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INSTITUTE FOR NUCLEAR SECURITY

RADIOCHEMISTRY Center of Excellence

Radiochemistry Center of Excellence

Dr. Howard L. Hall

University of Tennessee, Knoxville

Stockpile Stewardship Academic Alliance Program

February 16-17, 2016 -- Bethesda, MD

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Overview

Major Thrust Areas

- Advanced Radiochemical Separations/Melt Glass
- Nuclear Cross-Sections/Inverse Kinematics
- Bulk Actinide Oxide Materials Processing and Behavior
- Radiochemical Probes for Physical Phenomena

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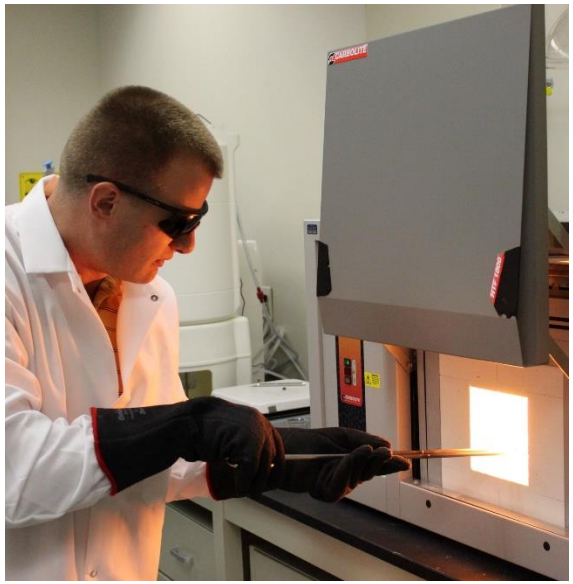
Development and Forensic Analysis of Nuclear Melt Glass Surrogates



Shown: CPT Joshua Molgaard (left) making surrogate trinitite samples
CDT Bremer (central) and Jon Gill (right) developing urban surrogates

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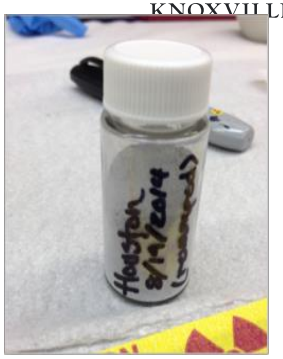


Scenario Selection

Estimates of Environment

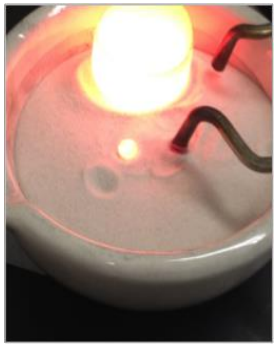
Develop Surrogate

Produce Event Surrogate Sample

Analysis Surrogate Material

Regional Production Comparison

Verification & Validation



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[1]*Development of Synthetic Nuclear Melt Glass for Forensic Analysis" Molgaard, Auxier et. al. J. Rad. Nucl. Chem., 2015*

[2]*Compositional Planning for Development of Synthetic Urban Nuclear Melt Glass, Giminaro et al. J. Rad. Nucl. Chem. 2015*

Trinitite Surrogate: Development and Synthesis

STF Composition (by mass fraction)

Trinitite Data		Synthetic Formulation	
Comp.	*Fraction*	*Comp.*	*Fraction*
SiO_2	6.42×10^{-1}	SiO_2	6.42×10^{-1}
Al_2O_3	1.43×10^{-1}	Al_2O_3	1.43×10^{-1}
CaO	9.64×10^{-2}	CaO	9.64×10^{-2}
FeO	1.97×10^{-2}	FeO	1.97×10^{-2}
MgO	1.15×10^{-2}	MgO	1.15×10^{-2}
Na_2O	1.25×10^{-2}	Na_2O	1.25×10^{-2}
K_2O	5.13×10^{-2}	KOH	6.12×10^{-2}
MnO	5.05×10^{-4}	MnO	5.05×10^{-4}
TiO_2	4.27×10^{-3}	TiO_2	4.27×10^{-3}
U	1.60×10^{-5}	UNH	3.37×10^{-5}
Total	9.81×10^{-1}	Total	9.91×10^{-1}
Element	*Fraction*	*Element*	*Fraction*
Si	3.00×10^{-1}	Si	3.00×10^{-1}
Al	7.55×10^{-2}	Al	7.55×10^{-2}
Ca	6.88×10^{-2}	Ca	6.88×10^{-2}
Fe	1.53×10^{-2}	Fe	1.53×10^{-2}
Mg	6.90×10^{-3}	Mg	6.90×10^{-3}
Na	9.24×10^{-3}	Na	9.24×10^{-3}
K	4.26×10^{-2}	K	4.26×10^{-2}
Mn	3.93×10^{-4}	Mn	3.93×10^{-4}
Ti	2.58×10^{-3}	Ti	2.58×10^{-3}
O	4.60×10^{-1}	O	4.69×10^{-1}
U	1.60×10^{-5}	U	1.60×10^{-5}
N	0	N	1.88×10^{-6}
H	0	H	1.10×10^{-3}

- Trinitite used as a benchmark
- Powdered oxides used to create sample matrix
- Matrix melted and vitrified

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Synthesis

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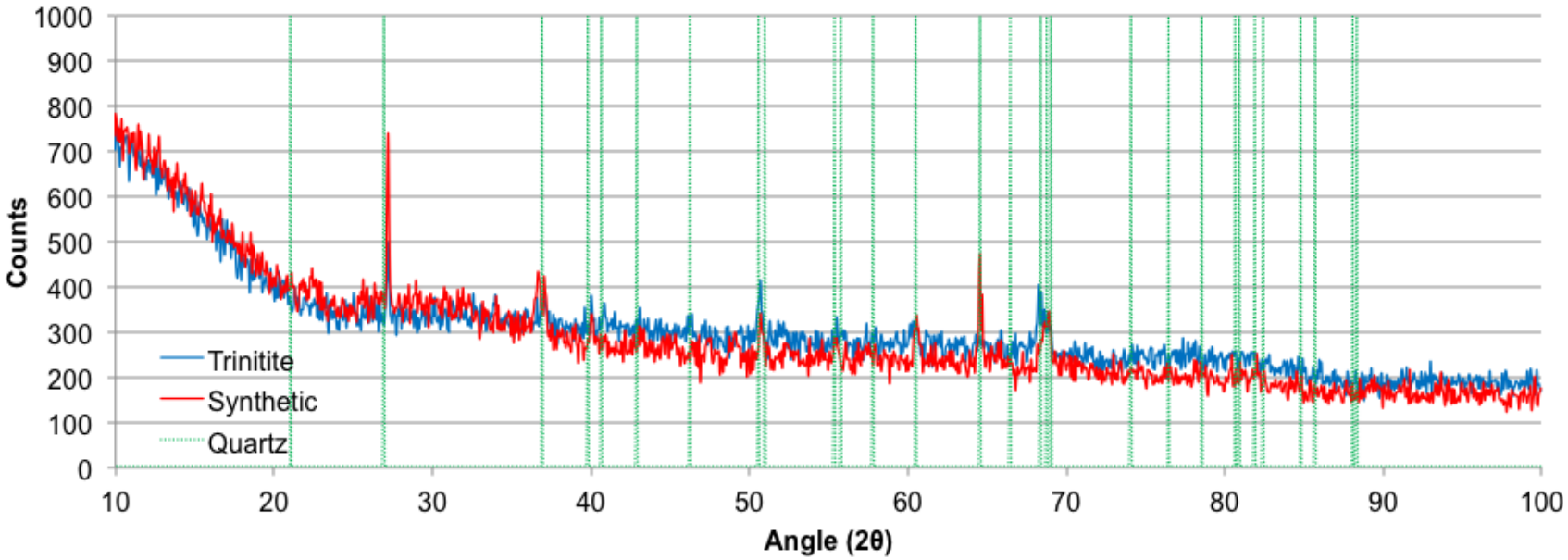
PXRD


Counts
1000
900
800
700
600
500
400
300
200
100
0
10
20
30
40
50
60
70
80
90
100
Angle (2θ)
Trinitite
Synthetic
Quartz

Gamma Spectroscopy (Cont.)

Nuclide	ROI	Half-Life (yr)	Energy (keV)	Branching Ratio (%)	Act. (Bq/g) - Trinitite	Act. (Bq/g) – STF
^{133}Ba[1,2,3]	5	10.51	356.01	62.05	27.1 ± 0.5	N/A
^{137}Cs[1,2,3]	8	30.05	661.66	84.99	32.1 ± 0.04	N/A
^{152}Eu[1,2,3]	3	13.522	121.7	28.41	69.9 ± 0.8	N/A
	4		334.2	26.59		
	10		778.9	12.97		
	11		964.08	14.50		
^{154}Eu[1,2,3]	*	8.601	123.07	40.40	158 ± 0.4	477 ± 9.3
	9		723.3	20.05		
	12		1,004.7	17.86		
	13		1,274.4	34.90		
^{155}Eu[1]	*	4.573	86.55	30.7	0.9 ± 0.6	0.38 ± 0.003
	*		105.31	21.1		
^{239}Pu[1]	1	24.1×10^3	51.62	0.02	11208 ± 3907	N/A
	*		129.30	0.002		
	6		375.05	0.0015		
	7		413.71	0.0015		
^{241}Pu[2]	*	14.35	103.68	1.0E-4	63.0 ± 1.8	N/A
^{241}Am[1,2,3]	2	432.2	59.94	35.92	13 ± 11	N/A
^{60}Co[1,2,3]	*	5.271	1,173.2	99.85	44 ± 4	N/A
	*		1,332.4	99.98		

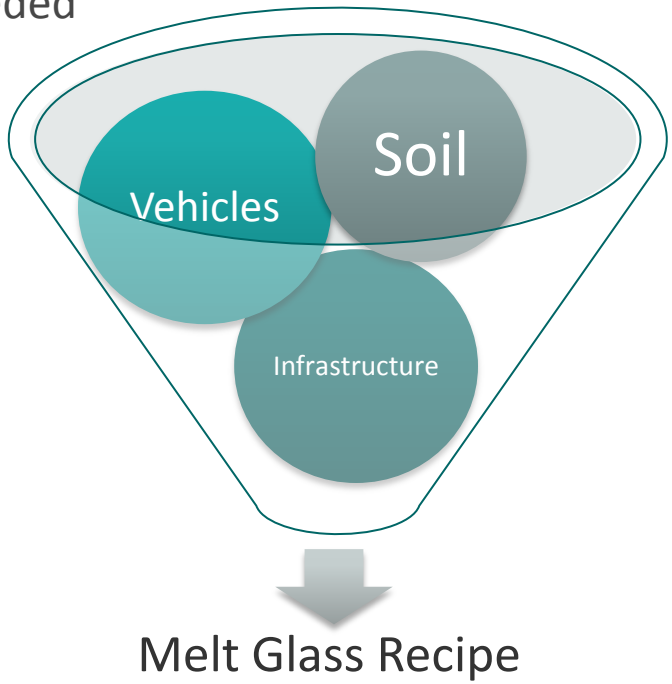
^{95}Zr is the actual isotope

^{126}Sn is the actual isotope

[1]P. P. Parekh *et al.*, "Radioactivity in trinitite six decades later.," *J. Environ. Radioact.*, vol. 85, no. 1, pp. 103–20, Jan. 2006
[2]J. J. Bellucci *et al* , "Distribution and behavior of some radionuclides associated with the Trinity nuclear test," *J. Radioanal. Nucl. Chem.*, vol. 295, no. 3, pp. 2049–2057, Sep. 2012
[3]D. Schlauf,,*et al*"Trinitite redux: Comment on 'Determining the yield of the Trinity nuclear device via gamma-ray spectroscopy,'" *Am. J. Phys.*, vol. 65, no. 11, p. 1110, 1997.

Urban Model: Mass Calculations

- Developed a 3-component system
- Flexibility allows for use in any area where data is available
- Can scale complexity of model as needed

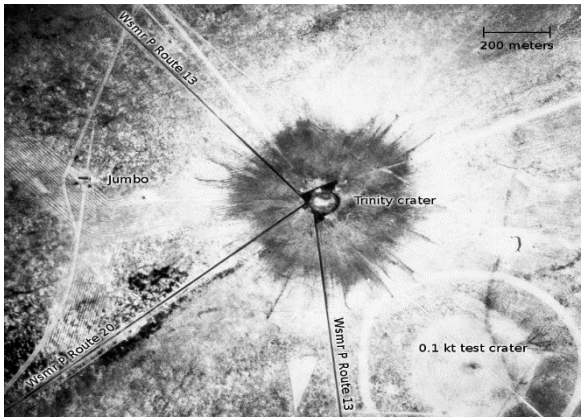


Major Elemental Composition by Weight Percent for a 1kT detonation

Element	NYC	Houston
Fe	9.88%	6.55%
Si	58.08%	63.30%
Ca	6.64%	7.56%
N	0.01%	N/A
S	0.06%	0.07%
C	0.01%	N/A
O	0.55%	0.14%
Al	14.55%	17.80%
Mg	2.68%	0.90%
K	3.39%	0.22%
Ba	0.05%	0.09%
Na	3.08%	0.74%
Mn	0.11%	0.06%
P	0.09%	0.03%
Ti	0.58%	0.60%

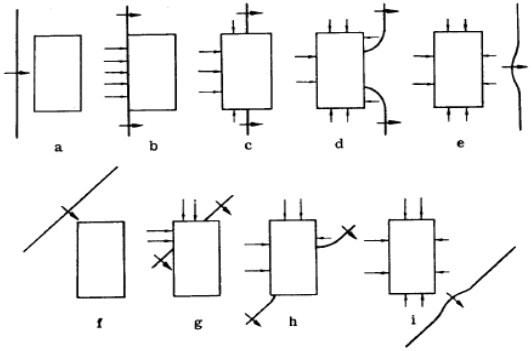
Local Fallout Modeling

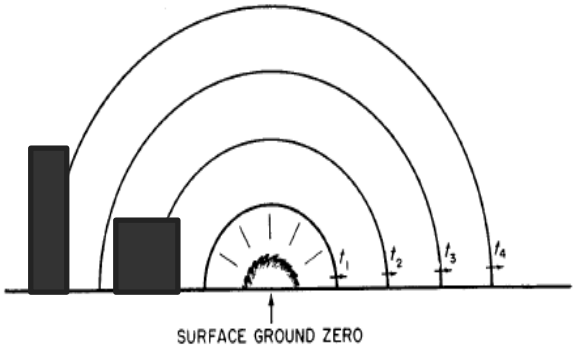
- From NTS data large particulates are distrusted in an approximately 1000m radius
  - Outside of Fireball Radius
  - Many buildings will remain after detonation



Local Fallout Modeling

- Blast Effects
  - Determine Buildings that are destroyed
  - Account for Damaged Buildings
- Shock Effects
  - Model Pressure Wave
  - Determine Damage of Buildings
- Simulate final Urban environment
  - Couple Map with CFD codes to predict fallout location



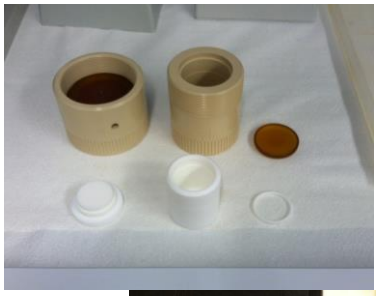


Advanced Separations

Approach – Pressure Method

$$X + 2HNO_3 + 5HF \rightarrow XF_a + X(NO_3)_b$$

- Heated 32 mL Parr Microwave Bomb, 35 sec @ 700 watts
- Cools for 20-30 mins
- Evaporated in Teflon @ 225 ºC



$$XF_a + X(NO_3)_b + 5HNO_3 + 2HClO_4 \rightarrow X(ClO_4)_c + X(NO_3)_d$$

- Evaporated in Teflon @ 225 ºC

$$X(ClO_4)_c + X(NO_3)_d + HCl \rightarrow XCl_e$$

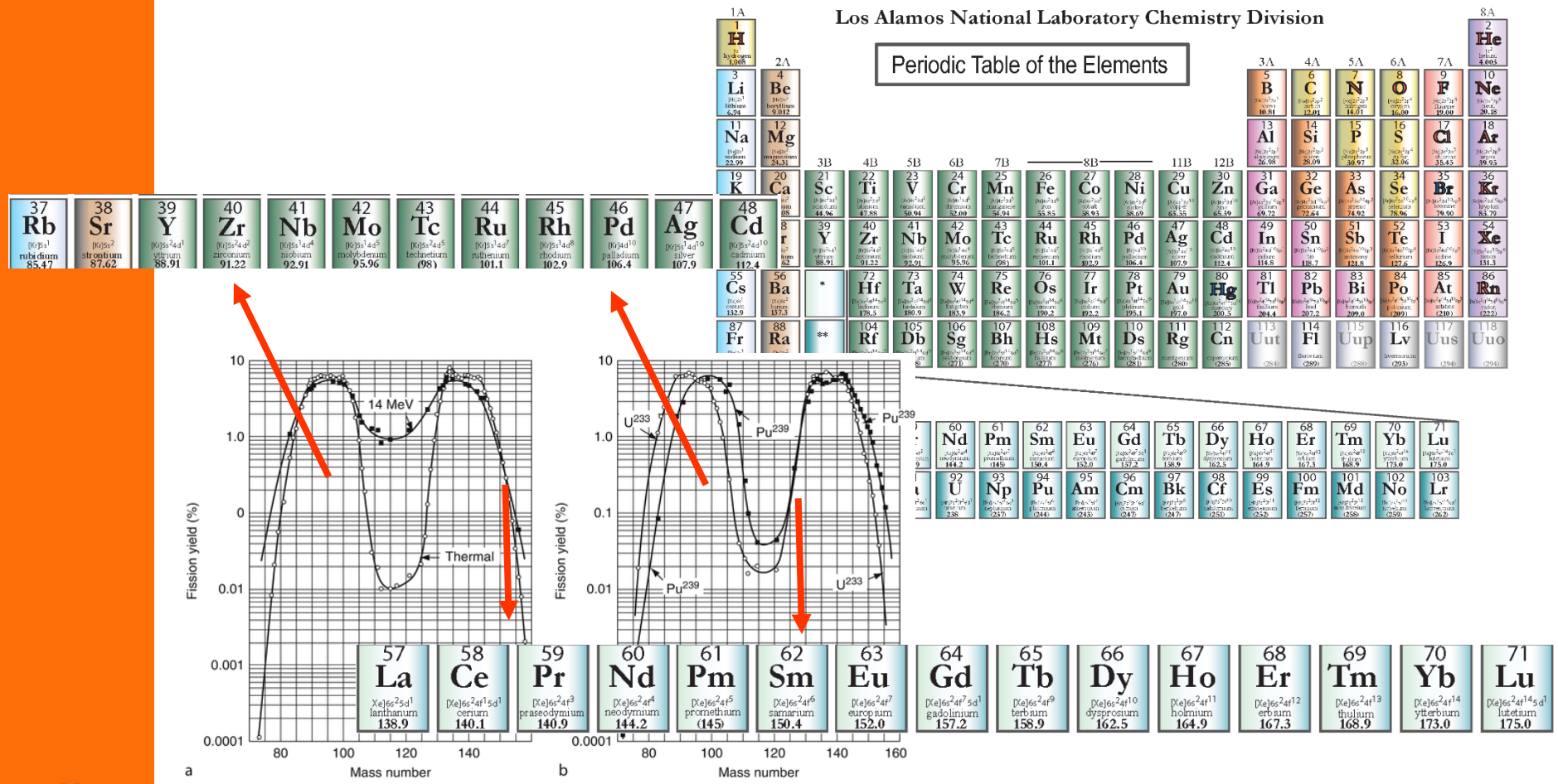
- Evaporated in Teflon @ 225 ºC

Process Time: ~4-6 hrs

* Reactive agents in concentrate form unless otherwise listed

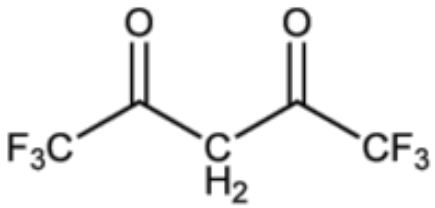
** a, b, c, d, e represent stoichiometric coefficient

Fission Products

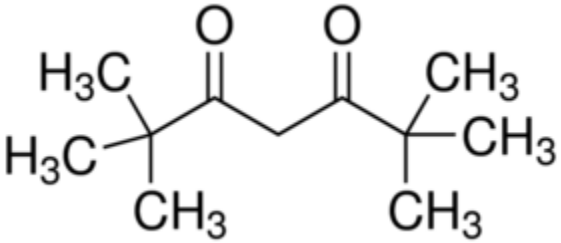


Background (*Cont.*)

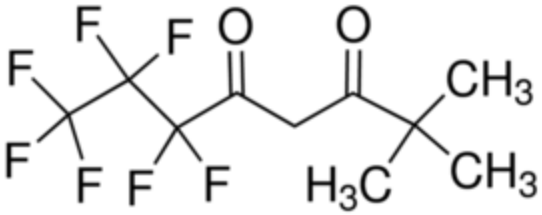
- Ligands for ease of volatilization and rapid separation



1,1,1,5,5,5 – hexafluoro – 2,4 – pentadione (denoted hfac)



2,2,6,6-tetramethyl-3,5-heptanedione (denoted hdpm)



6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (denoted hfod)

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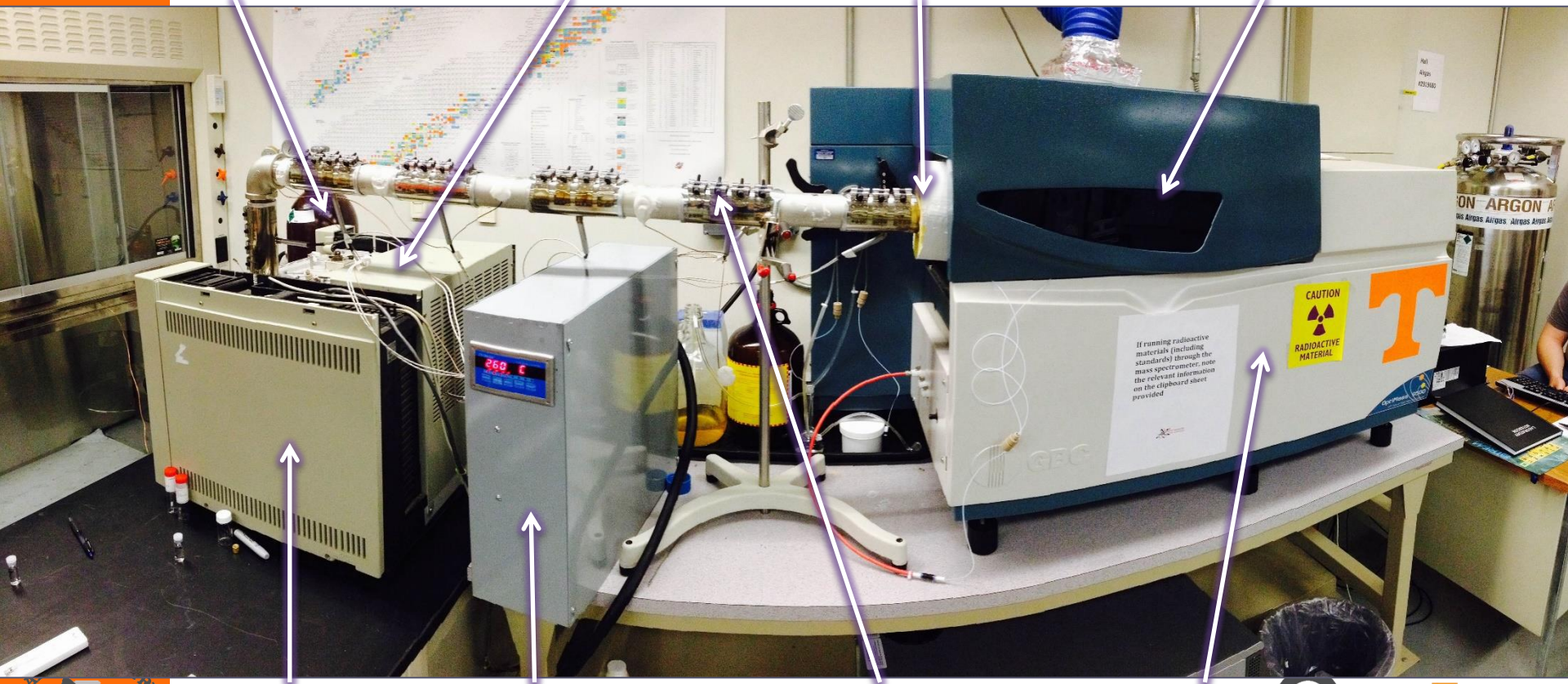
GC-ICP-TOF-MS



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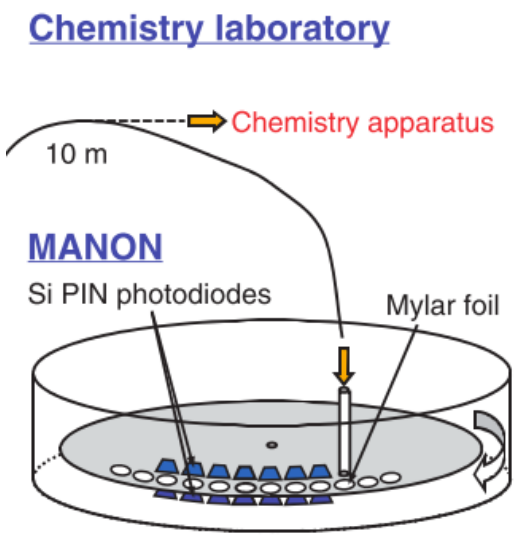
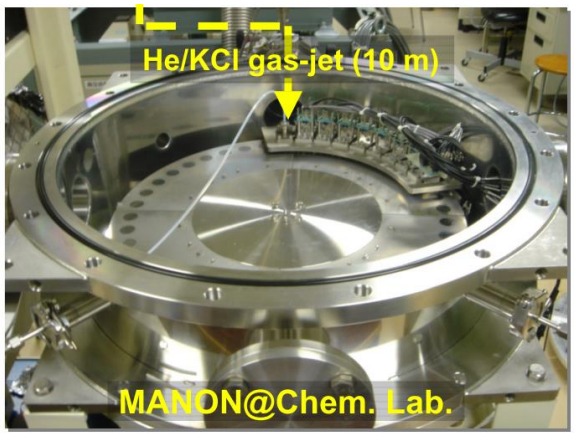
Additional characterization methods are under development

- Super heavy isotope measurement methods can be adapted to rapid gas-phase separations
- Alpha-particle spectroscopy provides a way to characterize samples with high-confidence
- Method currently employed at RIKEN to measure extremely short-lived isotopes in SH element separations

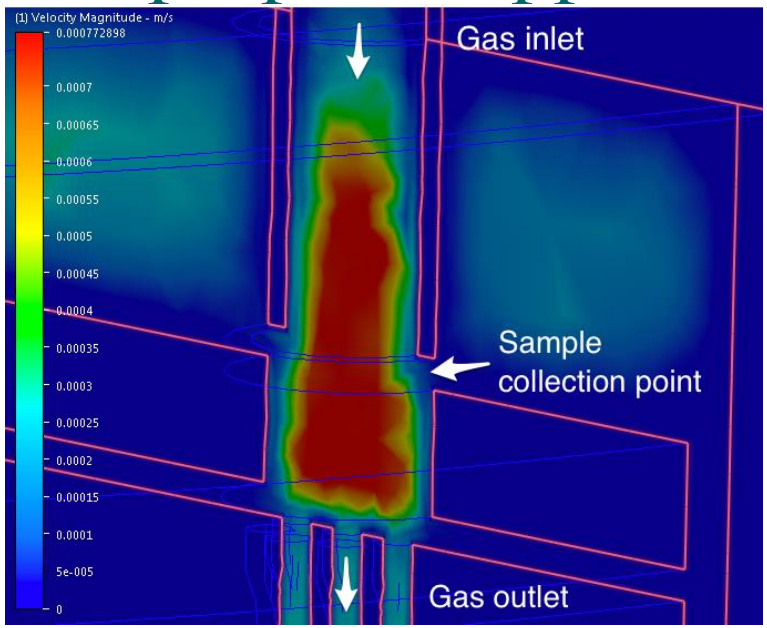


The MANON rotating wheel apparatus can be adapted to make alpha spectroscopy measurements for rapid gas-phase separations

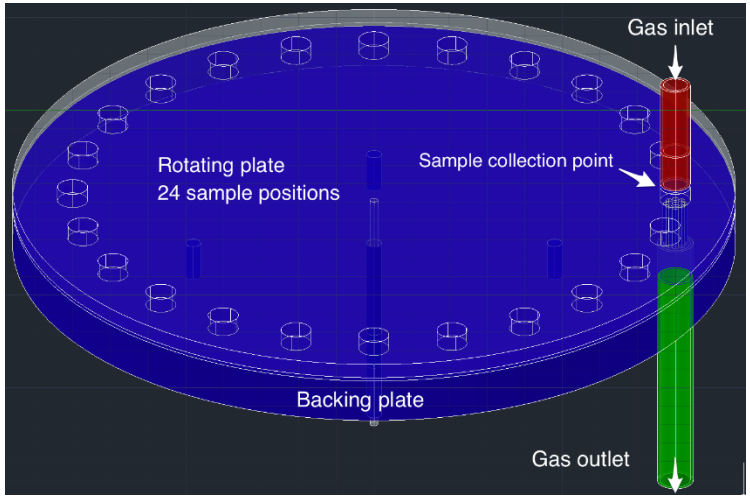


A rotating plate apparatus with a set rotational rate is proposed to partition elements for alpha-spectroscopy and/or further chemical analysis

Initial design and CFD simulation of the proposed apparatus



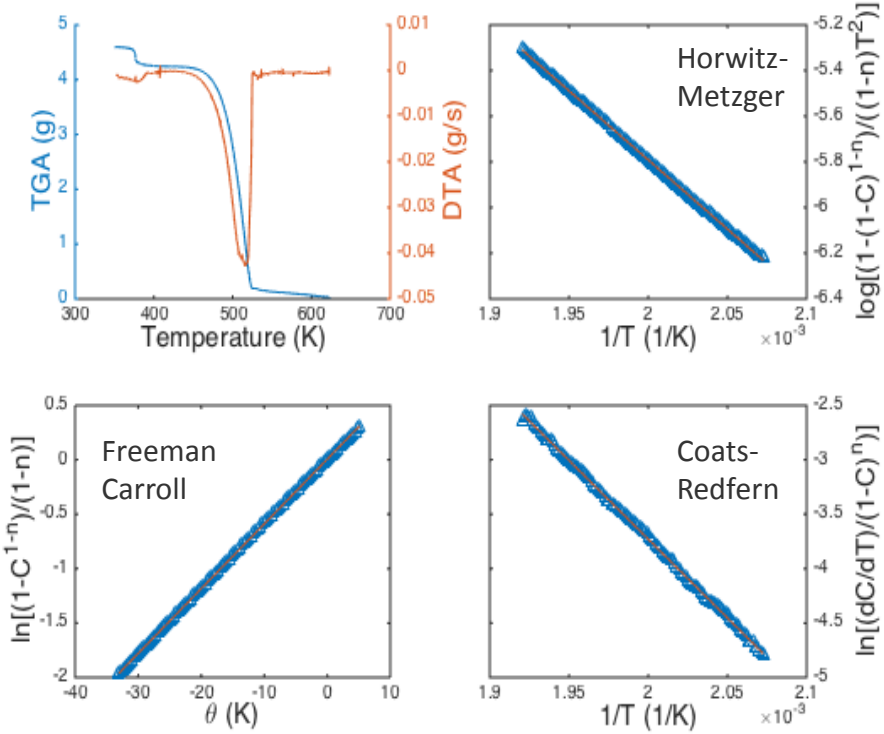
AutoCAD CFD is used to model how the gas will flow in the instrument for the initial design.



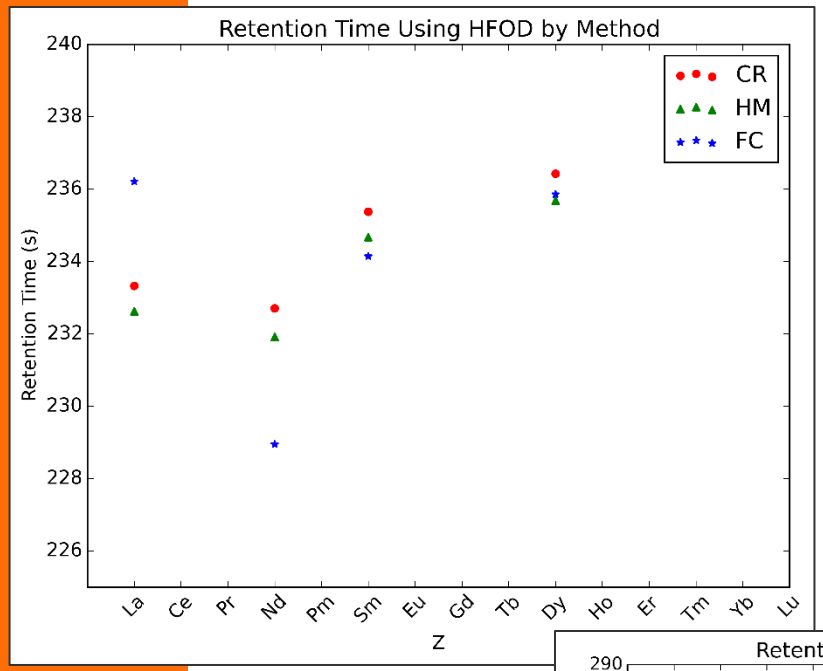
AutoCAD is used to produce an initial design for the UT sample collection system. Mylar film is placed over the sample collection points which then rotate under a semiconductor alpha-particle detector.

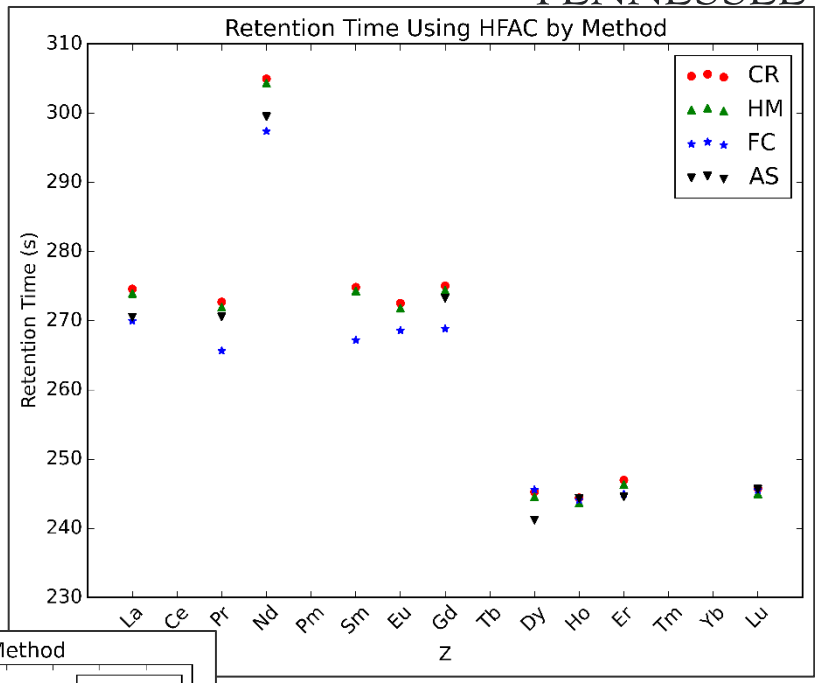
TGA Analysis (hfac)

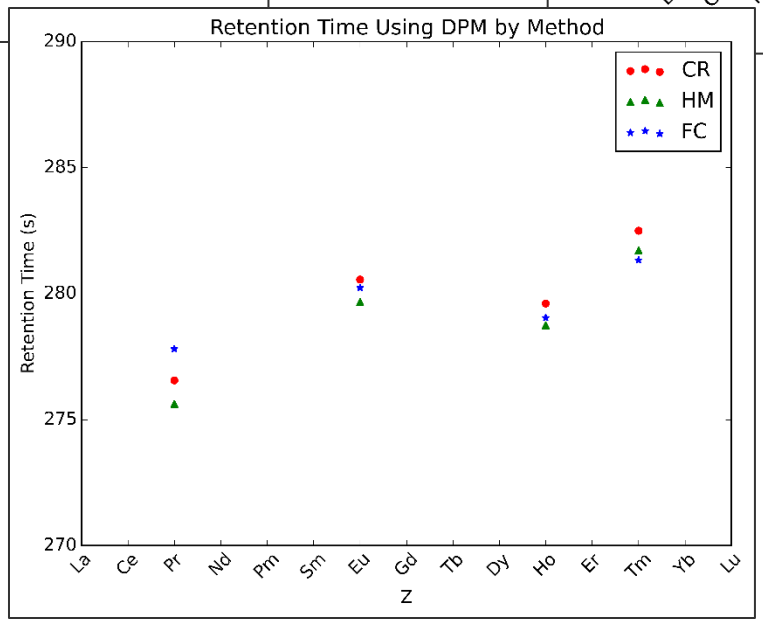
- Perform thermogravimetric analysis and differential thermal analysis
  - Fit data according to 4 model (Horwitz-Metzger, Freeman-Carroll, Coats-Redfern, and Ashcroft
- Derive ΔH_{subl} and ΔS_{subl} to solve for ΔH_{ads} and ΔS_{ads}
- Use adsorption values to predict retention time times of complexes on quartz column



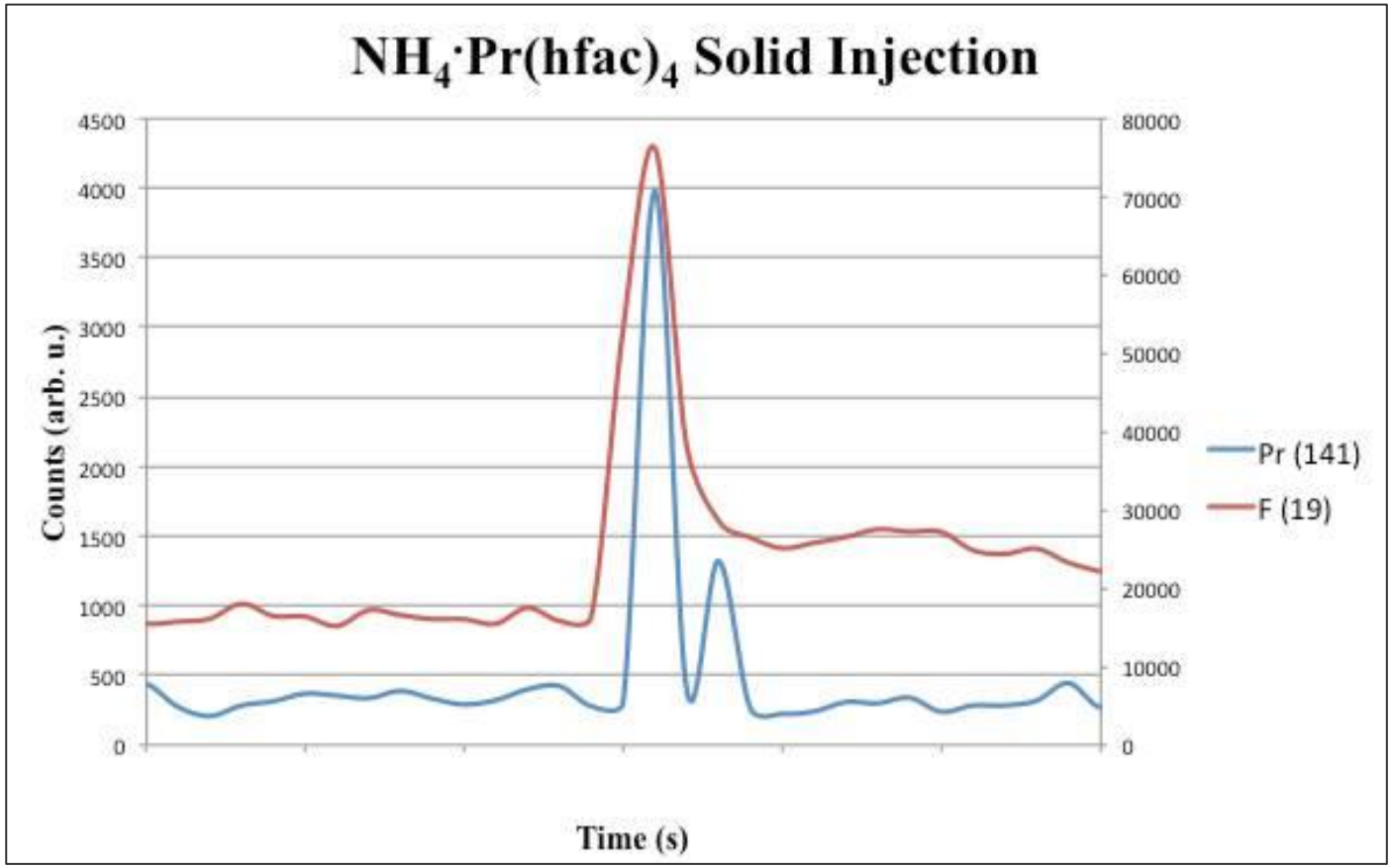
Predicted Retention Times







First Successful Solid Injection

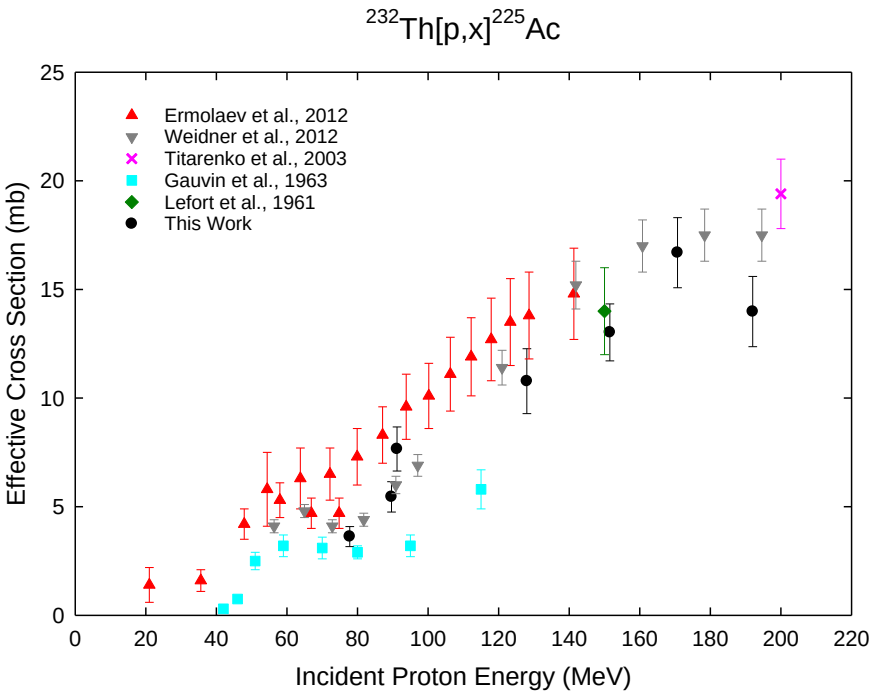


Nuclear Cross-Sections/Inverse Kinematics

Measurements of proton-induced actinide cross sections

Collaboration between ORNL, LANL and BNL (irradiations conducted at all three laboratories)

Radiochemical separations and gamma spectroscopy conducted at ORNL, LANL



Griswold 2015 DOE SCGSR awardee (BNL host lab)

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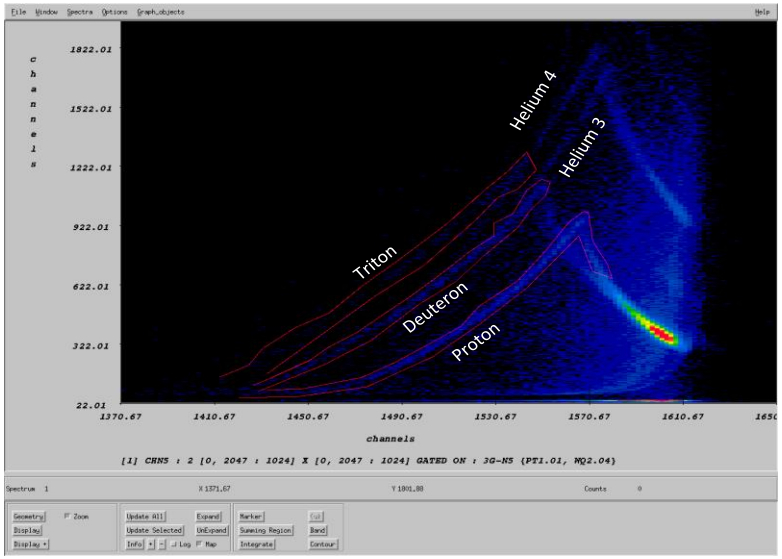
Measurements of light ion production cross sections and thick target yields

Motivation – uncertainties in inclusive light ion production cross sections and yields in transport model calculations



Experiments conducted at NSRL beam line
He, C, Ar, Fe ions between 0.4 and 2.5 GeV/nucleon
500 hours of beam time through 2017

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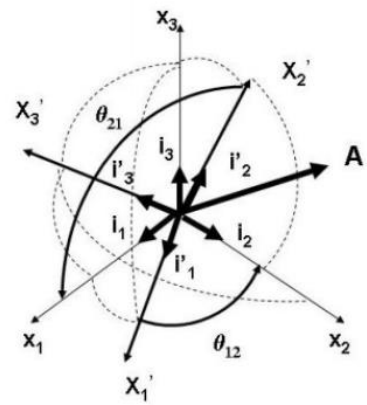
Cross sections group – other developments:

Inverse kinematics afterburner code for MCNP6 calculations (poster presentation)



a) x transformed into X'

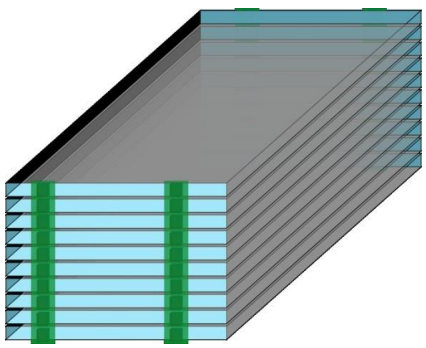
$$\boldsymbol{A} = A_1\boldsymbol{i}_1 + A_2\boldsymbol{i}_2 + A_3\boldsymbol{i}_3 = A'_1\boldsymbol{i}'_1 + A'_2\boldsymbol{i}'_2 + A'_3\boldsymbol{i}'_3$$

$$A'_j = A_1\boldsymbol{i}'_j \cdot \boldsymbol{i}_1 + A_2\boldsymbol{i}'_j \cdot \boldsymbol{i}_2 + A_3\boldsymbol{i}'_j \cdot \boldsymbol{i}_3$$

$$\begin{pmatrix} A'_1 \\ A'_2 \\ A'_3 \end{pmatrix} = \begin{pmatrix} \boldsymbol{i}'_1 \cdot \boldsymbol{i}_1 & \boldsymbol{i}'_1 \cdot \boldsymbol{i}_2 & \boldsymbol{i}'_1 \cdot \boldsymbol{i}_3 \\ \boldsymbol{i}'_2 \cdot \boldsymbol{i}_1 & \boldsymbol{i}'_2 \cdot \boldsymbol{i}_2 & \boldsymbol{i}'_2 \cdot \boldsymbol{i}_3 \\ \boldsymbol{i}'_3 \cdot \boldsymbol{i}_1 & \boldsymbol{i}'_3 \cdot \boldsymbol{i}_2 & \boldsymbol{i}'_3 \cdot \boldsymbol{i}_3 \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \\ A_3 \end{pmatrix}$$

$$\boldsymbol{i}'_2 \cdot \boldsymbol{i}_1 = cos\theta_{21} \text{ while } \boldsymbol{i}'_1 \cdot \boldsymbol{i}_2 = cos\theta_{12}$$

$$A'_j = A_1 \cos\theta_{j1} + A_2 \cos\theta_{j2} + A_3 \cos\theta_{j3}$$



Collaboration with Robert Grzywacz (RIBSS consortium) on development of NEXT – low energy neutron detector, energies between 0.1 and 10 MeV

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The separation of ^{213}Bi from the parent nuclide solution of ^{225}Ac and the sorption behavior of ^{221}Fr.

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Ion Exchange properties of Alkali Metal Cations

- Interested in the ion exchange properties of Fr.
- Performed experiments on Alkali metal ions to find the trend in the distribution coefficients (ratio of moles of ion on resin to moles of ion in solution).
- Will use this trend in distribution coefficients to predict the ion exchange properties of Francium.
- Will use this prediction to help design the test bed for the radioactive nuclides.

Cation	Distribution Coefficient	Uncertainty
Li^+	0.0113 L/g	0.00068
Na^+	0.0183 L/g	0.00104
K^+	--	--
Rb^+	--	--
Cs^+	0.0271 L/g	0.00034

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Bulk Actinide Oxide Materials Processing and Behavior

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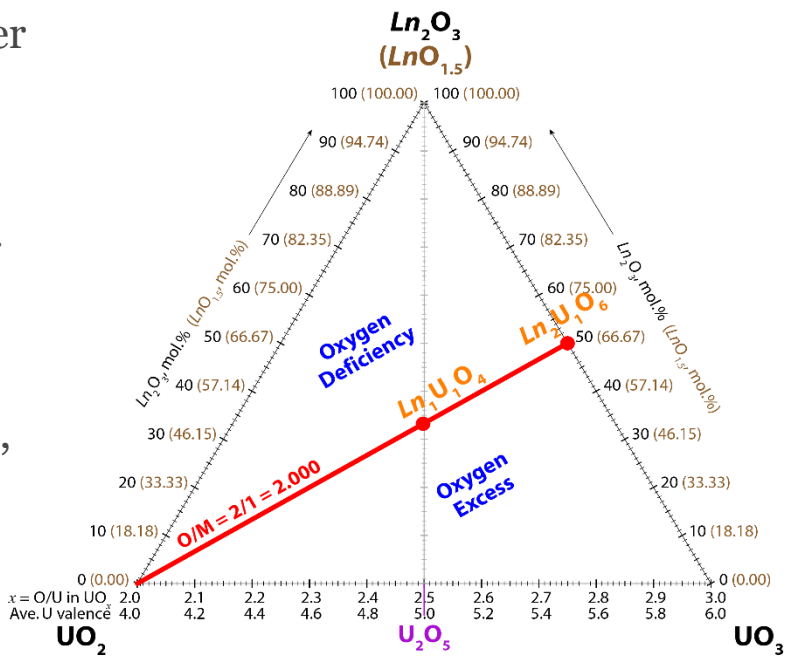
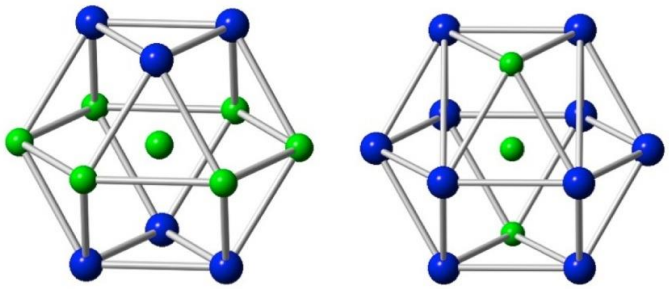
Compound formation, cation ordering, and defect chemistry in the UO_2-UO_3-Ln_2O_3 ternary system

- UO_2-UO_3-Ln_2O_3 compounds phase space are of technological interest in light water nuclear reactor fuel technology
- the chemistry of uranium dioxide (UO_2) fuel evolves to higher oxidation states of uranium with burn up
- Rare earth elements (as fission products, are incorporated into the fuel matrix.
- Oxidation of UO_2 is important for understanding fuel variations during reactor operation, and for predicting the chemistry of spent fuels.



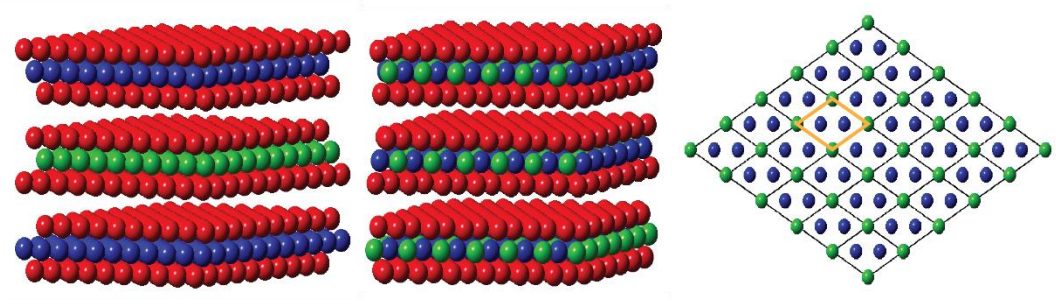
Compound formation, cation ordering

- Layered atom model approach to propose candidate ordered structures for compounds La_2UO_6, Ce_2UO_6, $LaUO_4$, $CeUO_4$



(a) (b)

(a) 2nd nearest neighbor cation coordination polyhedron in Ln_2UO_6, based on the ordered-*pure* layer model; (b) 2nd nearest neighbor cation coordination polyhedron in Ln_2UO_6, based on the ordered-*mixed* layer model.



(a) (b) (c)

(a) Inclined view of oxygen-metal-oxygen (O-M-O) blocks in the "pure" cation layer model for Ln_2UO_6. (b) Inclined view of O-M-O blocks in the "mixed" cation layer model for Ln_2UO_6. (c) Plan-view of one cation layer in the mixed cation layer model for Ln_2UO_6.

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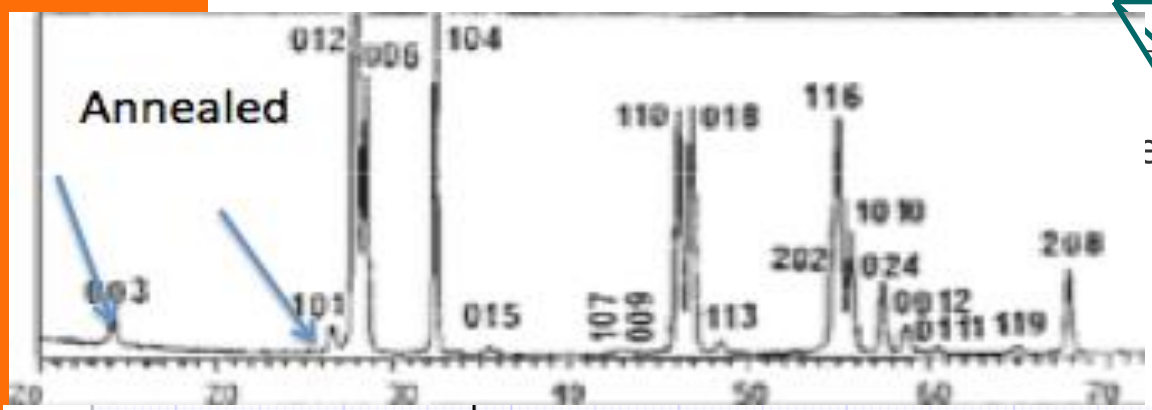
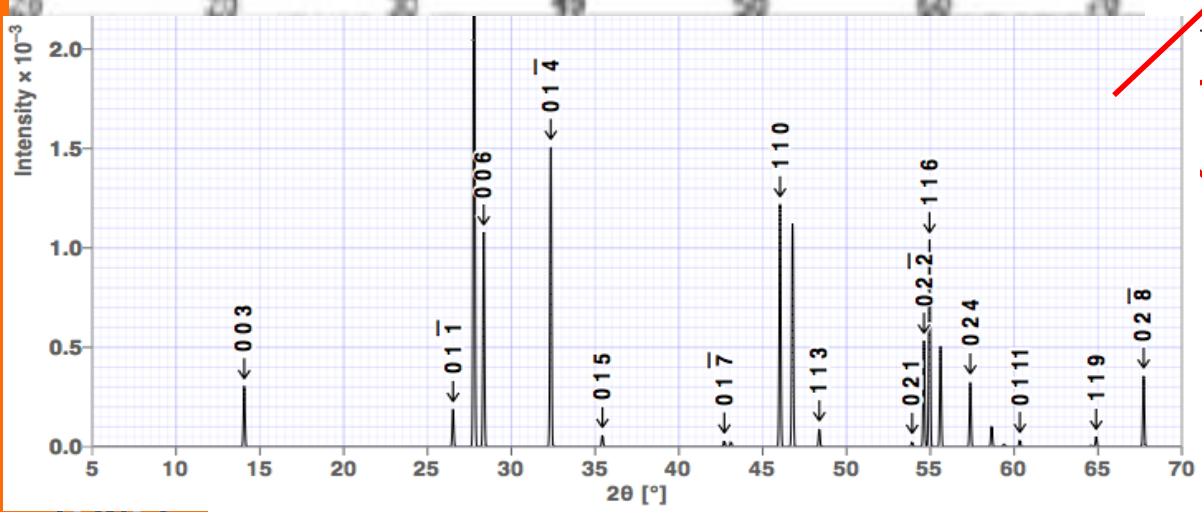
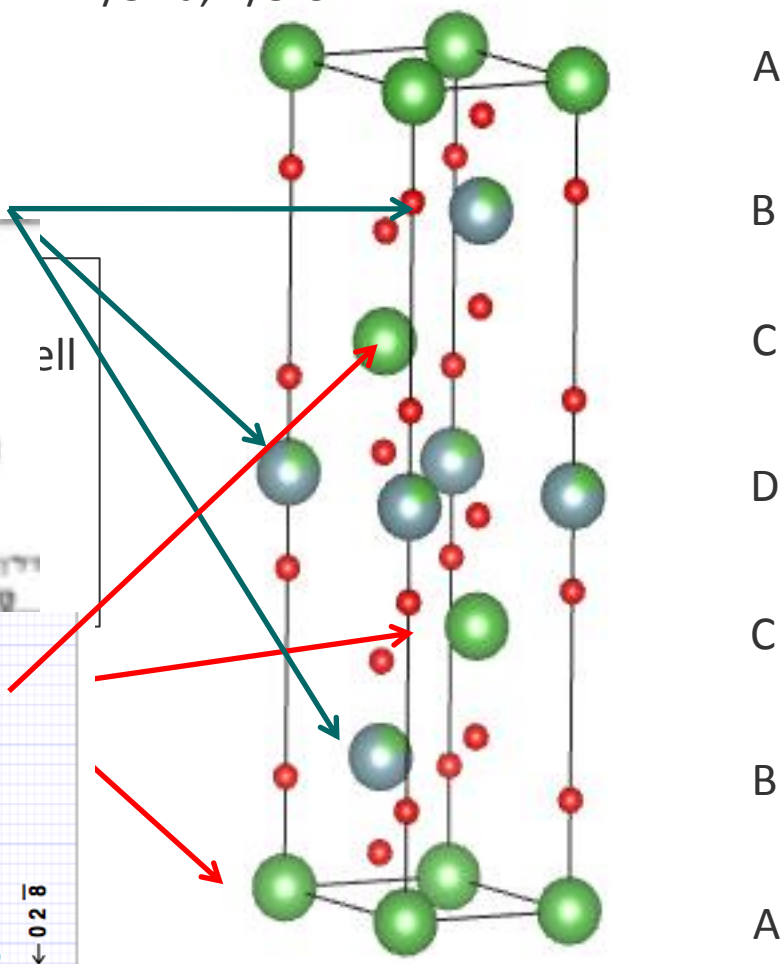
Using group-subgroup theory and experimental results from literature we have determined the crytallographic structure of real compounds $U_{0.40}La_{0.60}O_{1.98}$, $U_{0.26}La_{0.74}O_{1.89}$, $U_1La_6O_{12}$,

A=full lanthanum layer

B=1/5 La, 4/5 U







$U_{0.40}La_{0.60}O_{1.98}$

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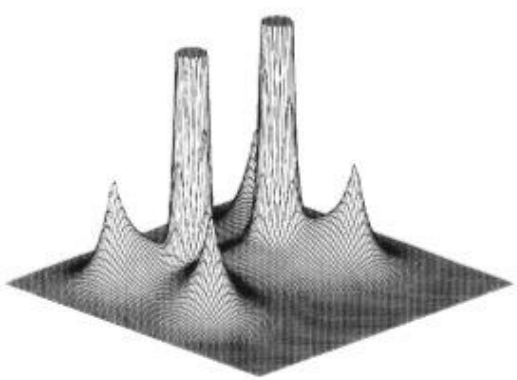
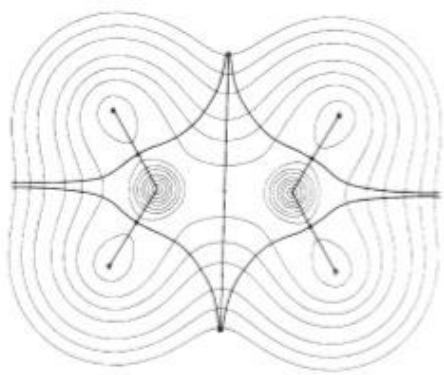
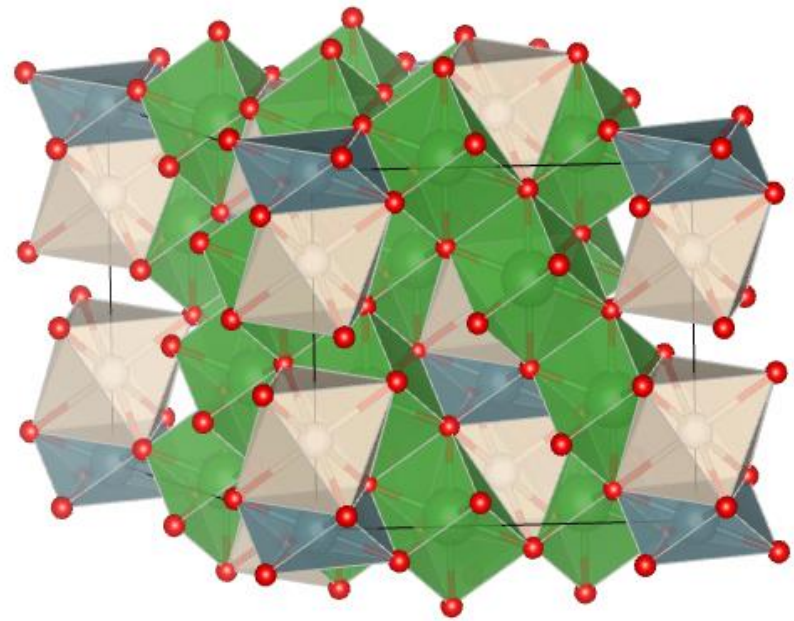
P. Garcia-Chain, R. Rojas, P. Herrero, and J. Günter, "Microstructural Characterization of the Fluorite Phase in the U-La-O System: II. Hexagonal Microdomain Formation in (U1-yLay) O2-x,

We explored the structural flexibility of the $(La,U)O_{2\pm x}$ system, with a particular focus on the La_6UO_{12} and we compare the uranium atoms local environment to two UO_3 polymorphs. To discuss those differences and their specific features in a quantitative way, we have assessed and applied atom-in-molecule type tools to the electron charge density obtained by DFT for each of those structures, and obtained robust estimates for Bader's charges and the characteristics of critical points of the laplacian of the charge density







Crystal structure of La_6UO_{12}.

R. F. Bader, *Atoms in molecules*: Wiley Online Library, 1990.

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Radiochemical Probes for Physical Phenomena

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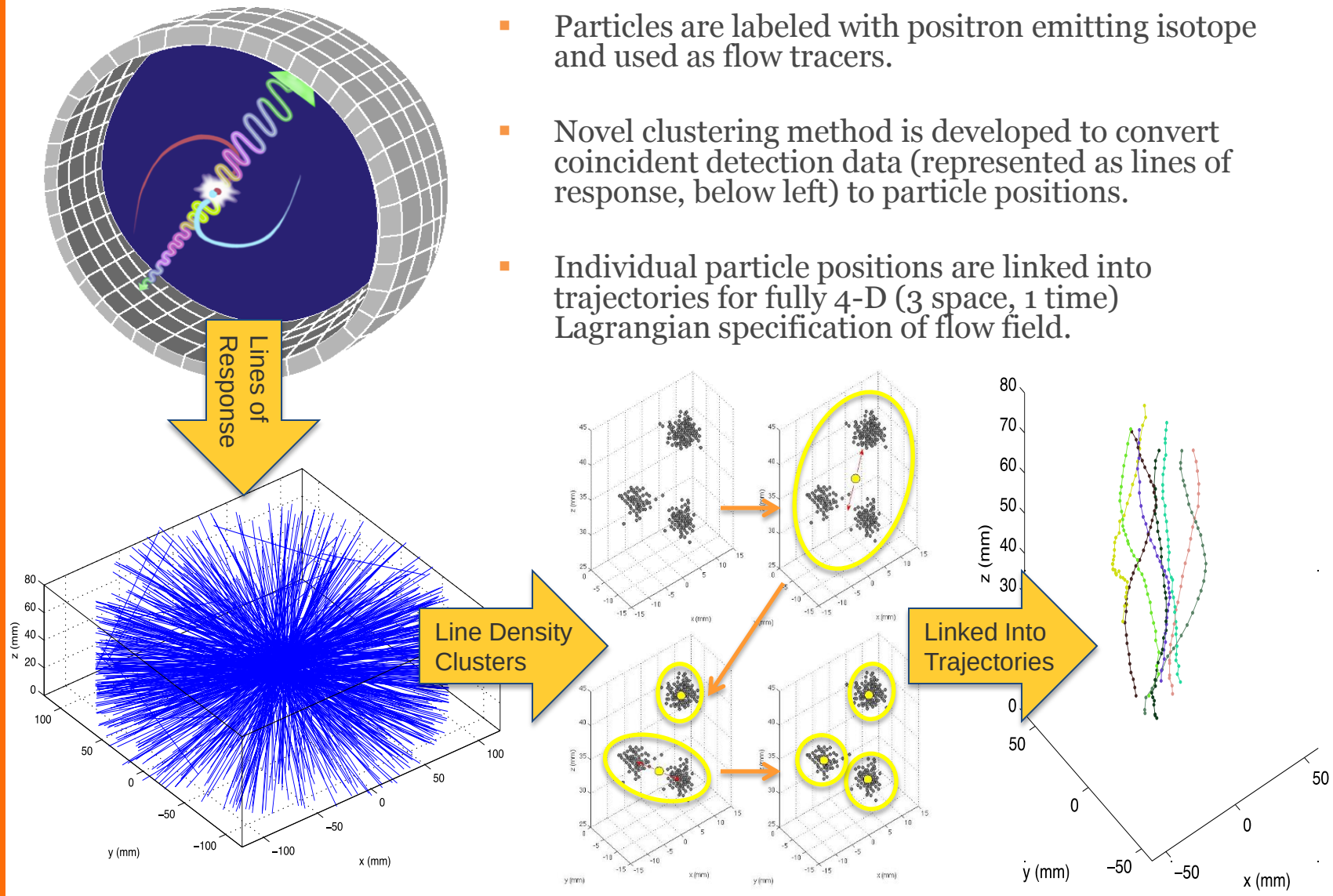
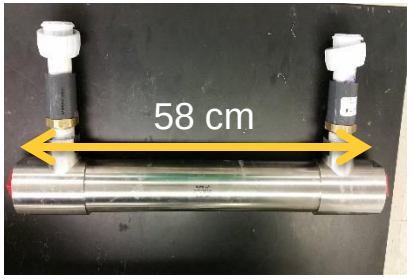
Positron Emission Particle Tracking (PEPT) for Flow Measurement

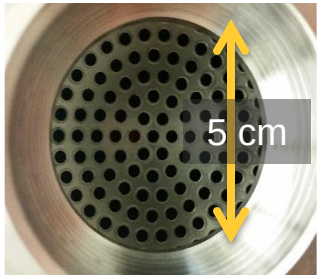


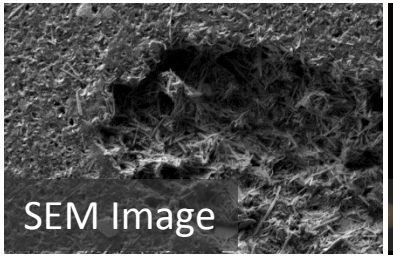
- Particles are labeled with positron emitting isotope and used as flow tracers.
- Novel clustering method is developed to convert coincident detection data (represented as lines of response, below left) to particle positions.
- Individual particle positions are linked into trajectories for fully 4-D (3 space, 1 time) Lagrangian specification of flow field.

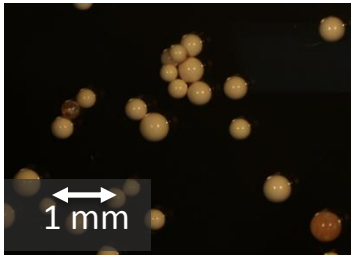
Example: Heat Exchanger Experiment

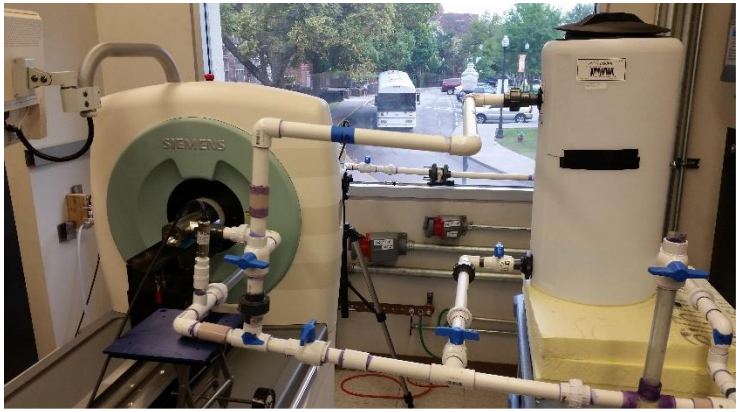
- Measurement performed in shell side of tube-in-shell heat exchanger (right, top).
- Working fluid is sugar water with density 1.225 g/cc and Reynolds number of 2300 (mean velocity 0.64 m/s).
- ^{18}F activated anion exchange resin beads (right, middle) used as tracers.
  - 500-750 micron diameter
  - ~1 mCi each
- Scan performed in Siemens Inveon Preclinical PET scanner (right, bottom) for 8 minutes.











Results Animation

- PEPT found capable of imaging through stainless steel.
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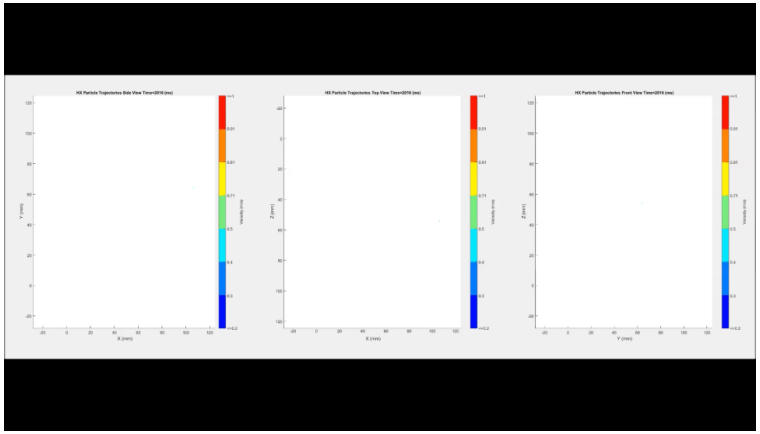
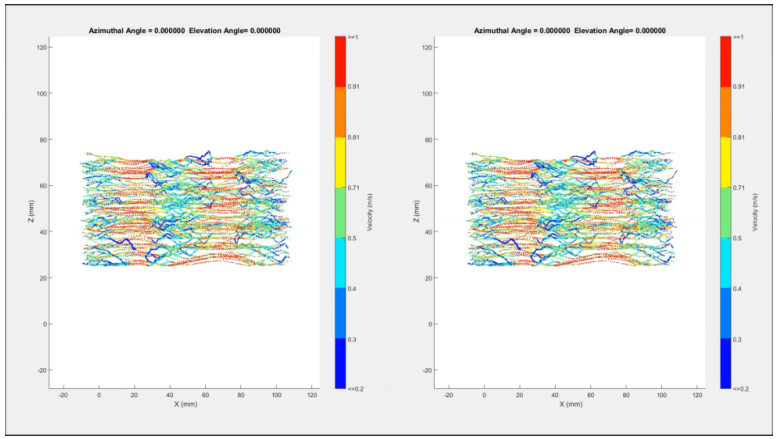


Time Resolved Trajectories



Rotated Trajectories

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Peer-Reviewed Publications

- J.J. Molgaard et al.; "Development of Synthetic Nuclear Melt Glass for Forensic Analysis", Journal of Radioanalytical and Nuclear Chemistry Vol. 304 (3), 2015. 1293-1301
- A. V. Giminaro et al, "Compositional planning for development of synthetic urban nuclear melt glass," Journal of Radioanalytical and Nuclear Chemistry, vol. 306, no. 1, pp. 175–181, Oct. 2015
- E. T. Peskie and H. L. Hall, "Radiation Damage as a Possible Metal Chronometer for Pre-Detonation Nuclear Forensics," International Journal of Nuclear Security, vol. 1, no. 1, p. Article 13, Jul. 2015
- E. T. Peskie and H. L. Hall, "Impurity Diffusion as a possible metal chronometer for pre-detonation nuclear forensics," International Journal of Nuclear Security, vol. 1, no. 1, p. Article 12, 2015.
- M. T. Cook et al; "A Comparison of Gamma Spectra from Trinitite vs. Irradiated Synthetic Nuclear Melt Glass", *Journal of Radioanalytical and Nuclear Chemistry*, vol. 307, no. 1, pp. 259–267, Jan. 2016.
- J. D. Auxier II et al; "Synthesis, Characterization, and Thermogravimetric Analysis of Lanthanide 6,6,7,7,8,8,8-Heptafluoro- 2,2-Dimethyl-3,5-Octanedione Complexes for Rapid Separation Applications", Under Review to Inor. Chem. Acta.
- J. D. Auxier II et al; "Thermochromatographic Analysis of Volatile Organometallic Fission Products"; *Journal of Radioanalytical and Nuclear Chemistry*, Dec. 2015. .
- Y. Wu et al; "Defect Engineering in SrI2:Eu2+ Single Crystal Scintillators"; J. Crys. Grow. Design. In Press.
- J. P. Auxier et al; "Development of a Gas Chromatography Inductively Coupled Plasma Time-of-Flight Mass Spectrometer" Under Review to J. Sep. Pur.
- J. J. Molgaard et al, "Production of Synthetic Nuclear Melt Glass," Journal of Visualized Experiments, no. 107, Jan. 2016. .
- L. Casillas-Trujillo et al; "Structure and cation ordering in ULa2O6, ULaO4,UCe2O6, UCeO4 by first principles calculation"; submitted to Scripta Materialia.

PLUS: 5 completed theses/dissertations, 42 conference presentations, 4 best student presentation awards (3 ANS, 1 INMM), 2 ACS Coryell Awards for UG Research

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Conclusions

- Scientific work is productive, impactful, and supporting numerous students in preparation for careers in NNSA missions or related areas
- RCoE is creating greater academic connectivity with the national labs and the broader USG nuclear security enterprise
- RCoE work is attracting new students and interest in nuclear and radiochemistry, a strategically important field that has suffered many losses of capability in the academic community

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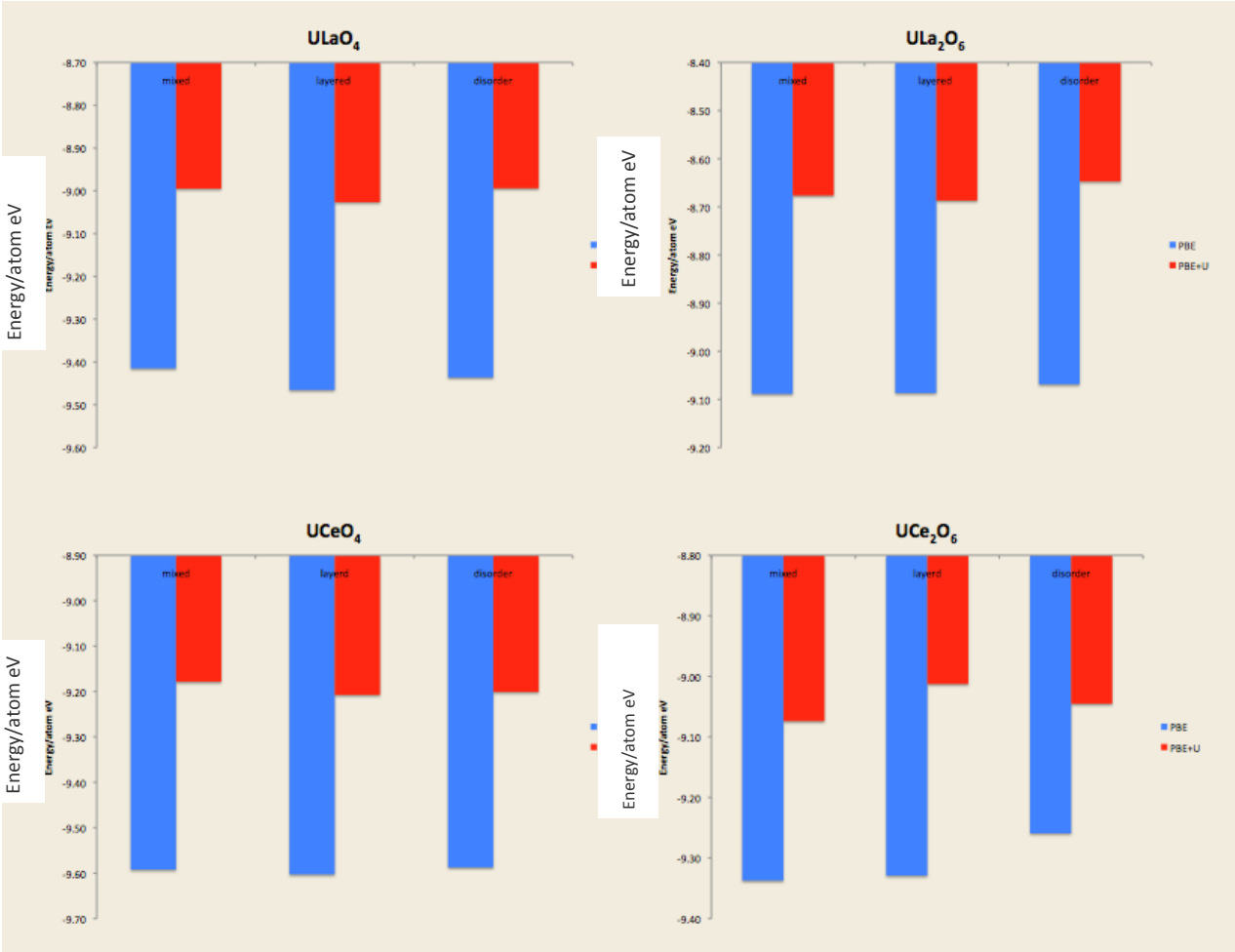
PANTEX
Thank You!

Extra Slides

Defect chemistry in the UO_2-UO_3-Ln_2O_3 ternary system



- Compounds La_2UO_6, Ce_2UO_6, $LaUO_4$, and $CeUO_4$. We then performed first principles calculations (DFT and DFT+U) to assess the relative structural stabilities of these model structures.
- For each of the *Ln*-U-O compounds, we examined distortions from ideality in the 1st and 2nd nearest neighbor polyhedra.

Ion Exchange Properties of Cs^+, La^+, and Bi^+

- Found the ion exchange properties of the ions La^{+3}, and Cs^+ with Isolute SCX-2 inorganic resin.
- These properties should be similar to the properties of the radioactive nuclides Ac and Fr.
- These properties will be used to design the shielded test bed for the radioactive nuclides.

Cation	Distribution Coefficient	Uncertainty
La^{+3}	18.0 L/g	2.18
Bi^{+3}	--	--
Cs^+	0.0271 L/g	0.00034

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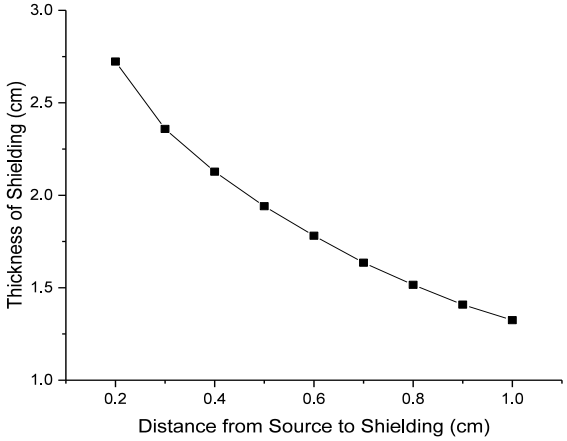
Shielding for Test Bed for Radioactive Nuclides

- Calculated the reduced exposure for the radioactivity of all the nuclides that will be used in the radioactive tests if the shielding is designed to to bring the exposure to the gamma radiation from ^{213}Bi to 5 millirems an hour.
- Calculated the thickness of the shielding needed as a function of the distance from the source to the shielding needed to reduce radiation exposure to 5 millirems an hour.
- Will use these values in the design for the test bed for radioactive nuclides.

Reduced Exposure		
Nuclide	Gamma Intensity MeV	Reduced Exposure mrem/hr
^{225}Ac	0.099 (?) 0.150 (?) 0.187 (?)	6.90×10^{-25} 1.1×10^{-24} 1.93×10^{-14}
^{221}Fr	0.218 (14%)	9.58×10^{-18}
^{213}Bi	0.437 (?)	5



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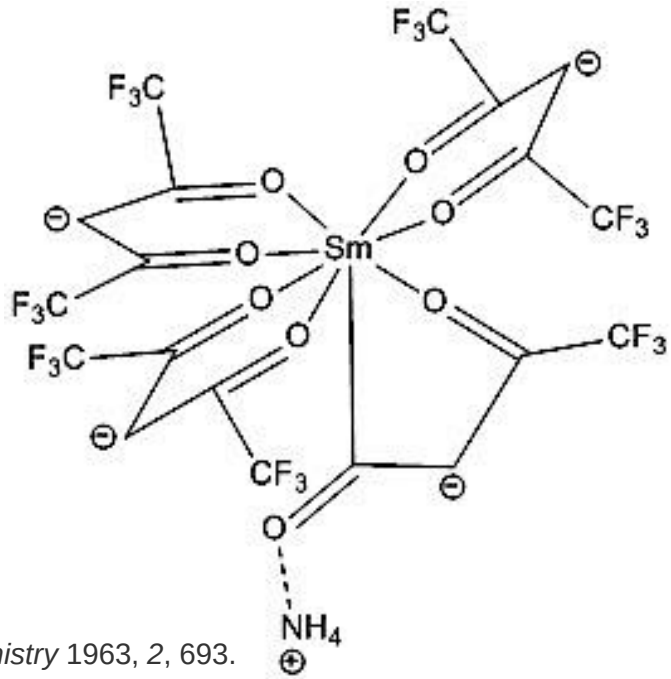
Synthesis of $Ln[hfac]_4$, $Ln[hfod]_x$, $Ln[hdpm]_x$ Compounds

Dissolution: $Ln_2O_{3(s)} + 6\ HCl \longrightarrow LnCl_{3(aq)} + 3\ H_2O_{(l)}$

Ligand Preparation: $NH_4OH_{(l)} + H_2fac_{(l)} \longrightarrow NH_4hfac_{(aq)} + H_2O_{(l)}$

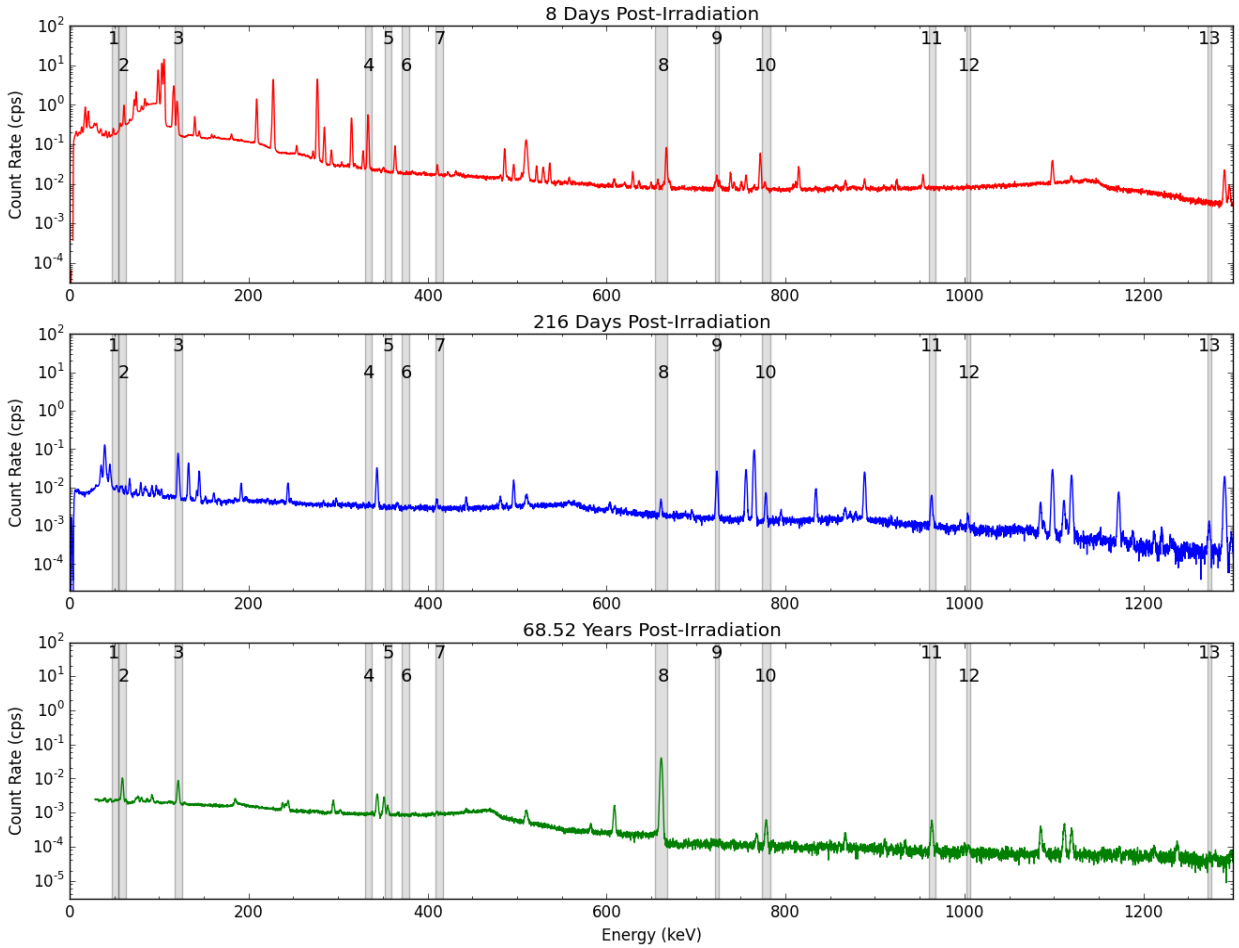
Combination/ Extraction: $LnCl_{3(aq)} + 6\ NH_4hfac_{(aq)} \xrightarrow[\text{ether}]{\text{extract into}} NH_4\ [Ln(hfac)_4]_{(org)} + 3\ NH_4Cl_{(aq)}$

Compound	% Yield
Sm	35.0-36.3
Gd	57.9-60.0
Tm	57.2-59.2

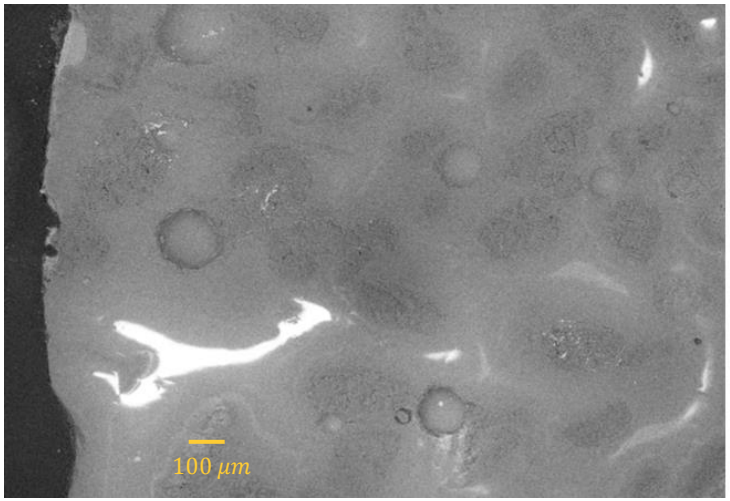


[1]Sievers, R. E.; Ponder, B. W.; Morris, M. L.; Moshier, R. W. *Inorganic Chemistry* 1963, *2*, 693.
[2]Eisentraut, K. J.; Sievers, R. E. *Journal of the American Chemical Society* 1965, *87*, 5254.
[3]Springer, C. S.; Meek, D. W.; Sievers, R. E. *Inorganic Chemistry* 1967, *6*, 1105.

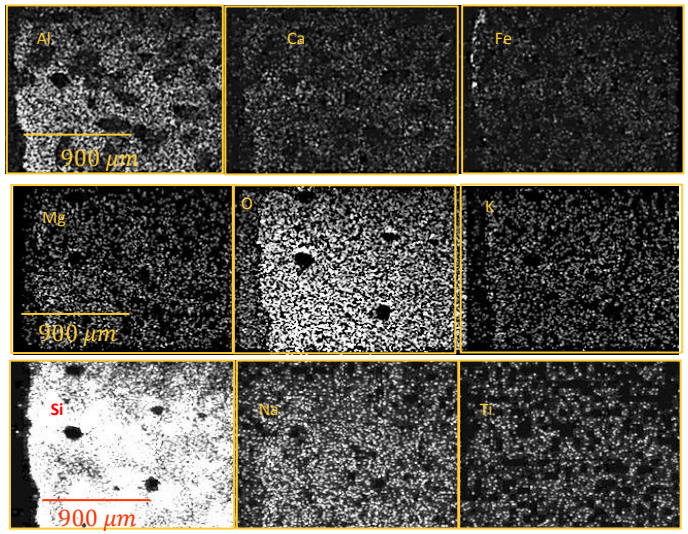
Gamma Spectroscopy



Urban Surrogate: Elemental Mapping



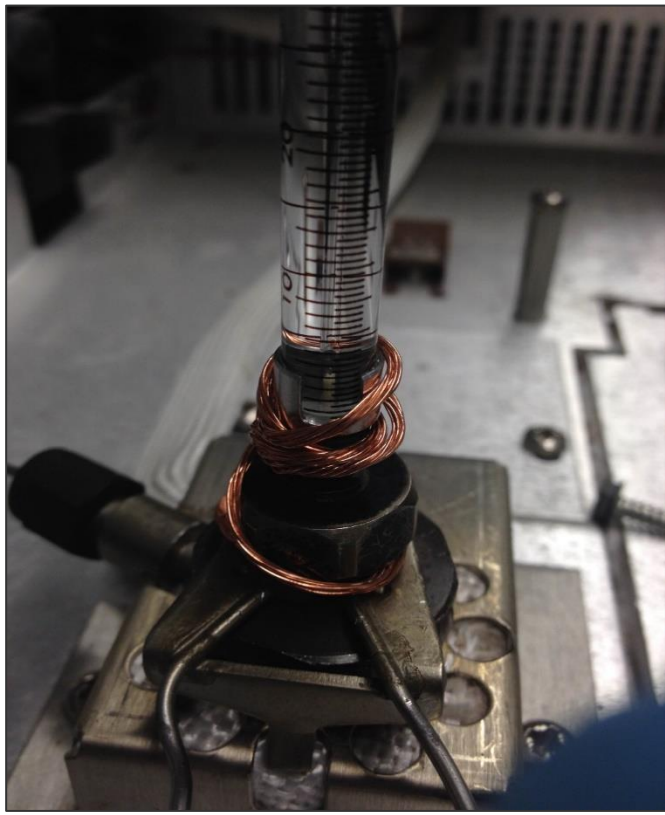
Samples ground and polished to 1μm using silicon carbide lapping paper



- Al and Si concentrations are inversely correlated
- Fe migrates migrates to the edge of the sample
- Other elements appear to have homogeneous distributions

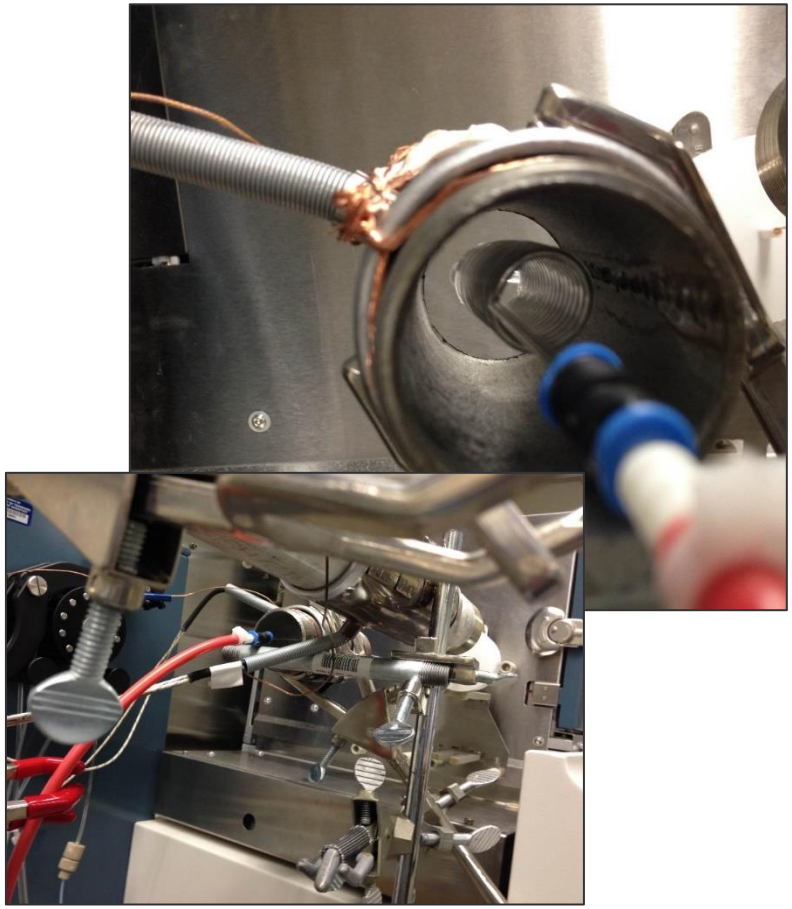
Solid Injection: Resolving Torch Blowout

- Solvents rapidly corroded torch cones and blew out the plasma
- Liquid injection completely infeasible
- New syringe solid injection method developed
- Widened sample injector to accommodate large syringes



Sample Condensation: Nebulizer Flow Heating

- These organometallics rapidly condense when not sufficiently heated
- Coupling between tube oven and MS produced a cold zone where sample condensed
- Argon nebulizer flow needed to be heated to fix this issue
- Quartz coil was designed and installed within a heating element to heat carrier gas flow



Results Animation (Alternate)

- PEPT found capable of imaging through stainless steel.
- 606 trajectories found with 1 msec temporal resolution and 0.25 mm average spatial resolution.
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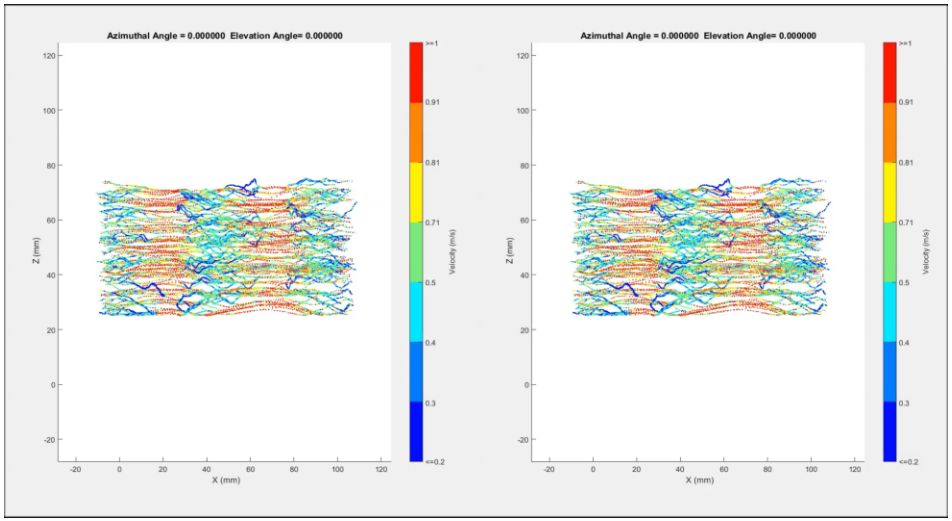
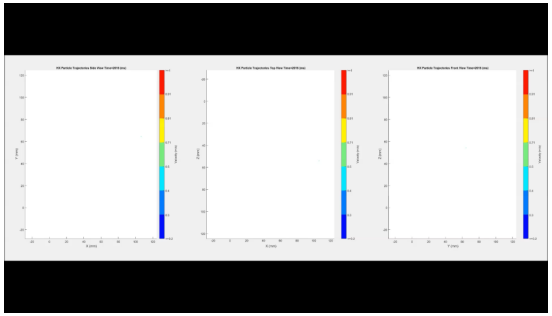
- Maximum velocity of 1.1 m/s measured in flow around baffle plates.



Rotated Trajectories



Time Resolved Trajectories

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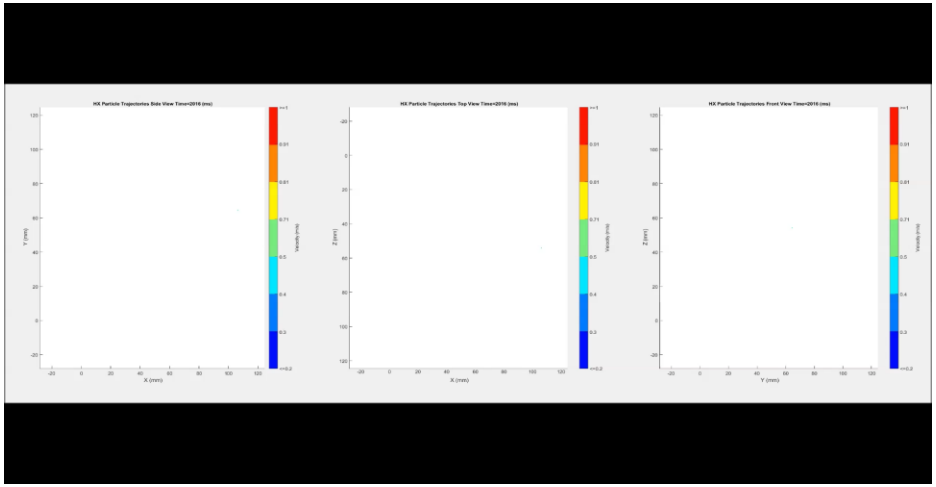

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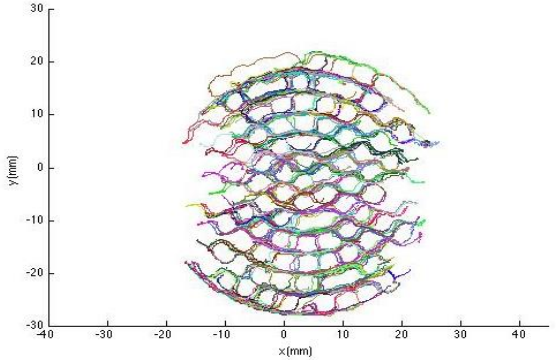

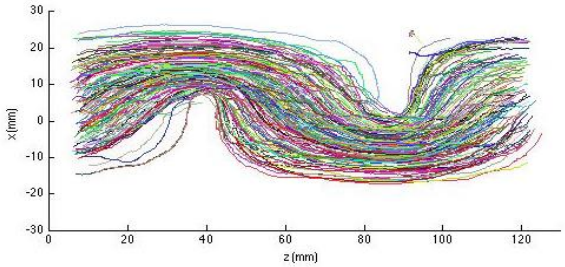

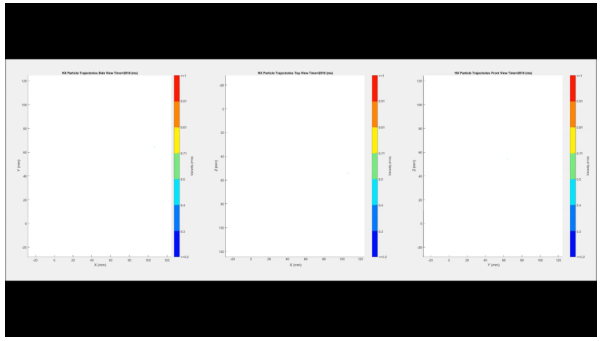

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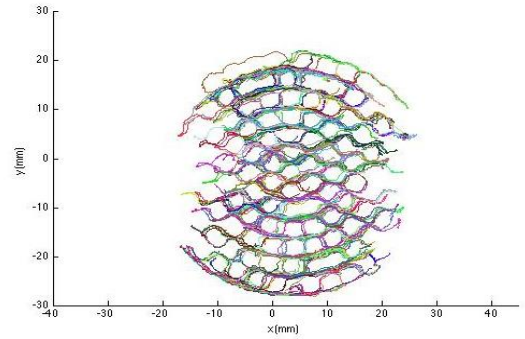
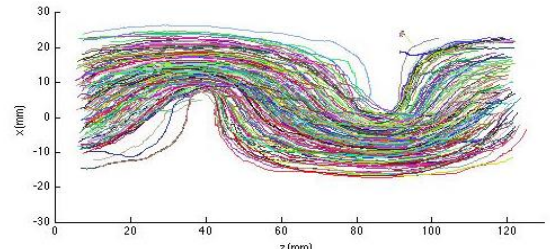
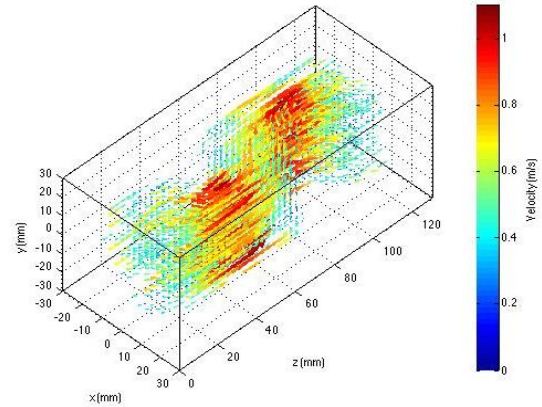
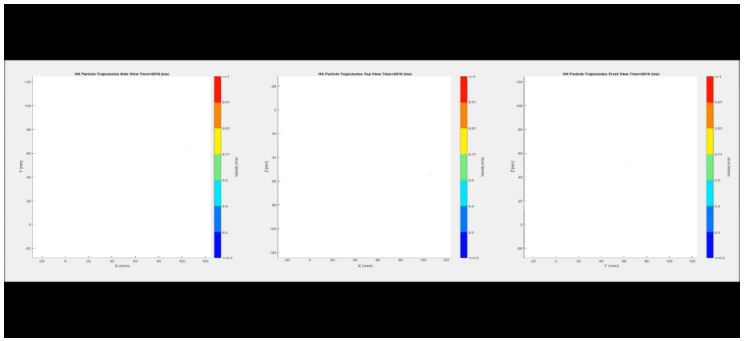






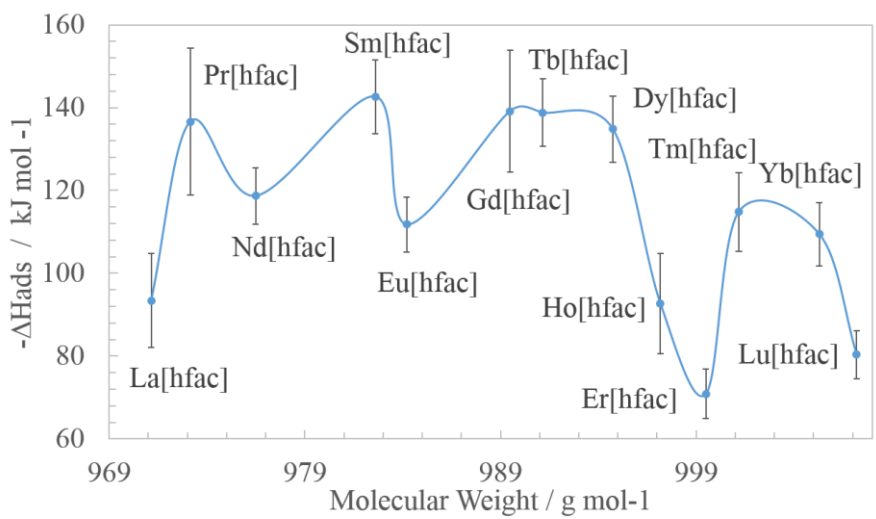


Time Resolved Trajectories

Thermal Analysis of Hfac complexes

Table 1. Thermodynamic results on Ln[hfac]$_4$ compounds

Compound	M_w (g mol^{-1})	*mp* (°C)†	Measured Range (°C)	$\Delta H_{sub} \pm \sigma$ (kJ mol^{-1})	ΔS_{sub} (J mol^{-1} K^{-1})	T_{sub} (°C)	$-\Delta H_{ads} \pm \sigma$ (kJ mol^{-1})‡	Decomposition Range (°C)		
								Onset	Peak	Endset
La[hfac]$_4$	971.15	140	110-130	119.9 ± 15.9	288.0	143	93.4 ± 11.3	165	195	213
Pr[hfac]$_4$	973.15	179	110-130	191.9 ± 27.1	466.4	138	136.6 ± 17.7	165	181	191
Nd[hfac]$_4$	976.48	173	120-140	161.9 ± 2.7	384.9	148	118.7 ± 6.8	161	176	192
Sm[hfac]$_4$	982.60	188	120-140	201.9 ± 8.7	483.2	145	142.6 ± 8.9	163	177	189
Eu[hfac]$_4$	984.20	175	120-140	150.4 ± 2.9	356.1	149	111.8 ± 6.7	176	192	200
Gd[hfac]$_4$	989.49	173	120-140	196.0 ± 21.5	468.9	145	139.1 ± 14.7	160	173	183
Tb[hfac]$_4$	991.17	193	120-140	195.4 ± 6.6	465.6	147	138.8 ± 8.2	175	197	210
Dy[hfac]$_4$	994.74	203	110-130	188.8 ± 6.4	458.2	139	134.8 ± 8.0	171	196	204
Ho[hfac]$_4$	997.17	220	130-150	118.7 ± 17.5	281.5	149	92.7 ± 12.1	174	193	200
Er[hfac]$_4$	999.50	221	110-130	82.3 ± 3.5	188.7	163	70.9 ± 6.0	168	188	194
Tm[hfac]$_4$	1001.17	202	110-130	155.5 ± 11.5	372.7	144	114.8 ± 9.5	165	185	194
Yb[hfac]$_4$	1005.29	214	110-130	146.6 ± 7.0	351.7	144	109.4 ± 7.6	164	185	193
Lu[hfac]$_4$	1007.21	217	120-140	98.0 ± 0.6	232.9	148	80.3 ± 5.8	159	173	181

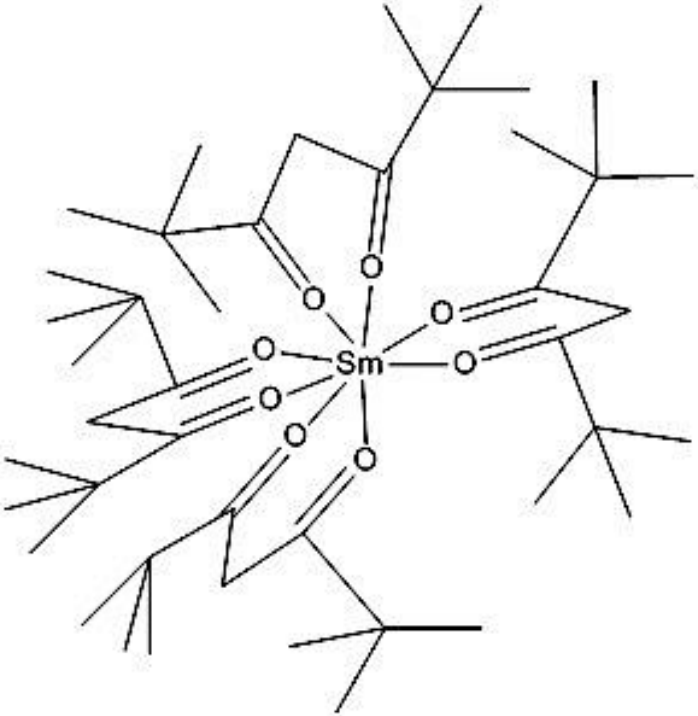


Synthesis of $Ln[hdpm]_x$ compounds

Ligand Preparation: $H(dpm)_{(aq)} + NaOH_{(aq)} \xrightarrow[\text{stirring, Ar}]{\text{50 \% EtOH}} Na(dpm)_{(aq)} + H_2O_{(aq)}$

Addition of Rare Earth: $X\ Na(dpm)_{(aq)} + LnCl_3 \xrightarrow[\text{stirring, 500 torr, Ar}]{\text{50\% EtOH}} [Ln(dpm)_x]_{(aq)} + NaCl_{(aq)}$

Compound	% Yield
Pr	72.1
Eu	80.7
Ho	82.4



Eisentraut, J. Am. Chem. Soc., 82(22), 1965

Thermal Analysis of Hfac complexes

- Thermogravimetric analysis using the isothermal Ashcroft method yields estimation of the sublimation enthalpy of the compounds

- Correlation of sublimation enthalpy to adsorption enthalpy:

$$-\Delta H_{ads} = (21.5 \pm 5.2) + (0.600 \pm 0.025)\ \Delta H_{sub}$$

- Adsorption enthalpy is one of the most important parameters in estimating experimental retention time of the compound on a chromatographic column

- Knowing the relative differences between adsorption enthalpy allows us to estimate the elution order of the compounds on a column, which is helpful when characterizing an unknown sample's composition via gas phase chromatography

- TGA also allows for analysis of the compound's metal content (purity), solvent impurities, atmospheric water uptake and the onset of decomposition.

National Nuclear Security Administration

THE UNIVERSITY OF TENNESSEE KNOXVILLE

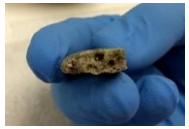
Dissolution Efforts

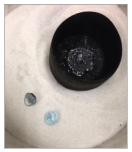
Methods / Samples	Eppich Method	Auxier Method	Lithium Method	Maxwell Method
Trinitite	Run 1 2 3	Run 1 2 3*	Run 1 2 3	Run 1 2 3
STF Gad Mod 1	Run 1 2 3	Run 1 2 3	Run 1 2 3	Run 1 2 3
NYC IND 1	Run 1 2 3	Run 1* 2 3	Run 1 2 3	Run 1 2 3
MAPEP MaS 32	Run 1 2* 3	Run 1 2 3	Run 1 2 3	Run 1 2 3

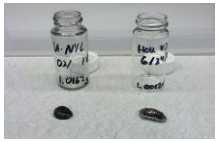
* Run was significantly inconsistent or failed

Samples Analyzed

- Trinitite
- STF using Gadget Mod 1 fuel debris
- Urban NYC using IND 1 fuel debris
- MAPEP MaS 32 (Prepared through melting procedure similar to STF)







Analysis

- Python Code used for comparison, GBC code is inadequate.
- Analyzes internal calibration standards to develop a new user defined calibration fit.
- Incorporates all mass spec data and can user define analytes in post process instead of prior to running samples.
- Final output is a user defined ideal mass spec output compared to an average from multiple runs.

Results

- Auxier Method is the fastest with the best yields for fissile materials and elements around daughter product masses
- Still not suitable for broad acceptance
- ICP-TOF-MS not suitable for these modifications to fusion methods
- No method with consistent yields across all elements
- MAPEP was not a suitable standard for comparison in this experiment

RADIOCHEMISTRY Center of Excellence

INSTITUTE FOR NUCLEAR SECURITY

The Fix: Quartz Coiling

- A quartz coil was designed to re-route nebulizer flow through an added heating element segment
- The argon gas is exposed to indirect heat at is spirals along the length of the heating element
- The heated nebulizer flow then surrounds the portion of the column extending into the mass spec

Total Output from the Center

- Publications
  - Total of 42 Conference Presentations
  - Total of 5 Master Thesis and 1 PhD Dissertation
  - Total of 7 Peer Reviewed Papers
- Patents
  - Total of 4 provisional patents
  - 1 Full Patent Awarded
- Students Supported

Synthetic Trinitite Results/Conclusions

- It is possible to produce melt glass that is similar to trinitite in:
  - Elemental Composition
  - Morphology
  - Radiological Signature
  - Chemical Behavior

- This melt glass can be used as a viable surrogate for radiochemistry/ nuclear forensic applications

Collaborators (Hall Group)

- Melt Glass
  - Joshua Molgaard (M.S. – now at USMA)
  - Andrew Giminaro, Jerrad Auxier, Jonathan Gill, CJ Oldham, Matthew Cook
- Advanced Separations
  - Daniel Hanson (now Ph.D. at SRNL)
  - Adam Stratz, Steven Jones (Bredesen Scholar)
  - UGS: Matthew Marsh (ACS Coryell Award Winner), Ashlyn Jones

Interdepartmental Collabotors

- UT Chemistry: Derek Cressy, Derek Mull, Dr. David Jenkins, Dr. Carlos Steren
- Materials Science Engineering: Dr. Stephen Young
- UT/ORNL Joint Institute for Computational Sciences: Dr. Deborah Penchoff

RCoE impact on the UT academic program

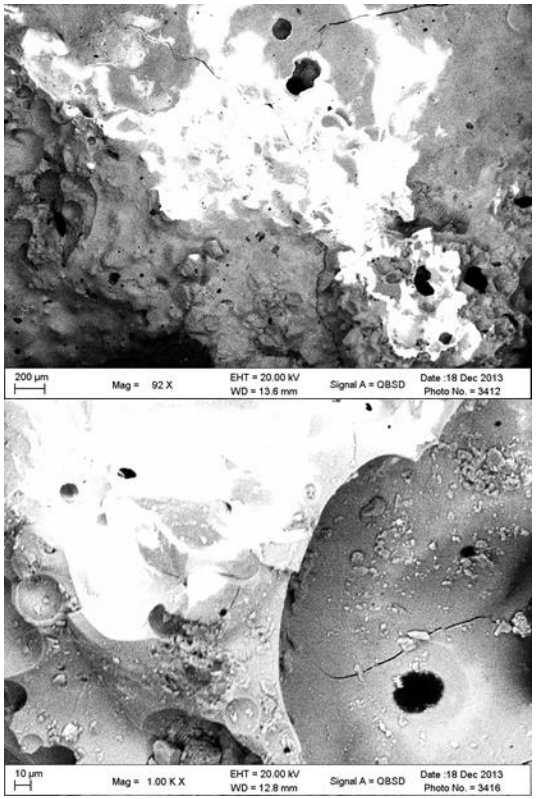
- Radiochemistry Certificate program
- Nuclear Engineering's Nuclear Security curricula
- New NE building programming

- Funding: U.S Dept. of Energy, National Nuclear Security Administration, Scientific Stewardship Academic Alliances Program
  - Special Thanks to Dr. Howard Hall and Dr. Lawrence Heilbronn

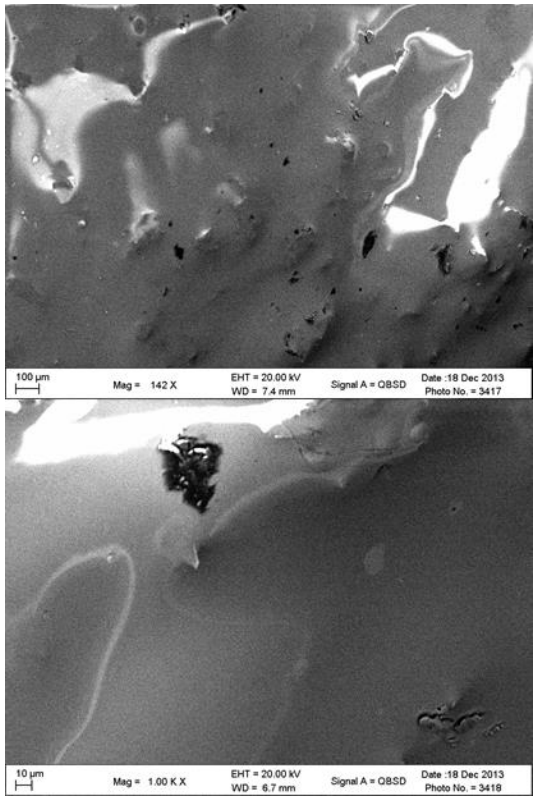
Synergistic Efforts

- Jonathan Gill (M.S. – now at BWXT in Lynchburg, VA) – developing novel fission materials detectors
- Edward T. Peskie (M.S. – Deployed at USMA) – helped to write a funded proposal for new pre-detonation signatures from DHS/DNDO
- Joshua Molgaard – (M.S. – Deployed at USMA) – helped to write a proposal between UT/ORNL.

SEM/EDS



Trinitite



Synthetic

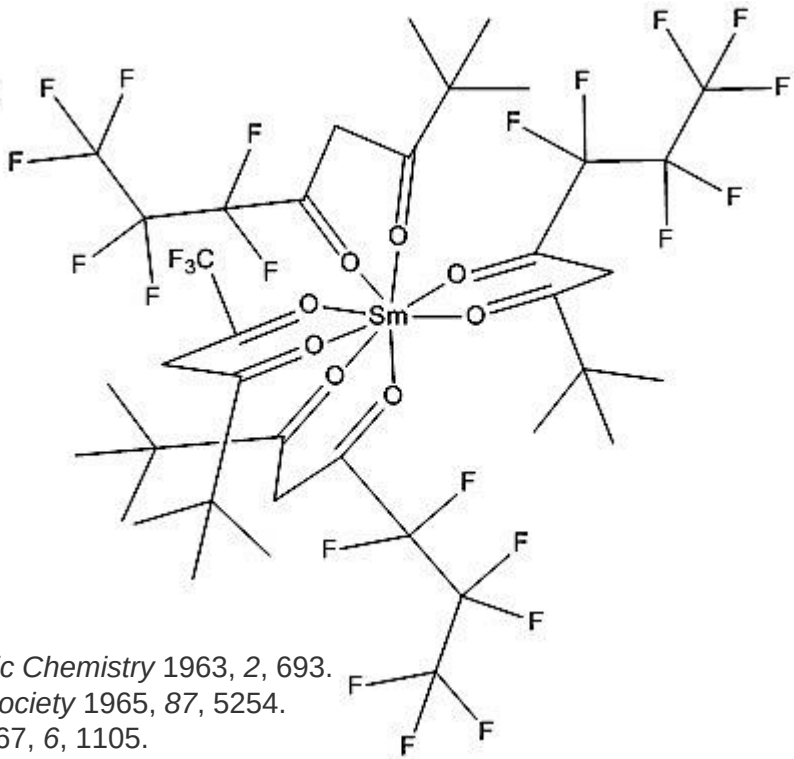
Synthesis of $Ln[hfod]_x$ compounds

Dissolution: $Ln_2O_{3(s)} + 6\ HCl \longrightarrow LnCl_{3(aq)} + 3\ H_2O_{(l)}$

Ligand Preparation: $NH_4OH_{(l)} + H_2fod_{(l)} \longrightarrow NH_4hfod_{(aq)} + H_2O_{(l)}$

Combination/ Extraction: $LnCl_{3(aq)} + 6\ NH_4hfod_{(aq)} \longrightarrow NH_4\ [Ln(hfod)_x]_{(org)} + 3\ NH_4Cl_{(aq)}$

Compound	% Yield
Nd	21.0-21.6
Sm	15.8-16.2
Dy	14.3-14.7



[1]Sievers, R. E.; Ponder, B. W.; Morris, M. L.; Moshier, R. W. *Inorganic Chemistry* 1963, *2*, 693.
[2]Eisentraut, K. J.; Sievers, R. E. *Journal of the American Chemical Society* 1965, *87*, 5254.
[3]Springer, C. S.; Meek, D. W.; Sievers, R. E. *Inorganic Chemistry* 1967, *6*, 1105.