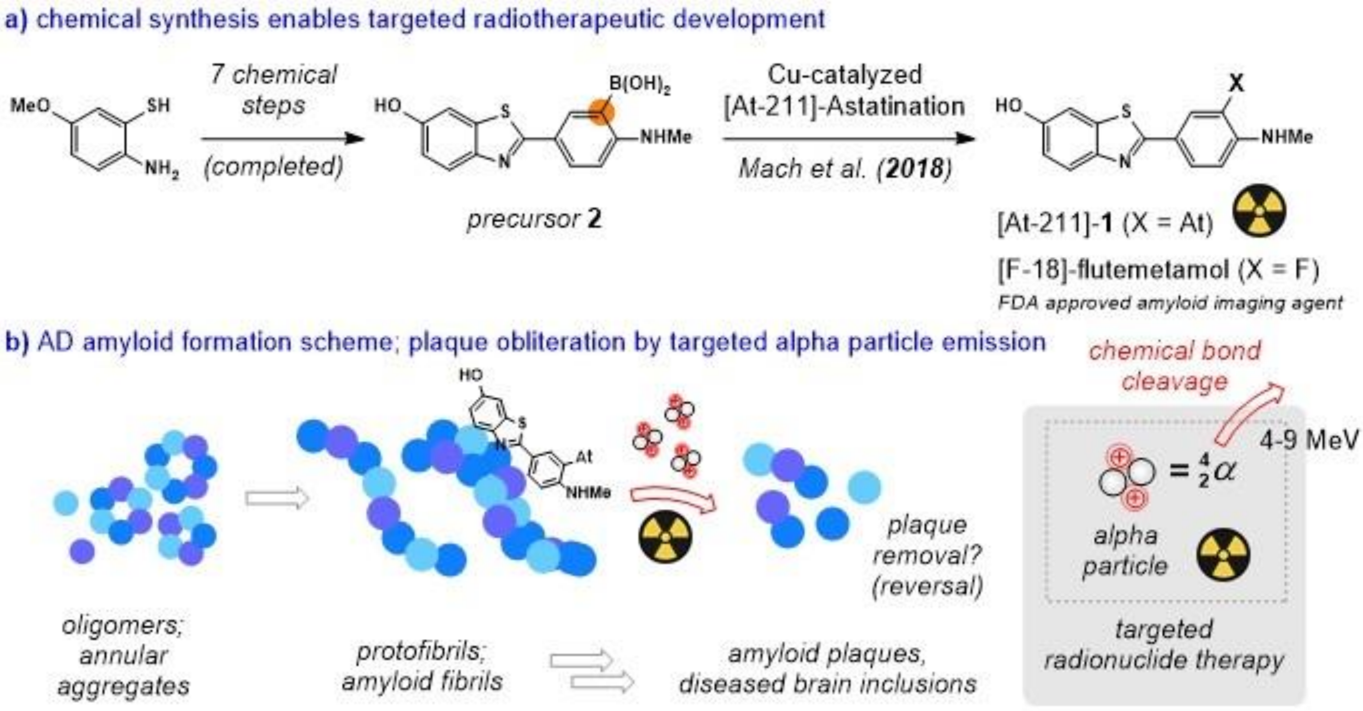

Figure 1. Small-molecule mediated targeted radionuclide therapy for the treatment of Alzheimer's disease.

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Silica nanoparticles as a vehicle for ^{225}Ac/^{89}Zr delivery for use as a theragnostic agent in targeted α-therapy

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Targeted α-therapy (TAT) is a promising treatment method for small tumors and metastases. The high linear energy transfer of α-particles causes double strand DNA breaks inducing cell death. With traditional chelators, the recoil effect during α-decay causes the chelation bonds to break. This is a problem for α-emitters that have long decay chains, like ^{225}Ac, because daughter radionuclides are released from the tumor site. This decreases the dose delivered in the tumor site and increases the dose delivered to healthy tissue throughout the body. Silica nanoparticles are a promising solution as additional layers of silica can be added after radiolabeling, increasing the retention of daughter radionuclides in the tumor site. Another challenge in working with ^{225}Ac is the inability to image the biological agent. Silica nanoparticles allow for the co-incorporation of PET radionuclide ^{89}Zr and TAT radionuclide ^{225}Ac resulting in a theragnostic agent. Silica nanoparticles are also cheap, biologically inert, and can be functionalized with peptides to target specific receptors expressed in tumors. Initial studies with mesoporous nanoparticles show ~90% labeling for both ^{225}Ac and ^{89}Zr. The retention of ^{225}Ac's daughter nuclei will be investigated with and without a thin layer of gold added to the nanoparticles. Additionally, incorporating ^{225}Ac and ^{89}Zr via co-precipitation with the Stöber method is being investigated.

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Radiochemistry and its applications in radioactive waste management and nuclear security

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This presentation is an overview of radiochemistry in complex systems ranging from groundwater to separations to radioactive waste processing streams. These systems are far from ideal, and often involve conditions that are driven far from equilibrium. Using multi-modal experimental approaches that include a strong theoretical foundation is resulting in a remarkable ability to understand behavior and chemical dynamics of ions in these systems. This knowledge is being applied to enable new approaches to radioactive waste processing and environmental monitoring.

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Panel discussion: Accelerating career development for radiochemists within the team science context

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Some of the challenges that societies face today are expansive radiochemical grand challenges, ranging from nuclear security to environmental cleanup. Accelerating innovative solutions to these grand challenges can be enabled by a team approach to discovery science, which provides an enduring foundation for technological progress. Today’s radiochemical team science involves the integration of experimental and computational contributors collaborating together, often at major scientific user facilities and with powerful supercomputers. This team science model must be effectively managed to provide productive career development and recognition opportunities for all team members, especially early career participants. This panel discussion will provide an opportunity to share experiences, describe the skills needed, and identify good practices within teams that drive forward careers for early career participants within the team science context.

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Educating the next generation of nuclear chemists and radiochemists in the U.S.

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Radiochemistry, the chemistry of radioactive materials where radioisotopes are used to study the properties of radioactive and stable elements, is becoming a lost art. Experts in nuclear chemistry, a branch of chemistry focusing on nuclear processes and transformation in the nuclei of atoms, are equally rare. The lack of experts in those fields – undoubtably based in part on a general mistrust towards scientists, fear of the nuclear field, and misinformation – is alarming. Although an accurate number of the students who graduate with a degree in the field of radiochemistry and nuclear chemistry in the U.S. is difficult to quantify, the lack of personnel in professional positions for which a solid academic foundation in these nuclear sciences is needed, is an indicator of the distressing situation. Unfortunately, this deficiency leads to dramatic consequences, as such knowledge is required in nuclear medicine applications, homeland security, non-proliferation and arms control, nuclear power, nuclear fuel cycle, and environmental remediation and management. We will discuss the status and possible solutions to address this problem.

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Sue Clark, an institute and team science

***James M. Boncella**, james.boncella@wsu.edu. Department of Chemistry, Washington State University, Pullman, Washington, United States*

In this talk, I will discuss the opportunities and challenges associated with the formation of an interdisciplinary institute that spans a University and a National Laboratory. Sue Clark had the vision for this type of endeavor, and she has played a pivotal role in the formation of the WSU/PNNL Nuclear Science and Technology Institute. I will also discuss the role of this Institute facilitating the training of graduate students while exposing them to the nuances of working in a national laboratory environment. Several examples of technical projects will be discussed including our own interests in fundamental organo-uranium chemistry.

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Nuclear science projects and our user facility model at the Washington State University Nuclear Science Center

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With less than 30 operational research reactors in the US, the WSU Nuclear Science Center (NSC) reactor facility serves a critical need for reactor-produced radioisotopes utilized in fundamental and applied nuclear research. The continued safe operations of the reactor facility and reactor operations currently meet critical needs in support of training and applied science at the DOE, the Department of Defense, Idaho National Laboratory, Pacific Northwest National Laboratory, Lawrence Livermore National Laboratory, Sandia National Laboratory, the Federal Bureau of Investigation, the National Guard Bureau, the National Nuclear Security Administration, and others.

In support of our mission, the NSC has adopted a user facility operational model to operate the facility research spaces, enabling all WSU faculty to utilize the facility for their nuclear-based research. Researchers can either perform experiments and gather data themselves, or collaborate with the Center's experienced personnel to perform, gather, and process data in support of their projects. The user facility is outfitting laboratory spaces for actinide thermochemistry, structural characterization of complex systems, and the establishment of the Radiological Science Laboratory (RSL) – a collaboration between the NSC, WSU/PNNL Nuclear Science and Technology Institute (NSTI), WSU Chemistry, and WSU School of Mechanical and Materials Engineering. The RSL will be home to a suite of instruments utilizing radiation scattering and absorption to probe solvation and material properties not otherwise achievable with other instruments or at other facilities on the Pullman campus.

Teaching and training students are a cornerstone to our Center's mission. NSC offers a student nuclear reactor operator training program to currently enrolled full-time WSU undergraduate and graduate students to prepare them for the nuclear workforce. The operator training program pursues four objectives, namely to: 1) Teach students; 2) Serve as a student-led workforce for reactor operations; 3) Serve as a workforce pool for full-time staff positions as they become available at the facility, and 4) Provide students with real-world experiential training in nuclear science and radiochemistry as well as options for internships and colloquia presentations to further their careers in nuclear science.

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Expanded uncertainties of instrumental, preconcentration and radiochemical neutron activation analysis methods for the measurement of nanogram levels of iodine in biological materials

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The expanded uncertainties associated with the measurement of nanogram levels of iodine in biological materials by various types of neuron activation analysis (NAA) technique were evaluated following ISO GUM procedures. The methods examined were conventional instrumental NAA (INAA), epithermal INAA (EINAA), pseudo-cyclic INAA (PC-INAA), pseudo-cyclic EINAA (PC-EINAA), preconcentration NAA (PNAA) and radiochemical NAA (RNAA) in conjunction with conventional and anti-coincidence (AC) gamma-ray spectrometry using both single comparator and k0 standardization procedures. Among the INAA methods, the lowest detection limit of 0.005 µg/kg was obtained by the PC-EINAA with anticoincidence counting (PC-EINAA-AC) method for 5 cycles of irradiation-delay-counting using a comparator standard. The expanded

uncertainty (κ=2, ~95% CL) of 1.81 ±0.48 µg/kg was obtained for the k0 procedure compared to that of 1.85 ±0.22 µg/kg for the single comparator procedure for NIST RM 8415 Whole Egg Powder with a certified value of 1970 ± 460 µg/kg. The value for the k0 procedure appears to be slightly influenced by the uncertainties in the nuclear constants and detector full photopeak efficiency determination. A PNAA method using a mixture of hexane and isopropanol was employed to measure extractable organo-iodine in bovine milk lipids. The samples were irradiated in a neutron flux of 2.5×10^{11} cm^2 s^{-1} for 10 min at the Dalhousie University SLOWPOKE-2 reactor facility, allowed to decay for 2 min, and counted for 10 min. A relative expanded uncertainty of 6.6% was obtained for the iodine mass fraction of 0.211 mg/kg in bovine milk lipids. A RNAA method involving microwave digestion after irradiation followed by bismuth sulfide coprecipitation gave a relative expanded uncertainty of 3.2% for the iodine mass fraction of 0.050 mg/kg in a milk sample. Many parameters were investigated in detail for the calculation of relative expanded uncertainties and will be presented.

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Characterizing technetium and plutonium in subsurface sediments for contaminant remediation

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Technetium-99 (Tc) and plutonium (Pu) have been released to the subsurface worldwide, including the release of ~2.59×10^{13} Bq of Tc and ~1.85×10^{15} Bq of Pu at the Hanford Site (Washington State, U.S.A.). Tc and Pu contamination remain a major environmental problem at legacy nuclear reprocessing sites as subsurface mobility is influenced by complex interactions with sediments and co-contaminants within waste streams. Developing enhanced attenuation and efficient remediation strategies for released Tc and Pu requires a complete understanding of retardation processes and mass flux, including the different mechanisms by which Tc and Pu are immobilized in the subsurface and the effect of localized subsurface conditions. Here, sediments from Hanford waste disposal sites have been selected, based on historical information and sediment composition, for characterization of Tc and Pu sediment associations. Characterization of Tc-containing phases in field-contaminated sediments using Tc K-edge X-ray absorption near edge structure spectroscopy revealed that Tc is present in vadose zone sediments as (i) TcO_4^- that remains in water films associated with fine-grained sediments; (ii) Tc co-precipitated with other lanthanides in phosphate mineral phases; and (iii) Tc present as $TcO_2.nH_2O$ in localized reducing zones.

Previous investigations at Hanford have shown that Pu is associated with discrete particles as PuO_2, as secondary phases formed from interactions with waste or as adsorbed/incorporated species associated with sediments. In this work, evidence is presented for the existence PuO_2, PuO_2-Bi_2O_3 composites, and burnt Pu metal particles in near-surface sediments where acidic waste was disposed. Pu and americium (Am), the long-lived daughter product of Pu-241, moved deeper into the subsurface and exhibit different behavior with depth, suggesting different mobility controlling phases. From these preliminary results, it is suggested that Pu and Am have limited mobility within the soil profile, and that stimulation of conditions that enhance Tc attenuation can be used to improve long-term Tc remediation strategies.

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Examination of actinide subsurface transport from lab to field scales: Influence of redox reactions and organic ligand complexation

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The migration of actinides in the environment is dependent on the chemical species which dominate under given geochemical conditions. The mobility can be enhanced or retarded by altering the oxidation state or forming soluble organic ligand-metal ion complexes. This work examines three case studies to evaluate the impacts of these changes in chemical speciation on the transport of trace elements through soil. Our approach seeks to characterize the time and length scales over which non-equilibrium states are maintained by rate-limiting (or rate-enhancing) reactions between radionuclides and co-reactants due to interactions between physical mass-transfer processes (i.e., flow, advection, diffusion) and (biogeo)chemical reactions.

A range of Np and Pu sources with varying chemical forms were deployed in multi-year lysimeter experiments. All plutonium sources are transforming to disordered PuO_{2+x} type phases regardless of the initial oxidation state and the extent of transformation to disordered PuO_{2+x} phases appears to be accelerated in the field lysimeter sources relative to the archived sources. Comparison of the downward migration of each source indicates some notable differences between lysimeters with different initial Pu and Np sources. The current working hypothesis to explain these differences is that colloidal PuO_{2+x} and NpO_2 phases are forming during the chemical/physical transformations of the source materials and downward migration is enhanced by these colloidal phases. Thus, the extent of transport appears to be somewhat dependent on the initial chemical/physical state of the source.

A second mechanism by which the mobility of ions can be altered is through complexation with organic ligands. This work has examined the influence of nutrient availability, plant roots and plant root exudates on preferential water flow through field lysimeters and dissolution of uranyl phosphate minerals through formation of soluble U(VI)-ligand complexes. Results indicate that less soluble phosphate sources lead to enhanced plant exudate production which in turn enhances uranium solubility and mobility. These results were verified using flow-through batch reactor experiments examining the dissolution of uranyl phosphate by citric acid (a common phytosiderophore). Comparable experiments examining the influence of organic matter on Pu sorption indicate similar processes control Pu migration.

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Spectroelectrochemistry as a tool for understanding the behavior of radionuclides in natural and engineered systems

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Fast, robust, and cost-effective methods are needed for nuclear processing and environmental applications where in-line and field applications are desired. Sensors need good selectivity for accurate measurements on complex samples such as found in process and environmental settings. A sensor based on spectroelectrochemistry is an excellent candidate to meet these needs as it can specifically target a single analyte in a sample containing many p+otential interferences.

The sensor consists of an innovative spectroelectrochemical configuration that we have developed by combining the following elements: spectroscopy, electrochemistry, device fabrication, thin film technology, and synthetic inorganic chemistry. In one type of spectroelectrochemical sensor the additional selectivity is provided by subjecting the analyte to electrolysis that electrochemically modulates an optical signal such as absorbance or fluorescence. The modulated signal can then be distinguished from the constant signals of the potential interferences, and the analyte quantified by the magnitude of the change in optical signal. The spectroelectrochemical sensor has been demonstrated on a variety of chemical systems including authentic radioactive waste samples. Specific examples of analyte detection including ferrocyanide, technetium and ruthenium will be presented.

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On-line monitoring and sensor development: Supporting the future of nuclear energy

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Development of reliable and fast methods for detecting and monitoring chemical composition of nuclear materials or related processing streams can facilitate maintenance of proper safeguards, ensure safe and efficient processing of materials, and support better informed decisions on environmental impacts. Optical spectroscopy-based approaches have the benefits of providing fast response while utilizing mature technology that is robust enough to withstand field applications. Furthermore, optical spectroscopy can be flexibly paired with complementary techniques to provide high fidelity analysis of multi-component samples that would otherwise be costly and time consuming to analyze. Combining optical spectroscopy with electrochemistry, or spectroelectrochemistry, can allow for the development of sensors that display high selectivity for target analytes. This enables accurate analysis despite optical interferences and can be further modified to enable detection of species with limited optical activity. Optical spectroscopy can also be paired with chemometric analysis, a multivariate form of analysis, to provide real-time analysis of process streams during processing operations. This talk will cover the applications of optical spectroscopy to sensor development and on-line monitoring to support needs within the field of nuclear energy.

NUCL

Exploring rapid radiochemistry separations

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With novel nuclear science applications continuously emerging in today’s society, the ability to design simple, tunable radiochemical separation approaches that can be tailored to meet the specific needs of a given research effort is of high value to the modern researcher. This presentation explores a variety of options available to modern radiochemists that can assist them with these efforts. The techniques primarily to be discussed in this presentation are founded on the coupling of traditional radiochemical concepts with the usage of simple, novel approaches for performing chromatographic separations; the combination of traditional wisdom with novel approaches can enable researchers to achieve high chemical yields and separation factors while simultaneously avoiding the need for complex, dedicated, expensive instrumentation. A variety of

examples from our laboratory for isolating short-lived radioisotopes for various applications will be presented in this work, with examples ranging from simple binary systems such as the isolation of short-lived, accelerator produced Sc-47 for medical applications, to more complex separations such as the isolation of individual lanthanide and fission product isotopes from highly complex uranium/short-lived fission samples.

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Microscale targets designed for simultaneous purification and production of isotopes

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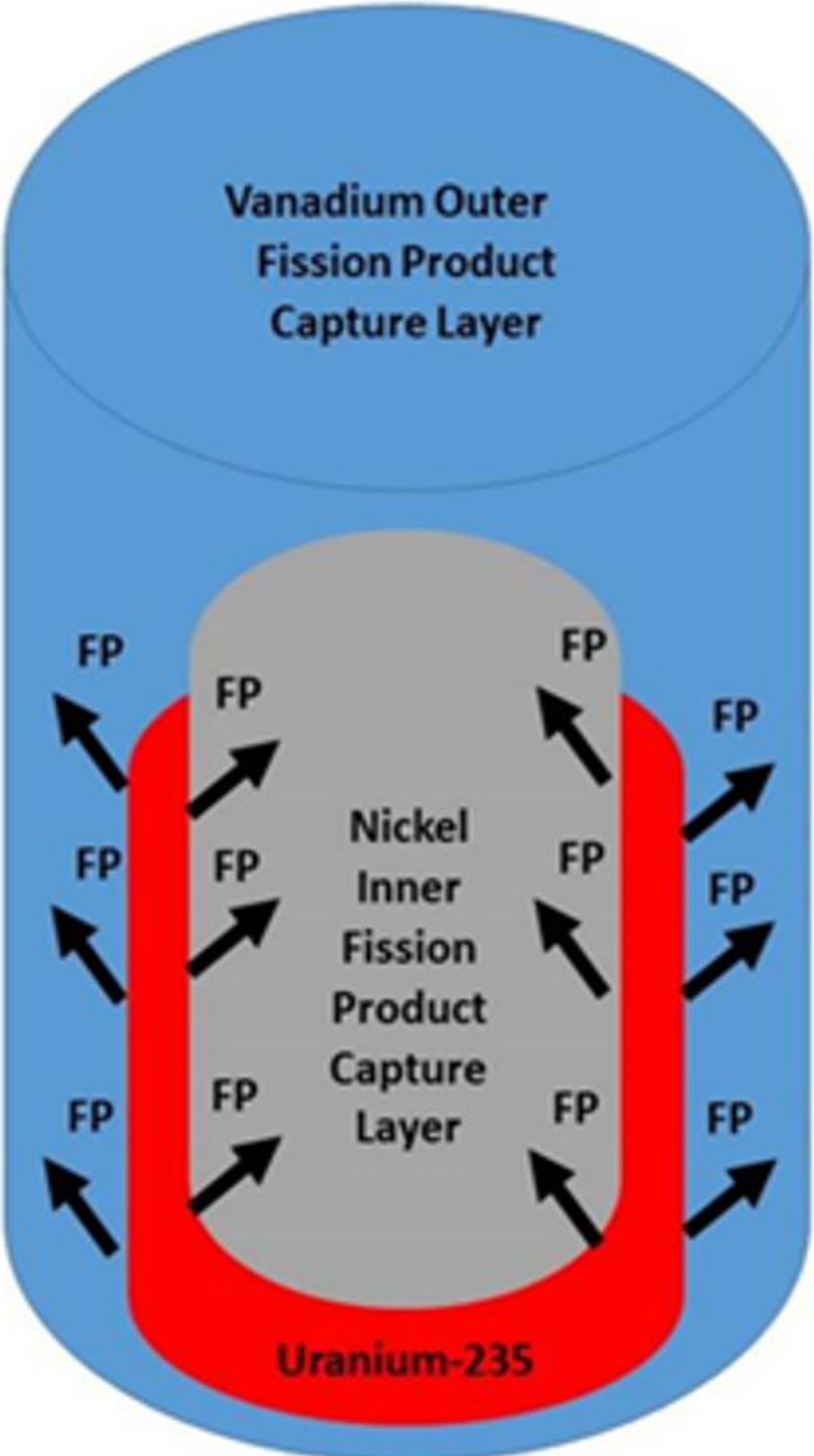
Microscale targets were designed and tested for fission product production and simultaneous separation from target material via kinetic separation. This target design facilitates cleaner and more cost-effective isotope production. The targets were designed with micron wide uranium fissile target layer, surrounded by various fission product capture layer materials. The optimal widths for the fissile target layer and the recoil capture layer were determined using Stopping and Range of Ions in Matter (SRIM) modeling for experimental conditions. The target manufacturing process was the layering of the uranium fissile layer by nitrogen trifluoride volatilization onto nickel wire as the inner capture layer, and a vanadium capsule as the outer capture layer. These targets were irradiated at the Washington State University research reactor to produce roughly $2x10^{11}$ fissions of the fissile material, followed by physical separation of the fissile layer and the nickel, and vanadium capture layers. Measurement of the fission products and the neptunium-239 activation product was achieved using gamma spectroscopy, the recovery of uranium in each layer was measured by inductively coupled plasma mass spectrometry. The microscale target design enabled physical separation of the fission products from the activation product and the initial target material with a separation factor of roughly $1x10^4$ by kinetic energy ejection of the fission products into the recoil capture layer. This target design can help alleviate supply issues of many chemotherapy and other isotope based medical products.


Vanadium Outer
Fission Product
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Nickel
Inner
Fission
Product
Capture
Layer
Uranium-235

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Expanding the toolbox in nuclear proliferomics to include oxygen isotope ratios

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The oxygen stable isotope composition of uranium oxides has been of interest in nuclear forensics and safeguards communities for decades for its potential as a signature of processing history and geolocation. Nevertheless, there has been a dearth of experimental work published to explain how oxygen isotopes fractionate in these materials during processing. At the University of Utah, a series of carefully controlled experiments, from the precipitation of yellowcake derivatives to calcination and fuel fabrication, have been performed to evaluate the incorporation and exchange of oxygen isotopes. Using a newly designed fluorination system at Utah, bulk oxygen isotope compositions of compounds from each processing stage were measured. In addition, a novel technique coupling thermogravimetric analysis and isotope ratio infrared spectroscopy (TGA-IRIS) was employed at Lawrence Livermore National Laboratory to isolate and analyze mineralization waters from uranium precipitates.

Following the peroxide precipitation route, analysis using TGA-IRIS revealed a consistent fractionation between water bound to uranyl peroxide and process water. Bulk fluorination of these precipitates did not show this same consistency however, suggesting a lack of equilibration between process water and the more tightly bound uranyl oxygen. Moving further through the nuclear fuel cycle, calcination and reduction processes were shown to significantly alter the oxygen signature of uranium compounds as a result of atmospheric composition, temperature, and heating and cooling rates. These results provide new insight into the poorly understood relation of oxygen isotope composition to production practices of uranium materials and illuminate promising new avenues for signature development.

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Covalent bonding in actinide compounds

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The covalent mixing of metal and ligand orbitals makes an important contribution to the properties of actinide compounds, yet there is a dearth of estimates that quantify the

extent and the energetic importance of the covalent character of these compounds. Novel theoretical methods have been developed to provide reliable information about the covalent bonding and their application to selected actinide compounds is presented. Compelling evidence is presented for important aspects of the covalent mixing: (1) The contributions of both the actinide 6d orbitals and the actinide 5f orbitals to form covalent bonds with the ligand frontier orbitals are both important and the 6d covalency should not be neglected. (2) The covalent mixing depends on the nominal oxidation state of the actinide cation. It is larger for higher oxidation states. (3) The relative importance of the 6d covalency increases as the 5f occupation increases. And, (4) the extent of the covalent mixing depends strongly on the separation of the actinide cation and the ligand. While this distance dependence is not surprising, the extent of the changes in the covalency with bond distance and the consequences for an observable are discussed. The focus will be for differences between oxides of U and Pu. The theoretical analysis of the covalency is based on the use of wavefunctions for cluster models of the compounds and of the fragments. The extent of the covalency is estimated from projections of fragment orbitals on the orbitals of the compound. The energetic importance is estimated by constraining the variation of the orbitals of the compound where the covalent mixing is allowed or forbidden.

NUCL

Overview of computational image techniques for characterizing the surface morphology of lanthanide and actinide materials

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While analytical imaging techniques and qualitative surface morphology descriptions can deliver valuable insight into a material's properties, additional analysis techniques are often needed to quantify or further characterize key morphology features. Computational image analysis techniques for segmentation, texture analysis, and deep learning are introduced and described, emphasizing their applications to lanthanide and actinide chemistry. The size and shape morphology features can be quantitatively measured with high precision from micrographs through particle segmentation analysis. In this presentation, several common segmentation methods will be implemented and compared, including image texture analysis techniques and convolutional neural networks (CNNs).

For example, image texture analysis techniques, such as gray-level co-occurrence matrices (GLCM) or angle measurement technique (AMT), can be used to characterize more abstract morphology features. These texture techniques might also be instrumental in identifying heterogeneities or material defects. Alternatively, CNNs are complex and powerful deep learning tools capable of pattern recognition, image

classification, automatic feature segmentation, and more. Key aspects of the CNN architecture, and their specific roles, are introduced to demystify the “black box” method. The challenges faced in developing CNNs for surface morphology analysis, specifically for nuclear forensics applications, are addressed.

NUCL

Interfacial behaviors of ALSEP organic extractants: An atomic perspective derived from molecular dynamics simulation

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With the continued generation of nuclear power, management of high-level waste is becoming increasingly relevant. Transuranium actinides (e.g. neptunium, americium, and curium) are of particular interest as these elements have been identified as the major contributors to long-term radiotoxicity of nuclear waste and are the main targets for transmutation. Even so, satisfactory transmutation can only be achieved after the separation of the actinides from lanthanide fission products – a herculean task that has daunted scientists since the discovery of transuranium actinides. Herein, an extractant mixture of *N*,*N*,*N'*,*N'*-tetra(2-ethylhexyl)diglycolamide (T2EHDGA) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEHEHP), proposed for the Actinide-Lanthanide Separation (ALSEP) process, were investigated in biphasic *n*-dodecane + water solution. Molecular dynamics simulations were performed on systems composed of 0 M to 6 M HNNO3 to understand the effects of varying aqueous acidity on surface behaviors and coordination environments near the Gibbs dividing surface. Specifically, this work aims to provide a complete molecular picture by probing the respective chemical interactions, spatial distribution of extractants, interfacial orientation, and extractant conformation of HEHEHP and T2EHDGA.

NUCL

Impact of Pb^{+2} on the structural and optical properties of uranyl complexes

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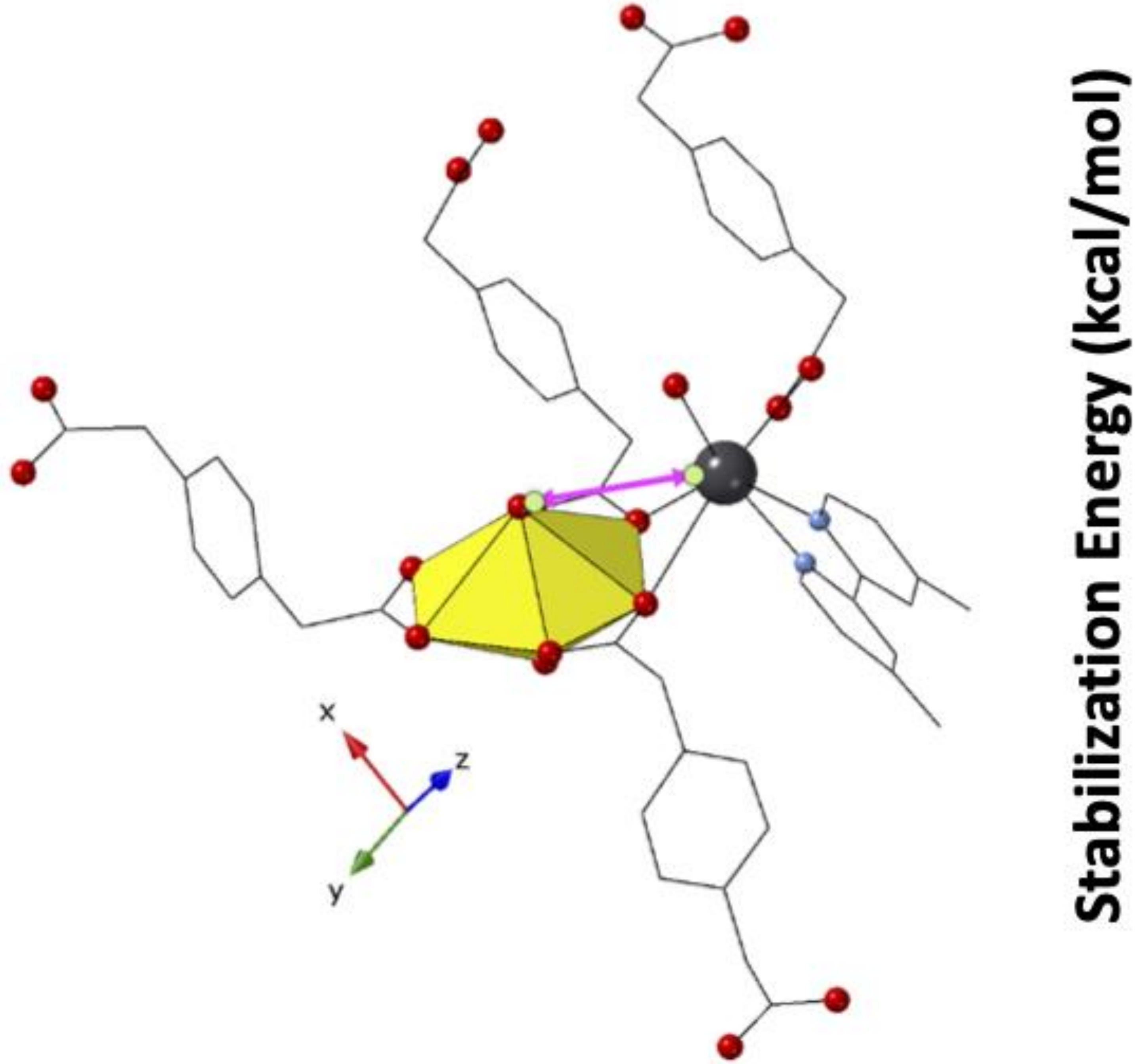
The synthesis and characterization of six heterometallic UO_2^{2+}/Pb^{2+} compounds were performed to study the effect of closed-shell metal influences on U=O bonding and photophysical properties via second sphere coordination. Structural determinations were made using single-crystal X-ray diffraction whereas optical properties were measured using temperature variable luminescence. Our findings correlate uranyl emission quenching to -yl interaction strength as determined via Pb-O distances, natural bonding orbital (NBO), and quantum theory of atoms in molecules (QTAIM) calculations.

We find an increase in Pb-O_{yl} stabilization energy, i.e interaction strength, lends to weakening of U=O bonding and increased instances of emission quenching. To rationalize these observations, we propose the formation of an excited state complex, i.e. an exciplex, involving the Pb^{2+} and the uranyl unit which can only form if the interaction strength is sufficient. The formation of this short-lived species introduces non-radiative relaxation pathways for U(VI) emission quenching. This study provides a platform to interrogate U=O bonding chemistry in the presence of closed-shelled heavy metal ions such as those that occur as fission products.



NUCL

Magnetic properties of cubic plutonium hydrides: A density functional theory study

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The understanding of long-term storage of nuclear materials, including plutonium, is essential to avoid risks to human, wildlife and environment. Hydrogen corrosion of plutonium produces plutonium hydride, PuH_x, which is a pyrophoric material.
We used Density Functional Theory, PBEsol + U approach and Hybrid DFT based on HSE06sol to study fluorite structured PuH_2 and cubic PuH_3. We explicitly considered spin-orbit coupling and noncollinear magnetic contributions to systematically identify the stability of the magnetic ordering of the hydride structures, resolving the controversy around their magnetic structure. Our findings show that PuHx crystal structures are coupled by spin-orbit interactions to the magnetic states, and that ferromagnetic and antiferromagnetic (longitudinal and transverse) ordering have similar stability and dependent on the Hubbard U parameter used. This result is confirmed by the hybrid DFT. Given the experimental difficulties of handling plutonium hydrides, our results have significant implications in future computational studies of model PuHx systems and related actinide hydrides.

NUCL

Impact of tritium valence and impurities on chemical structure and transport in fluoride salts

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In advanced fission and fusion reactors, high heat capacity fluoride molten salts allow operation at high temperature and atmospheric pressure, which could dramatically increase efficiency, reduce capital cost, and enable passive safety features. In these systems, tritium is of particular importance due to its ability to corrode structural materials as $^3H^+$ in fluoride salts, and its potential to cause significant radioactive release as diffusive $^3H^0$, which are cited as key barriers to technological deployment. Yet, the chemistry and transport behavior of the hydrogen species remain poorly understood due to the difficulties in handling and controlling experimental impurities in toxic and radioactive materials. To address these challenges, we used ab initio molecular dynamics to examine the coupled effects of tritium speciation and transport in prototypical salts 66.6%LiF-33.3%BeF_2 (Flibe) and 46.5%LiF-11.5%NaF-42%KF (Flinak). Using extensively validated calculations on the local structure and dynamics, we find significant difference between $^3H^0$ and $^3H^+$ transport behaviors that are usually overlooked. We find that $^3H^0$, which always exists as molecular H_2 diffuses 3-5 times faster than $^3H^+$ due to differences in their bonding and complexation in solution.

Moreover, we examine the interactions between corrosion and atmospheric impurities and tritium atoms. We find that tritium is able to isotopically exchange with H_2O (from moisture ingress) and bind to dissolved CrF complexes (corrosion product) reducing their transport mobility. This work explains contradicting experimental results and provides useful species data for predicting tritium transport and chemistry in fluoride salts.

NUCL

Adsorption of water, carbon dioxide and hydrogen peroxide on PuO_2 surfaces: A density functional theory study

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The handling of radioactive plutonium oxide, and its safe long-term storage and subsequent reprocessing or disposal pose significant challenges to the nuclear industry. There is evidence of gas build-up in storage containers, which may be due to small residual molecules, including water, hydrogen and products of radiolysis. Knowledge on the interaction of such species with the surface of the oxide will aid handling of the long-term storage of PuO_2. In our study, we used Density Functional Theory calculations (PBEsol + U) including the effect of spin-orbit interactions coupled with the complex 3k antiferromagnetic longitudinal ordering to understand the surface composition and energetics of PuO_2 surfaces when water, carbon dioxide and hydrogen peroxide are adsorbed. We found that strong chemical adsorption is favoured. Water and hydrogen peroxide dissociate while carbon dioxide forms surface carbonate groups on all the most relevant PuO_2 surfaces including the {111}, {110} and {100} surfaces. Finally, we used a thermodynamic strategy to evaluate the surface free energy of adsorbed surfaces, from which we mapped the PuO_2 surface phase diagrams as a function temperature, water and oxygen partial pressure. These free energies have also been used to predict equilibrium nanoparticle morphologies and infer how external conditions may drive particle morphology evolution between the polyhedral shaped nanocubes, truncated octahedra and octahedra.

NUCL

Radiation damage in embedded tungsten nanoparticles

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Tungsten is currently one of the leading candidates for use as a plasma-facing material in fusion reactors. With a high melting point and thermal conductivity, tungsten is particularly well suited to withstand high energy neutron collisions and high heat flux. However, neutron collisions induce collision cascades in structural materials, leading to

the accumulation of point defects and the degradation of the mechanical properties of the material. One possible method to improve the radiation resistance of the material is to introduce a high number of interfaces and grain boundaries into the system. These interfaces can act as a defect sink to trap and recombine point defects, which could reduce the defect accumulation. However, the annealing of such interfaces due to radiation damage may have a detrimental impact on the structure.
In our research we have utilized classical molecular dynamics to carry out collision cascades in bulk tungsten systems with embedded tungsten nanoparticles. Our results show that collision cascades occurring in close proximity to the interface appear to have improved long term defect recovery despite initial high defect production. Furthermore, we show that the collision cascade can shift the bulk/nanoparticle interface, facilitating a decrease in size of the nanoparticle and enhancing void production.

NUCL

Theoretical study on the coordination and structural chemistry of actinium-HOPO complexes

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Actinium-225 (^{225}Ac) is a highly promising radiopharmaceutical agent for targeted α therapy (TAT) for cancer treatment. For successful application of TAT, the ^{225}Ac in the form of Ac^{3+} has to be stabilized by a bifunctional chelator to be delivered and retained around the targeted cancer cells. A class of compounds, mutidentate hydroxypyridinonate (HOPO) ligands, was found to have high affinity for Ac^{3+}. Based on the structure of a known octadentate HOPO ligand 3,4,3-LI(1,2-HOPO), a novel decadentate HOPO ligand, 3,4,3,3-LI(1,2-HOPO) was designed and synthesized in Dr. Caterina Ramogida's lab at Simon Fraser University and TRIUMF. The purpose of this project is to compare the binding affinities of the known and novel ligands to Ac^{3+} using computational chemistry (density functional theory, DFT). The structures of conformers for the ligands and complexes were optimized. According to the Gibbs Energy of the designed ligand exchange reactions, the stabilities of the complexes were compared, and it was found that the novel ligand has more affinity to Ac^{3+} than the known one does. For purification and further application purposes, Lanthanum complexes were also studied and their stabilities were compared with the Actinium complexes through the designed metal exchange reactions.

NUCL

Comparative DFT analysis of $HTcO_4$ and H_5TcO_6

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Properties of pertechnic acid have been reported by Soderquist et al. [1]. They have proposed the existence of acidic species of $H_2TcO_4^+$ and H_5TcO_6 for an aqueous solution of $HTcO_4$. In this study, these structures and their related structures have been analyzed within the DFT combined with Quantum Theory of Atoms in Molecules (QTAIM) [2]. The structures in gaseous and aqueous phases have been optimized employing nonempirical meta-GGA functional, TPSSTPSS [3].
The standard basis set, 6-31G(d,p), is used for the elements other than Tc. Stuttgart RSC 1997 together with its effective core potential (ECP) has been used for Tc. This basis set has been obtained from the EMSL basis set exchange library, https://bse.pnl.gov/bse/portal [4]. Gaussian 09 [5] has been used for the optimization and additional analyses of the optimized structures have been done by Multiwfn 3.8 dev [6]. The optimized structures of $H_2TcO_4^+$ and $HTcO_4$ with Mulliken charges in an aqueous solution are given in Fig.1. In particular, O-H bonds covering acidic protons have been explored by analyzing their bond orders, dipole moments, real space functions relating to QTAIM. In general, higher Fuzzy Bond Order (FBO) values have been obtained for aqueous phases. The FBO values in ascending order were obtained as $H_2TcO_4^+ < H_5TcO_6 < HTcO_4$ and species derived from H_5TcO_6 by releasing their protons. Other O-H bonding properties were analyzed as a function of structure and its position in the structure.

NUCL

Harvesting radionuclides from heavy ion-beam irradiated tungsten at the NSCL

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The effort of Isotope harvesting has been of interest because of the massive quantities of radioisotopes that will be produced during routine operation of the Facility for Rare Isotope Beams (FRIB). The harvesting of radioactive isotopes from an aqueous beam stop has been successfully demonstrated in a series of experiments carried out by delivering beams from NSCL (National Superconducting Cyclotron Laboratory) into a dedicated aqueous endstation. Solid isotope harvesting approaches have been probed into to a much lesser extent, but, they have great potential because of the flexibility they offer in collection material, location and time, which can greatly simplify the post irradiation chemistry needed to isolate the radioisotopes. In this work, 0.2 μCi of ^{88}Zr ($t_{1/2}$ = 83.4 d, E_γ= 392.8 keV) was collected when ^{88}Zr beam (produced from the fragmentation of a 10-pnA, 140-MeV/u ^{92}Mo primary beam) impinges on a tungsten target. Isotopes of Y, Sr, Nb and Rb were also implanted and ^{88}Y and ^{85}Sr were used as tracers. The collection of ^{88}Zr through solid harvesting approaches was important for comparison to aqueous harvesting results which shows an increase in the collection percentage by three times.

The produced radionuclides ^{88}Zr, ^{88}Y ($t_{1/2}$= 106.6 d, E_γ= 1836 keV, 898 keV) and ^{85}Sr ($t_{1/2}$= 64.8 d, E_γ= 514 keV) were separated from the tungsten matrix and captured on the columns containing cation exchange resin and extraction chromatography resin with ^{88}Zr being collected in a low molarity H_2SO_4. Harvesting these long-lived radionuclides are important because they are otherwise very difficult to produce. Through this experiment, we established radiochemical methodologies for separating Zr, Y, and Sr from the tungsten collector material, and from each other; built a solid isotope harvesting endstation; and completed a solid isotope harvesting experiment at the NSCL.

NUCL

Deducing coupling constants from molecular iodine hyperfine spectra

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An iodine saturated absorption spectrometer has been constructed to calibrate a laser for precision laser spectroscopy studies at the Facility for Rare Isotope Beams at Michigan State University. Accurately modeling and fitting experimental iodine hyperfine spectra is imperative for a precise determination of laser frequency. For a given rovibrational level in iodine, the hyperfine spectrum consists of 15 or 21 hyperfine levels that are described by the effective hyperfine Hamiltonian. Coupling between many hyperfine levels must be considered. Thus, the energy of each hyperfine level is obtained by diagonalizing a Hamiltonian matrix, comprised of either 45 or 63 states for both the lower and upper levels of the iodine transition. In this work, a Python-based program was written to construct and diagonalize the hyperfine Hamiltonian. After matrix diagonalization, the spectrum can be modeled as a function of four hyperfine coupling constants for both the ground and excited levels. Additionally, a nonlinear curve fitting routine was implemented to fit a full iodine hyperfine spectrum and deduce the hyperfine coupling constants and hyperfine spectrum centroid. The coupling contributions from the 45 or 63 states are considered during the fitting routine, which allows precise fitting of all 15 or 21 hyperfine transitions simultaneously to deduce a single centroid value for the transition. The creation of this application will be presented, and future prospects using this tool for laser frequency calibration will be discussed.

NUCL

Electronic population manipulation of transition metal ions in an RFQ ion trap

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Collinear laser spectroscopy (CLS) is commonly used for determination of the charge radii and electromagnetic moments of radioactive nuclei. These fundamental properties of the nucleus provide information about the evolution of the shape and structure across an isotopic chain. CLS has been applied across broad swaths of the chart of the nuclides. However, certain elements have proven difficult to study, including the first and second-row transition metals due to low production rates and inaccessible electronic transitions. To overcome this situation, an electronic population manipulation technique using optical pumping in an RFQ ion trap has been developed at the BEam COoling and LAser spectroscopy (BECOLA) facility at the National Superconducting Cyclotron Laboratory (NSCL), allowing for studies of most transition metal isotopes towards the nucleon driplines. The optical pumping technique was demonstrated using stable ^{90}Zr ions captured in an RFQ ion trap. Pulsed laser light irradiated the ions for population manipulation followed by laser-resonant fluorescence (CLS) measurements. Details of the technique, performance characteristics, and implications for future studies at the Facility for Rare Isotope Beams (FRIB) will be discussed.

NUCL

Process for the recovery of Mo-99 from the accelerator-induced fission of uranium

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Technetium-99m (Tc-99m) is the most used diagnostic imaging agent in nuclear medicine. The majority of the world’s Tc-99m is generated by the decay of molybdenum-99 (Mo-99), usually produced by uranium-235 fission in a nuclear reactor. One proposed alternative approach to manufacturing Mo-99 involves inducing fission in natural or low enriched uranium targets with an electron accelerator. A new separation process for the recovery of Mo-99 from these irradiated uranium targets has been developed at Argonne National Laboratory. Following dissolution of the target in nitric acid, uranium is recovered for reuse by extraction with tributyl phosphate (TBP). The subsequent isolation of Mo-99 from the remaining fission product mixture is achieved by extraction with di-2-ethyl hexyl phosphoric acid (HDEHP) and stripping with acetohydroxamic acid (AHA). A strong base anion exchange resin column is used as a final purification and concentration step.

NUCL

Hydroxypyridinone-based stabilization of Np(IV) enabling efficient U/Np/Pu separations in the adapted Purex process

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Neptunium (Np) is produced by uranium (U) in nuclear fuel and ^{237}Np is far more in quantity than the combination of all other Np isotopes. ^{237}Np is the longest-lived member of the 4n + 1 radioactive decay series and thus an important long-term constituent of high-level liquid waste (HLLW). First, its transport in geologic environment is not as hindered as other actinides (An) and it is highly mobile upon leakage. Second, its radiotoxicity is high due to the decay daughters. Np was used to be treated as a waste that goes to HLLW vitrification but it has become more worthy of recovery, not only because of mitigating the above-mentioned problems but also because of its application in the production of ^{238}Pu that is an excellent heat source for thermoelectric devices.

Np^{4+}, NpO_2^{+}, and NpO_2^{2+} are the existing forms in acid-dissolved used nuclear fuel, of which Np^{4+} and NpO_2^{2+} are greatly extractable while NpO_2^{+} hardly so. The conditions of PUREX process create an environment where most Np exist as NpO_2^{+} and NpO_2^{2+}. In the first cycle of PUREX process where Np is co-extracted with Pu and U the more extractable form NpO_2^{2+} is the major species thanks to the oxidation by the indigenous HNO_3 and HNO_2. The rest of Np stays with trivalent fission-produced lanthanides (Ln). In the second cycle where Pu is separated from U reductants must be added to reduce Pu^{4+} to Pu^{3+} and NpO_2^{2+} to NpO_2^{+} if Np is chosen to follow Pu instead of U, most favorable route in the Adapted PUREX process. The main issues in this step is the sensitivity to HNO_3/HNO_2 concentration and the incomplete separation caused by the production of Np^{4+} that stays with U. Previous studies have shown that an aqueous complexant called 3,4,3-LI(1,2-HOPO) has high affinity to Np^{4+} and is feasible in assisting the separation of Np both from U and from Ln. Extraction and stripping profiles of Np were determined as a function of acidity. Valence profiles of Np are concluded by UV-Vis and cyclic voltammetry (CV). The thermodynamics and kinetics of the Np reduction and complexation by HOPO were assessed.

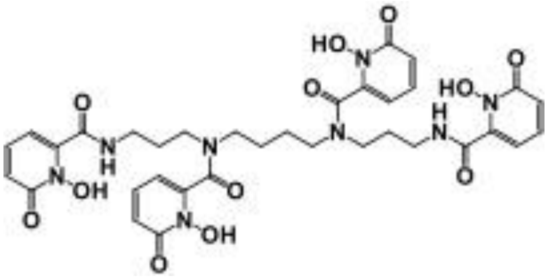

Fig 1. Structure of 3,4,3-LI(1,2-HOPO)

NUCL

Superheavy element chemistry and the residual gas effects on the chromatographic yield of homologs Hg and At

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Principal challenges in the study of transactinide elements ($Z \geq 104$) are production rates as low as single-atoms per week and shortening half-lives as Z increases. The frontier of transactinide research uses on-line gas adsorption chromatography (GC), such as the Cryo-OnLine Detector (COLD) as the primary method of element identification and chemical investigation. These state-of-the-art GC experiments provide the necessary detection sensitivity for single atoms, while allowing experiments to be performed on radioisotopes with half-lives of ≈ 500 ms. The Superheavy elements Cn ($Z = 112$) and Fl ($Z = 114$) can thus be studied. During our experiments, Hg is produced simultaneously in nuclear fusion evaporation reactions for homolog studies of Cn, while acting as a tracer to monitor experimental conditions. At is a by-product of multinucleon-transfer reactions but similarly provides useful data. Recent upgrades in the equipment with the inclusion of mass spectrometry for the gas composition analysis have shown that there is a strong correlation between the composition of unwanted residual trace gases and transport yields of different elements (Fig. 1).

We present the observed influences of impurities in the carrier gas on the chromatographic yield and the importance of accurately knowing potential contaminants in similar experiments. These observations are of high significance as they highlight the importance of tightly controlling the purity of gases used in experiments at the single-atom scale. This knowledge can therefore be used to prevent unwanted side-reactions, or to increase transport yields in the future and has initiated the development of a new experimental setup ‘Trace-gas Reaction Analysis for Chromatography (TRACY)’ designed specifically for this purpose.

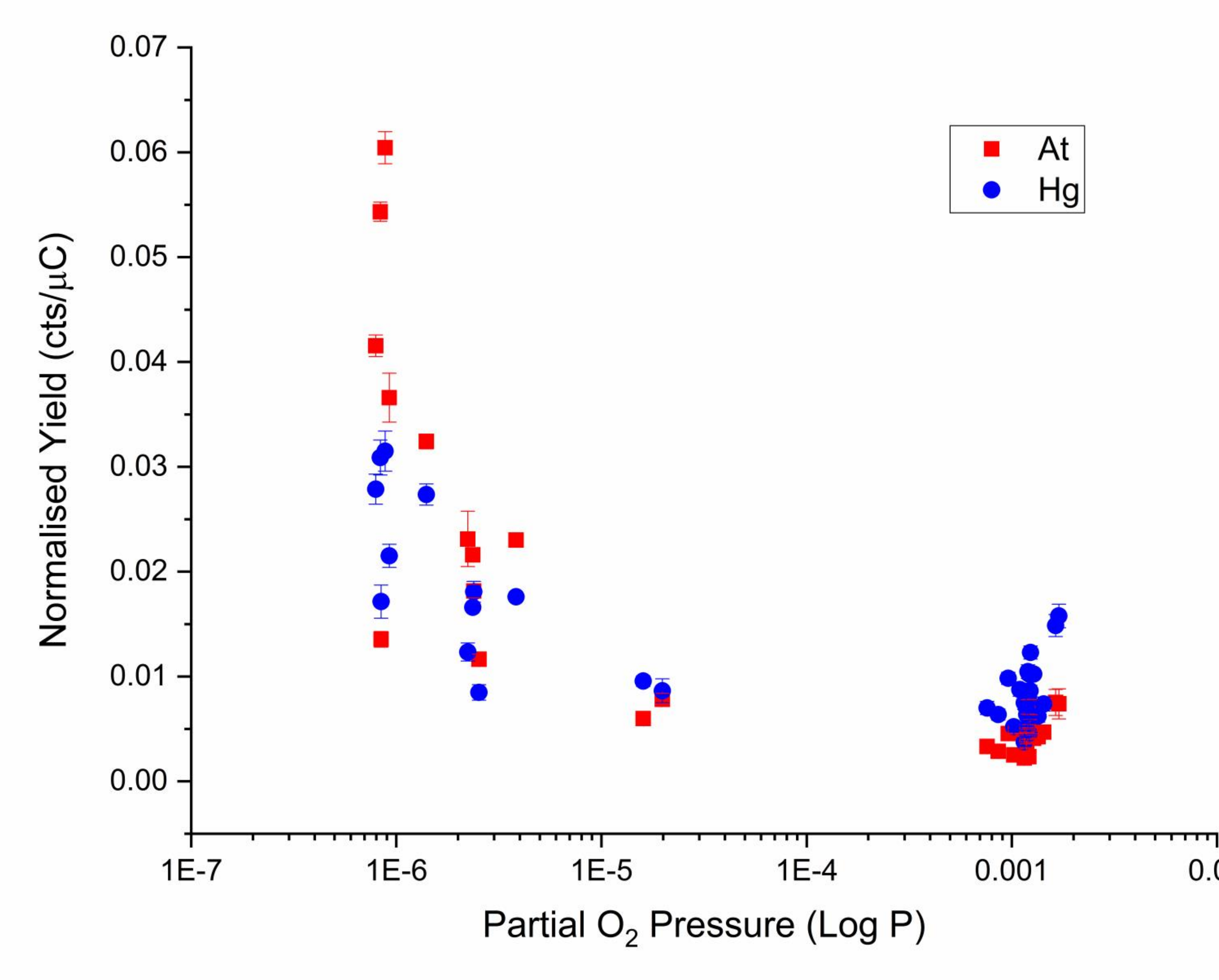

Fig. 1: Normalized yield of At & Hg radioisotopes in relation to oxygen content in the carrier gas; decreasing detection of reaction products as oxygen content increases. Partial pressure values are relative, not absolute.

NUCL

Characterization of 1-(11-Mercaptoundecyl)imidazole self-assembled monolayers on gold-coated silicon chips for future detection of radioactive isotopes

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Traditionally, silicon detectors, utilized in the field of studying the chemical properties of superheavy elements, are coated with gold. However, enhanced reactivity of element 113, Nh, towards gold disabled the proper chemical characterization of this element. Therefore, a need for new chemically modified gold-coated silicon detectors that will selectively bind the atoms of interest, but with weaker interactions, has emerged. Meitnerium is expected to be a member of Group 9 of the periodic table, and a brand new chemical research is needed to confirm this classification. Initially, we aimed to study the self-assembly of a commercially available thiol, 1-(11-Mercaptoundecyl)imidazole, on gold-coated silicon chips that mimic functionalized detectors. The main goal of such devices is to capture radioactive isotopes of iridium and rhodium (meitnerium's homologs) during online Cyclotron-based experiments. Self-assembled monolayers (SAMs) can be easily prepared in the liquid phase by immersion of a substrate into an ethanolic thiol solution.

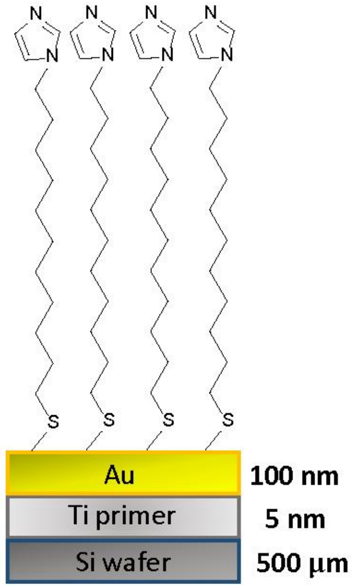
Several techniques were used to characterize the functionalized chips. Atomic force microscopy was used to evaluate the roughness of pure gold and substrates with self-assembled monolayers (SAMs).

We obtained satisfactory results on the average surface coverage with SAMs (≥ 90%) using cluster secondary-ion mass spectrometry.

X-ray photoelectron spectroscopy was employed to study the chemical state of SAMs. The H_2O_2-mediated liquid UV-light photooxidation was found to be an effective treatment to remove SAMs.

Ellipsometry was used to determine the thickness of SAMs, which indicated the presence of a single monolayer.

Finally, neutron activation analysis was performed to conclude that iridium and rhodium bind to SAMs on gold from hydrochloric acid solutions (sorption efficiency ≥ 55%). Details and results of the experiments mentioned above will be discussed.



Schematic diagram of the substrate investigated in this study

NUCL

Solid-phase isotope harvesting of ^{88}Zr

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At the Facility for Rare Isotope Beams (FRIB), high-purity radioactive ion beams will be produced for user experiments in nuclear science research. During normal operation, excess radionuclides will accumulate along the beamline from the beam purification process. Due to the significant demand for many radionuclides, there is interest in collecting, purifying, and using byproduct isotopes produced at FRIB, called isotope harvesting. Preliminary isotope harvesting efforts have been ongoing at the National Superconducting Cyclotron Laboratory (NSCL), such as the aqueous collection of ^{24}Na, ^{67}Cu, ^{48}V, and ^{88}Zr. In this work, the viability of isotope harvesting using solid collection of ^{88}Zr, an isotope relevant to stockpile stewardship, was examined. Through a proof-of-concept experiment at the NSCL, ^{88}Zr beam was stopped in a series of collectors comprised of Al, Cu, W, and Au. ^{88}Zr was radiochemically recovered from each of these collectors and yields compared to previous aqueous harvesting efforts. Results of the harvesting experiment and the radiochemical recovery from Cu and Al collectors will be discussed. For elements of interest that readily hydrolyze in near-neutral pH aqueous conditions, such as Zr, harvesting through solid-phase collection may allow for higher recovery yields compared to aqueous harvesting.

NUCL

Environmental fate of actinide-siderophore complexes: Desferrioxamine B promoted sorption of U(VI) on manganese minerals

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Anthropogenic activities related to the mining and industrial use of U(VI) have led to significant contamination of the environment. As a result, there is a need to understand better the factors that govern the fate and transport of contaminants. The adsorption of U(VI) to minerals is a potential pathway for natural remediation however, this process is influenced by various environmental factors including the presence of naturally occurring organic molecules.

The current work examines the complexation of U(VI) with desferrioxamine B (DFOB - a hydroxamate type siderophore), and the interactions of this complex with common manganese minerals (pyrolusite and manganite). Adsorption experiments with U(VI)-DFOB complex were performed with each mineral at pH 6 and 8. Control adsorption experiments were also performed with U(VI) and DFOB. DFOB promotes the sorption of U(VI) on pyrolusite under circumneutral conditions and DFOB undergoes degradation allowing us to detect organic molecules-fragments in the aqueous phase (e.g. acetate and succinate). On the other hand, when manganite is used as a substrate, U(VI) sorption is not affected by the presence of DFOB and no degradation of DFOB was observed. These results indicate that uranium sorption can be influenced by the presence of siderophores, which can assist in natural attenuation, decreasing uranium mobility in the environment. Furthermore, the results suggest that multiple adsorption mechanisms of the U(VI)-DFOB complex could be occurring involving active sites on the mineral surface interacting with both DFOB and U(VI).

NUCL

Pyrrol-based ligands as Salen relatives: Complex synthesis, characterization and comparison

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Schiff bases like the mixed *N, O* donor ligands of the salen (Bis(salicyliden)ethylendiamin) family are gladly taken systems for complexation studies. Advantageous is their ability to stabilize a great amount of metals including actinides, as well as the tuneable electronical and sterical properties. Pyrrol-based ligands only exhibit *N* donor functionalities. Nevertheless, they can be considered as structural relatives. This provides the possibility to investigate the binding situation between early Actinides and *N* atoms in different environments.
In this study a complex series from Th to Pu with the pyrrol-based ligands 1,2-ethylenediamine-*N,N*'-bis(1H-pyrrol-2-yl)methylene (pyrenH_2) L^1H_2 and 1,2-benzenediamine-*N,N*'-bis(1H-pyrrol-2-yl)methylene (pyrophenH_2) L_2H_2 was synthesized. Characterization in solution (NMR) and solid state (SC-XRD) in combination with quantum chemical calculations reveal different binding situations to the different *N* donors, as well as unique paramagnetic behaviour in solution.

Molecular Structure of the U(pyren)$_2$ complex.

NUCL

Electrochemical reduction of Eu^{3+} using tetra-*n*-octyl diglycolamide functionalized ordered mesoporous carbon electrodes

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The relative concentration of each lanthanide in uranium ore varies geographically and does not change during uranium processing. These lanthanide patterns serve as a nuclear forensic signature which can aid in determining the origin of uranium materials. Tetra-*n*-octyl diglycolamide (TODGA) has an unusually high extraction efficiency and selectivity for trivalent lanthanides. This amidic extractant has shown promise for actinide-lanthanide solvent extraction and extraction chromatographic based separations. However, obtaining the lanthanide pattern for uranium material requires intralanthanide separations. Adjacent lanthanide separations are notoriously difficult due their predominant trivalent oxidation state and similar ionic radii. One way to manipulate adjacent lanthanide separations is through the redox properties that some of these *f*-elements possess, such as the relatively stable divalent oxidation state of Eu. Using voltammetric methods, the Eu(III/II) redox couple was measured using TODGA physisorbed on ordered mesoporous carbon in a cavity microelectrode. These results show the preference TODGA has for Eu^{3+} over Eu^{2+} and the prospect for selective electrochemical stripping.

NUCL

Preparation for harvesting ^{48}V from an aqueous beam dump for neutron capture cross section studies

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The upcoming Facility for Rare Isotope Beams (FRIB) at Michigan State University will be able to regularly produce many potentially useful exotic radionuclides as byproducts of spallation and fragmentation reactions of unused primary beams in an aqueous beam dump. One such radionuclide is ^{48}V, which is important for enhancing the neutron capture cross section data of V isotopes for the Stockpile Stewardship Program. For accurate data to be obtained in neutron capture studies with ^{48}V, the ^{48}V target must be isotopically pure with minimal ^{49}V impurity (^{48}V/^{49}V = 10^4). Prior studies completed at FRIB's precursor, the National Superconducting Cyclotron Laboratory (NSCL), have

shown that V can be chemically separated from various types of aqueous solutions, but none have shown ^{48}V can be isolated with high isotopic purity.

One way of obtaining ^{48}V in high isotopic purity is by setting up a ^{48}Cr/^{48}V generator by harvesting ^{48}Cr. To meet this goal, efforts will be made to develop the protocols for constructing a ^{48}Cr/^{48}V generator starting with stable Cr and V separations and ending with proof-of-concept experiments at FRIB. Experiments completed so far have shown solutions can be made with stable Cr and V in the same oxidation states as those observed with Cr and V produced in prior experiments at NSCL. Results from elution studies with AG1-X8 anion exchange columns loaded with stable Cr and V from these solutions suggest that 93.3(20) % Cr and 89.9(24) % V can be eluted with 2 M HNO_3 and 1 M HCl respectively. Additional results from elution studies performed with AG1-X8 columns loaded with Cr and V from mixed Cr and V solutions suggest that it would be difficult to achieve good separation of Cr and V given the loading conditions. So, recent experiments have focused on secondary separation methods with the aim of producing a ^{48}Cr/^{48}V generator.

NUCL

Total kinetic energy (TKE) release in the fast neutron induced fission of ^{237}Np(n,f)

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The total kinetic energy (TKE) release in the fast neutron induced fission of ^{237}Np was measured for neutron energies from E_n = 2.6 – 100 MeV at the LANSCE-WNR facility. The post TKE release decreases non-linearly with increasing incident neutron energy and can be represented as TKE(MeV) = (174.38 ± 0.72) – (5.11 ± 0.5821) $\log_{10} E_n$ for $E_n > 1$ MeV. Analysis of the fragment mass distributions indicates that the decrease in TKE with increasing E_n is a consequence of the fading out of shell effects at high excitation energies (resulting in an increase of symmetric fission) and the decrease of the total kinetic energy associated with asymmetric fission with increasing E_n.

NUCL

Saturated absorption spectrometer for laser frequency calibration

Eleanor K. Ronning, *ekronning17@ole.augie.edu,* ***Eleanor Weckwerth***, *ecweckwerth19@ole.augie.edu. Augustana University, Sioux Falls, South Dakota, United States*

A saturated absorption spectroscopic setup was constructed to measure hyperfine spectra of molecular iodine. The well-known absorption features of molecular iodine will be utilized to calibrate probe lasers used for collinear laser spectroscopy of rare

isotopes at the Facility for Rare Isotope Beams on the campus of Michigan State University. A pump and probe beam, split from a common laser, were counter propagated through a 60-cm-long iodine vapor cell. The frequency of the laser light was scanned, and the probe laser beam was modulated on-and-off. A lock-in amplifier was used to demodulate the probe laser light signal to eliminate the Doppler-broadened background and obtain the saturated absorption spectrum. An external cavity diode laser (ECDL) emitting near 780 nm light was constructed and optimized as the laser system for the setup; the ECDL was characterized with a monochromator and a Michelson interferometer was assembled to ensure its stability. An electro optic modulator was tested and characterized and is planned to be integrated into the setup to either independently scan the probe laser frequency, or alternatively to perform frequency modulation spectroscopy. A data acquisition system was developed to monitor temperature and pressure shifts using Python to interface with a LabJack U3 streaming unit. The design and setup of the spectrometer will be presented, and future applications of the apparatus will be discussed.

NUCL

Enabling future scientists to always ask why

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Prof. Clark was an inspiration to work for in graduate school. She provided constructive feedback that always instilled creativity, independence, and integrity. No science question was too great, though it may be at 10,000 feet, and you need to see it from the surface. These lessons have continued to push me to ask questions and pursue new research avenues, including particle morphology and stable isotope ratios.

Particle morphology is an emerging signature that could aid in safeguarding and preventing the illicit trafficking of nuclear material. Our recent studies have demonstrated that U-oxides' morphological features are a product of processing parameters such as starting material, intermediate material, oxidation rates, precipitation conditions, and calcination history. While these studies demonstrate that morphology could help identify the process history of nuclear materials, an additional signature is needed to help identify the geographic origin of unknown nuclear materials. Oxygen isotope ratios can potentially provide these unique signatures as the interaction between uranium and oxygen-containing substrates are nearly ubiquitous within the nuclear fuel cycle. Results highlighting the development of these signatures and future research needs will be presented.

NUCL

Generalizability of convolutional neural networks to out-of-distribution uranium morphology image data

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Past research efforts have shown that the factors affecting the surface morphology characteristics of uranium ore concentrates (UOCs) are numerous and complex. While driven largely by the route of precipitation and calcination product of the UOC, the solution precipitation conditions, the extent to which precipitates are washed, the presence of elemental impurities, and the conditions under which the materials have been aged will all impact the morphology of the UOC. The variety of factors that can impact the morphology results in large datasets often with overlapping variables making cause and effect correlations challenging to find. Nonetheless, convolutional neural networks (CNNs) have proven useful in classifying scanning electron microscopy (SEM) images of the UOCs. They have been used as a rapid means of processing large sets of images, classifying them into fine-grained labels representing specific aging parameters, elemental impurities, or as pure, unaged “unperturbed” materials from different precipitation routes.

This work ties together past UOC morphology studies to determine the ability of CNNs trained on image sets of unperturbed materials to generalize to impure, aged, partially converted, or otherwise altered UOCs that might have been imaged under varying SEM parameters and image scales. The results identify specific challenges that will need to be addressed as CNN techniques join the nuclear forensics analysis toolbox for characterizing the surface morphology of nuclear materials. Specifically, the CNNs performed well when classifying materials precipitated from different uranium solutions and images of unperturbed materials acquired at different scales, but failed to accurately predict aged, impure, and partially calcined materials. These results highlight the need for additional research into surface morphology as a nuclear forensics signature; principally, in developing SEM image databases that could be used to characterize the process history of nuclear materials.

NUCL

Impact of controlled storage conditions on the hydrolysis and surface morphology of amorphous-UO_3

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The hydrolysis and morphological effect of amorphous (A)-UO_3 following aging under varying temperature and relative humidity has been studied. This work provides insight to U-oxide speciation following storage, the U-oxide quantitative morphology database, and the overall characterization of nuclear material provenance. A-UO_3 was synthesized by the washed uranyl peroxide synthetic route and aged by a 3-factor circumscribed central composite design of experiment. Target aging times include 2.569, 7, 14, 21, and 25.431 days, temperatures of 5.505, 15, 30, 45, and 54.495°C, and relative humidities of 14.175, 30, 55, 80, and 95.825% were investigated. Following storage, crystallographic changes were quantified via powder X-ray diffraction (p-XRD) and an internal standard Rietveld refinement method. Particle morphology from scanning electron microscopy (SEM) images was quantified via Morphological Analysis of MAtierals (MAMA) software. Largely hydrated samples were found to have a much larger, plate-like morphology compared to the unaged control samples. Predictive modeling via response surface model determined that, while aging time, temperature, and relative humidity all have a quantifiable effect on A-UO_3 crystallography and morphology, relative humidity is the greatest driving factor.

NUCL

Cr(III) adsorption mechanism and the effect on boehmite dissolution in highly alkaline solutions

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Boehmite (γ-AlOOH) is an important aluminum oxyhydroxide in nature that also plays diverse roles across a plethora of industrial applications. It comprises a major portion of the solid fraction in nuclear waste stored at the Department of Energy (DOE) Hanford Site, where it exists in contact with highly caustic sodium hydroxide solutions and sludges. Tests have showed that the surface area-normalized dissolution rate of boehmite nanomaterials in the tank waste sludge is at least an order of magnitude lower than that predicted for those conditions, ostensibly attributed to the role of various possible doped trace metals. We have examined Cr(III), an abundant species in the tank waste, as an adsorbate on boehmite particle surfaces, which adheres at saturation coverages as submonolayer nano-to-micron sized precipitates or as an adsorbed complex, the latter of which may or may not ultimately lead to its incorporation as a substituent for Al in the boehmite structure. Using well-defined synthetic 40-60 nm boehmite nanoplates as a model system, the dissolution rates of pure versus Cr(III)-adsorbed boehmite were investigated. Results showed that the dissolution rate of the Cr(III)-adsorbed boehmite is several times lower than that of pure boehmite, with a dissolution activation energy (E_a) 16 kJ mol^{-1} higher. The behavior is tentatively attributed to an armoring effect by adsorbed Cr(III) that reduces the number of dissolution-active sites on particle surfaces, a hypothesis currently under examination with high-resolution electron and scanning probe microscopies. The findings should

help improve kinetics models and ultimately provide a stronger foundation for the development of robust waste processing strategies.

NUCL

Evaluation of actinium-225 radiolabeled cyclized alpha-melanocyte stimulating hormone (CycMSH) peptide for targeted alpha therapy (TAT)

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With four alpha ($^{4}He^{2+}$) particles in its decay chain, actinium-225 (^{225}Ac, $t_{1/2}$ = 9.9 d) is ideal for incorporation into radiopharmaceuticals for targeted alpha therapy (TAT) of cancer. Tumour targeting biomolecules allow for site-specific delivery of radioactive emissions to the disease cell. Lactam-bridged cyclized α-melanocyte stimulating hormone (CycMSH) peptide has high affinity for over expressed surface receptors on most malignant melanomas, making it a promising target for melanoma therapy. Herein, ^{225}Ac-labeled CycMSH derivatives were evaluated as novel TATs for melanoma in a preclinical mouse model. DOTA- and macropa-CycMSH conjugates were radiolabelled with ^{225}Ac with radiochemical yields (RCY) of <10 and >99 %, respectively. Low % RCY of the DOTA-conjugate precluded in vivo evaluation. The biodistribution of ^{225}Ac-macropa-CycMSH (molar activity, S.A. = 1.38 kBq/pmol) in B16F10 tumour-bearing mice (n = 4) was evaluated for 2 different injected radioactivities (103.6 kBq and 51.8 kBq) 2 h post-injection and was found to be 2.50 and 0.67 % injected dose/gram in tumour. The moderate-to-low tumour uptake highlights the need for development of efficient and robust ^{225}Ac chelators that produce high S.A. radiopharmaceuticals with favourable biodistribution.

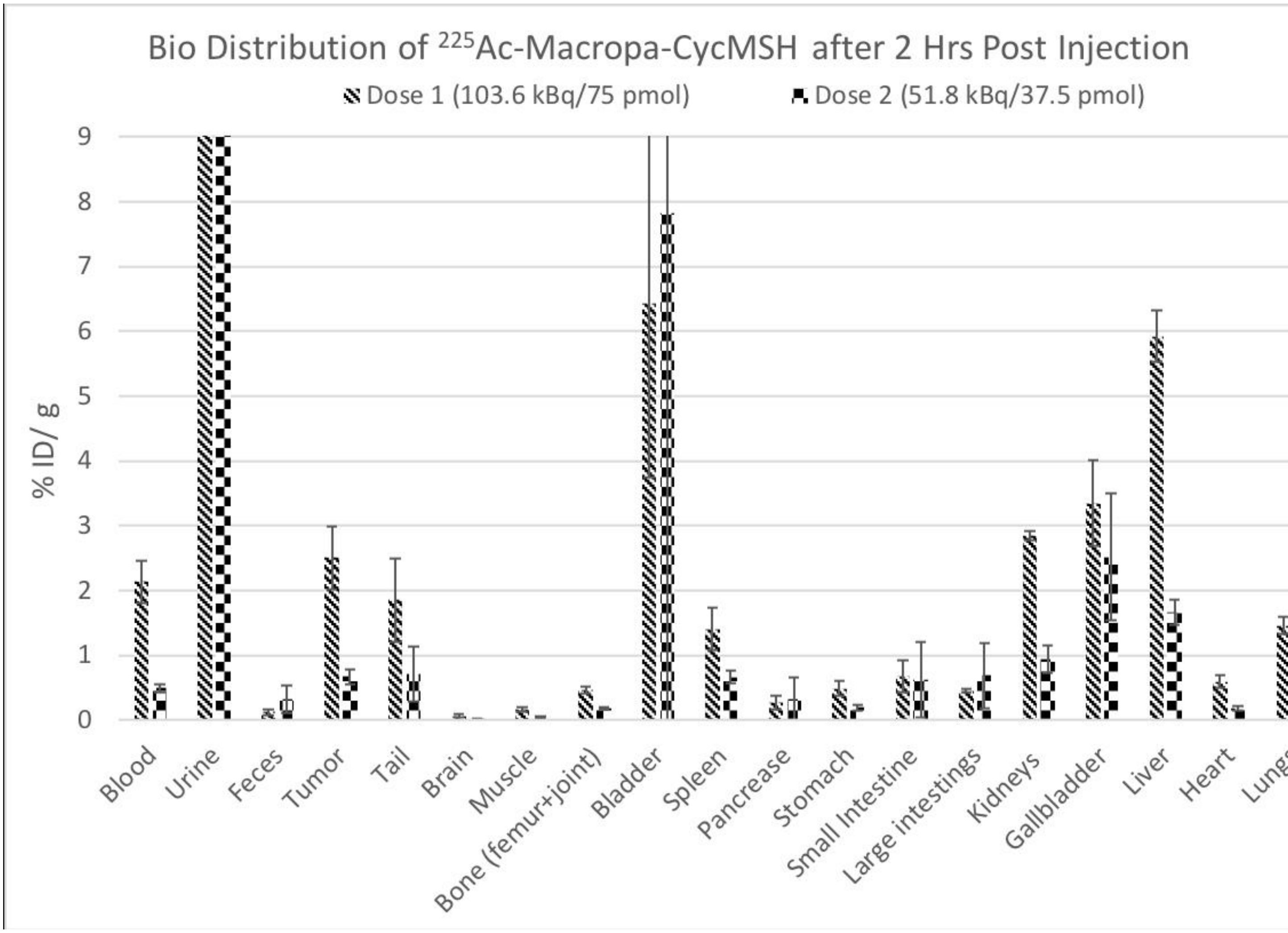

Figure 1: The biodistribution 2 hours post injection of ^{225}Ac-Macropa-CycMSH in B16F10 tumour-bearing mice (n = 4) for dose 1 (diagonal lines) and dose two (checkered).

NUCL

Single-dose of 212Pb-YS5 significantly inhibits tumor growth in prostate cancer xenograft mouse model

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Introduction: We have developed a new human monoclonal antibody that selectively targets CD46 in all subtypes of prostate cancer. The objective of this study is to test if this antibody can deliver 212Pb radionuclide for effective radioimmunotherapy in prostate cancer.

Methods: The human antibody YS5 was first conjugated with a chelator TCMC followed by radiolabeling with 212Pb. The 212Pb-YS5 was evaluated binding with tumor cells (PC3) in vitro to confirm the cell binding. For in vivo studies, five dosages of 212Pb-YS5 were administered in mice without tumors to identify the safe dose. Finally, the safe dose of 212Pb-YS5 was used to evaluate the therapeutic efficacy for 60 days post-injection in PC3 xenograft tumor mouse models with measures of tumor growth, body weight, survival, and health status.

Results: The labeling yield of 212Pb-YS5 was 65-75% and final products after purification was 99% in radiochemistry purity. The in vitro cell study confirmed the tumor cell binding with a binding affinity of 27-35Nm. Among the dose tested (5 µCi, 10 µCi, 20 µCi, and 50 µCi), 5-20 µCi were safe without any death while 50 µCi resulted in 80% death in one week. Compared with the control group with tumor growing and 80% within 3 weeks and 100% death within 40 days, the radiotherapy study group with a single dose of 20uCi showed significant tumor inhibition with no tumor growth for 40 days post-administration of 212Pb-YS5 and 0% death even after 60 days.

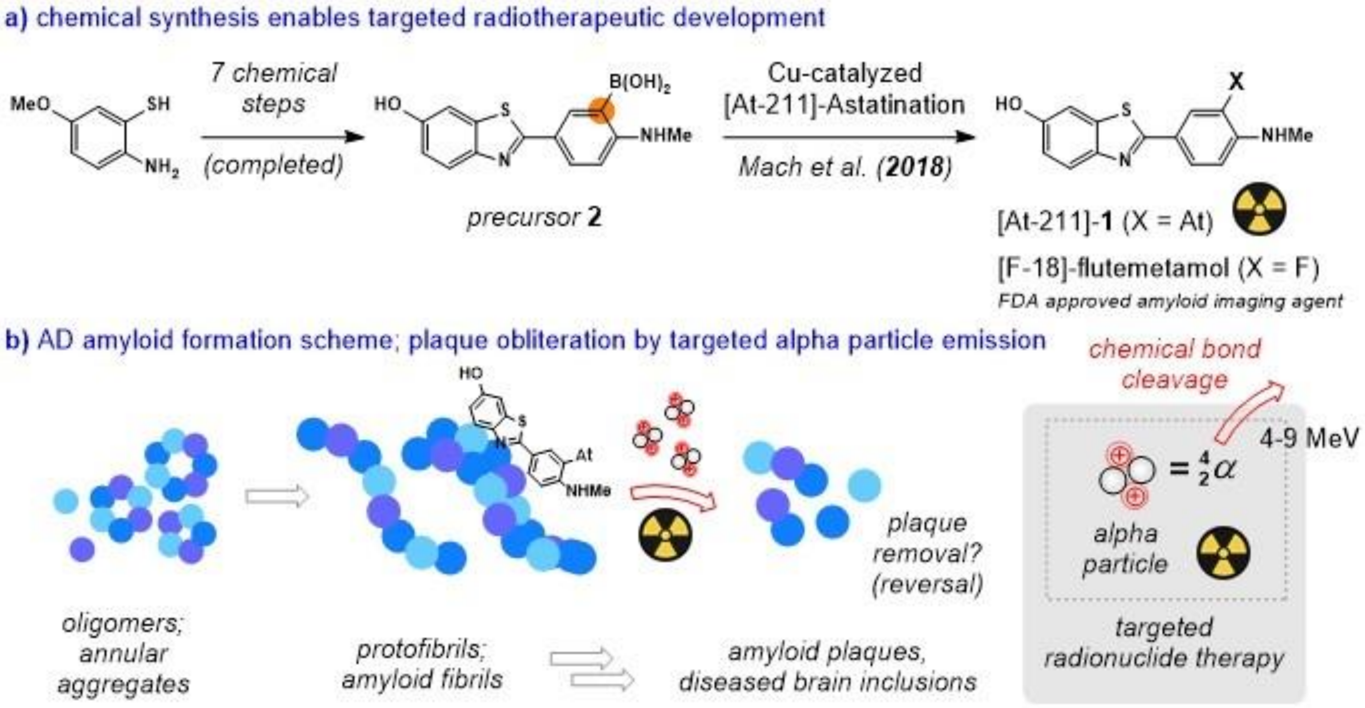
Conclusion: This initial radiotherapeutic study demonstrated that 212Pb-YS5 exhibited excellent therapeutic efficacy and warrant further extensive investigation.

NUCL

At-211 labeled small molecule based on the flutemetamol scaffold: Potential theranostic for Alzheimer’s disease

Emily K. Kirkeby[1], *Emilykirkeby@gmail.com, George Diehl*[2], *Andrew G. Roberts*[3], *Tara Mastren*[4]. *(1) Chemistry , University of Utah, Salt Lake City, Utah, United States (2) Civil Engineering, The University of Utah College of Engineering, Salt Lake City, Utah, United States (3) Chemistry, University of Utah, Salt lake city, Utah, United States (4) Nuclear Engineering, University of Utah, Salt Lake City, Utah, United States*

Recently, targeted alpha-particle therapy (TAT) has garnered recognition for the treatment of various cancer types. The high linear energy transfer of emitted alpha-particles enables targeted cleavage of chemical bonds at proximal distances (micrometer range), leaving neighboring healthy tissues unharmed. We propose this strategy can be applied for the treatment of Alzheimer's disease using astatine-211 (At-211) as a covalently bound alpha-emitting radionuclide. Flutemetamol (X = F-18) is an FDA-approved radiopharmaceutical for positron-emission tomography (PET) imaging of beta-amyloid deposition, a diagnostic tool for Alzheimer's disease. The incorporation of astatine-211 onto the derivative thioflavin scaffold (X = At-211) could result in a novel theranostic agent (1) for the targeted obliteration of amyloid aggregates. Here, we report on the synthesis and characterization of flutemetamol I-127 and At-211 derivatives. (This abstract was updated from a previous submission to a 2020 symposium canceled due to the COVID-19 pandemic.)


a) chemical synthesis enables targeted radiotherapeutic development

b) AD amyloid formation scheme; plaque obliteration by targeted alpha particle emission

Figure 1. Small-molecule mediated targeted radionuclide therapy for the treatment of Alzheimer's disease.

NUCL

Saturated absorption spectrometer for laser frequency calibration

Eleanor K. Ronning, *ekronning17@ole.augie.edu*, ***Eleanor Weckwerth***, *ecweckwerth19@ole.augie.edu. Augustana University, Sioux Falls, South Dakota, United States*

A saturated absorption spectroscopic setup was constructed to measure hyperfine spectra of molecular iodine. The well-known absorption features of molecular iodine will be utilized to calibrate probe lasers used for collinear laser spectroscopy of rare isotopes at the Facility for Rare Isotope Beams on the campus of Michigan State University. A pump and probe beam, split from a common laser, were counter propagated through a 60-cm-long iodine vapor cell. The frequency of the laser light was scanned, and the probe laser beam was modulated on-and-off. A lock-in amplifier was used to demodulate the probe laser light signal to eliminate the Doppler-broadened background and obtain the saturated absorption spectrum. An external cavity diode laser (ECDL) emitting near 780 nm light was constructed and optimized as the laser system for the setup; the ECDL was characterized with a monochromator and a Michelson interferometer was assembled to ensure its stability. An electro optic modulator was tested and characterized and is planned to be integrated into the setup to either independently scan the probe laser frequency, or alternatively to perform frequency modulation spectroscopy. A data acquisition system was developed to monitor temperature and pressure shifts using Python to interface with a LabJack U3 streaming unit. The design and setup of the spectrometer will be presented, and future applications of the apparatus will be discussed.