ADVANCED REACTOR SAFEGUARDS & SECURITY

Process monitoring for MC&A: Optical spectroscopy

PRESENTED BY

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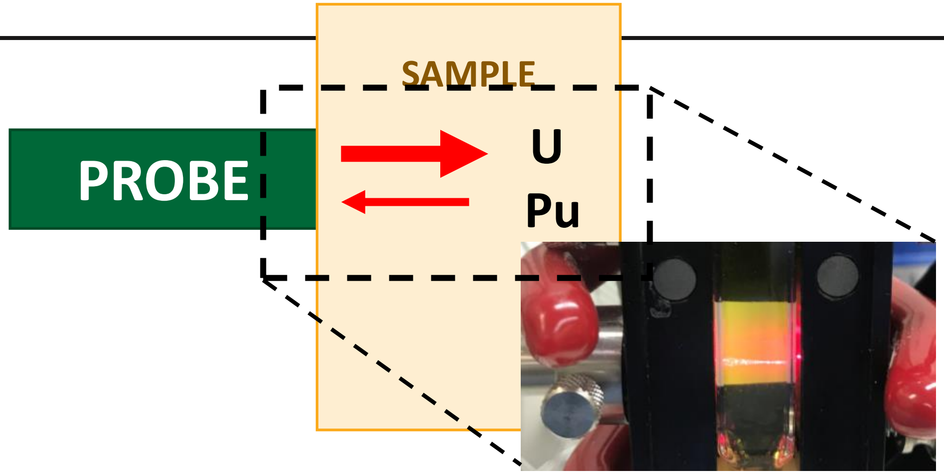
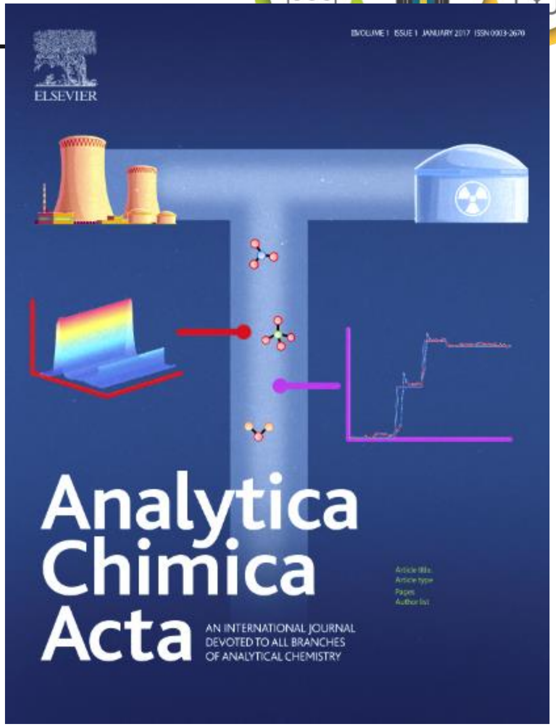
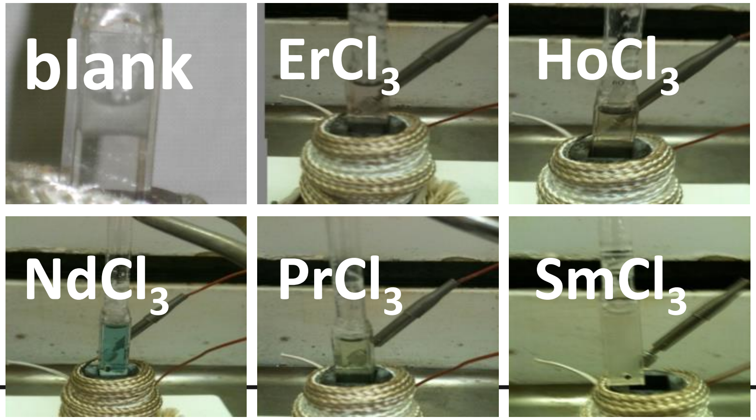
Common process monitoring goals in industry

- Fundamental characterization
  - Insight into system processes
- Design phase
  - Informed and optimized R&D
- Deployment phase
  - Process optimization
  - Process control
  - Material accounting

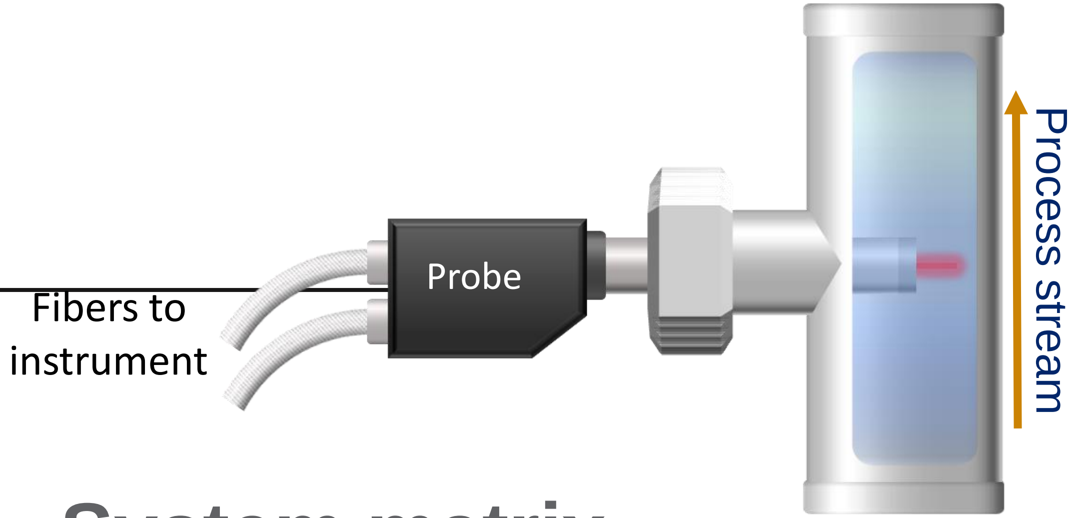






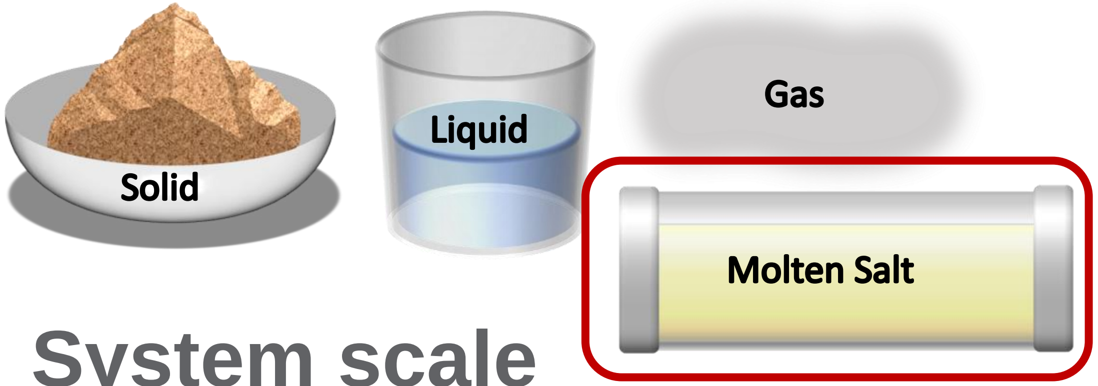
Tse, P., N.P. Bessen, S.A. Bryan, A. M. Lines, J.C. Shafer. *Analytica Chimica Acta*, 2020, 1107:1-13,

Chemical characterization: Optical spectroscopy



- Provides chemical information
  - Identification and quantification
  - Oxidation State
    - Essential information for control of systems
  - Molecular and elemental species
    - Essential information to control general system behavior (e.g., precipitation, species interaction)

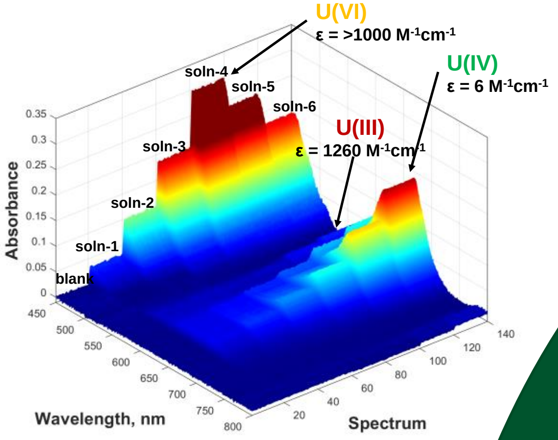
System matrix



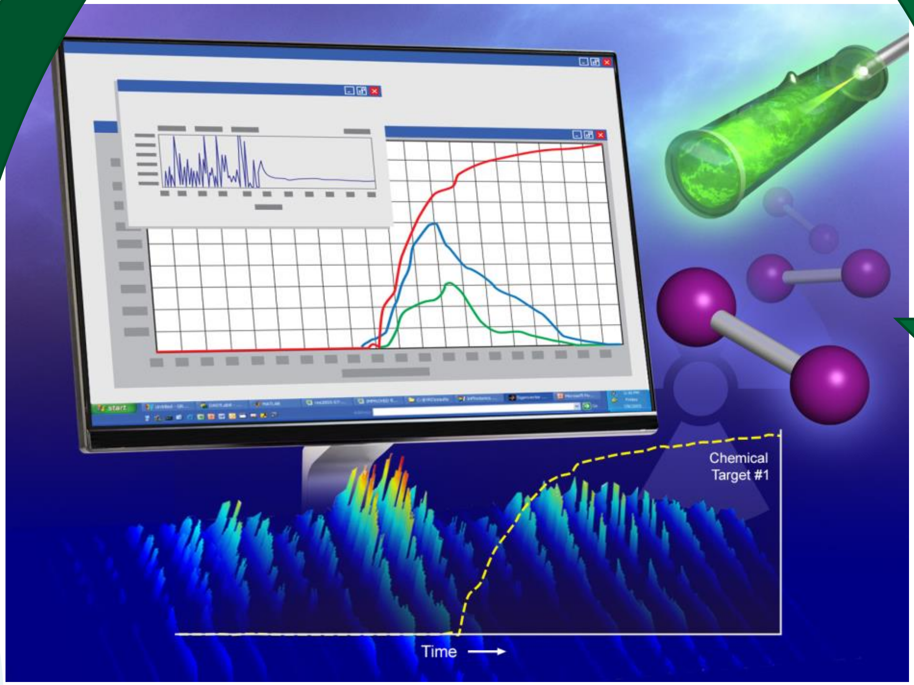
- Highly mature technology
- Simplistic integration
- Versatile
- **Real time insight into complex chemistry**

System scale

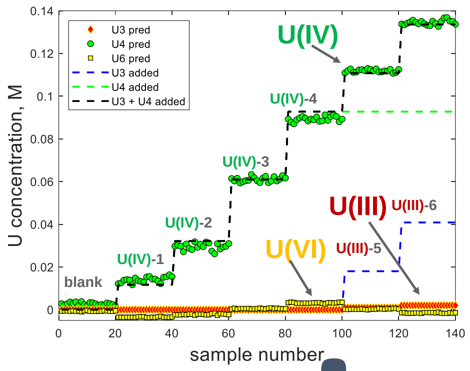
Chemometric Model Building



Data



Enabling researchers and operators to understand complex processes with *in situ* and real-time feedback on process conditions



Information

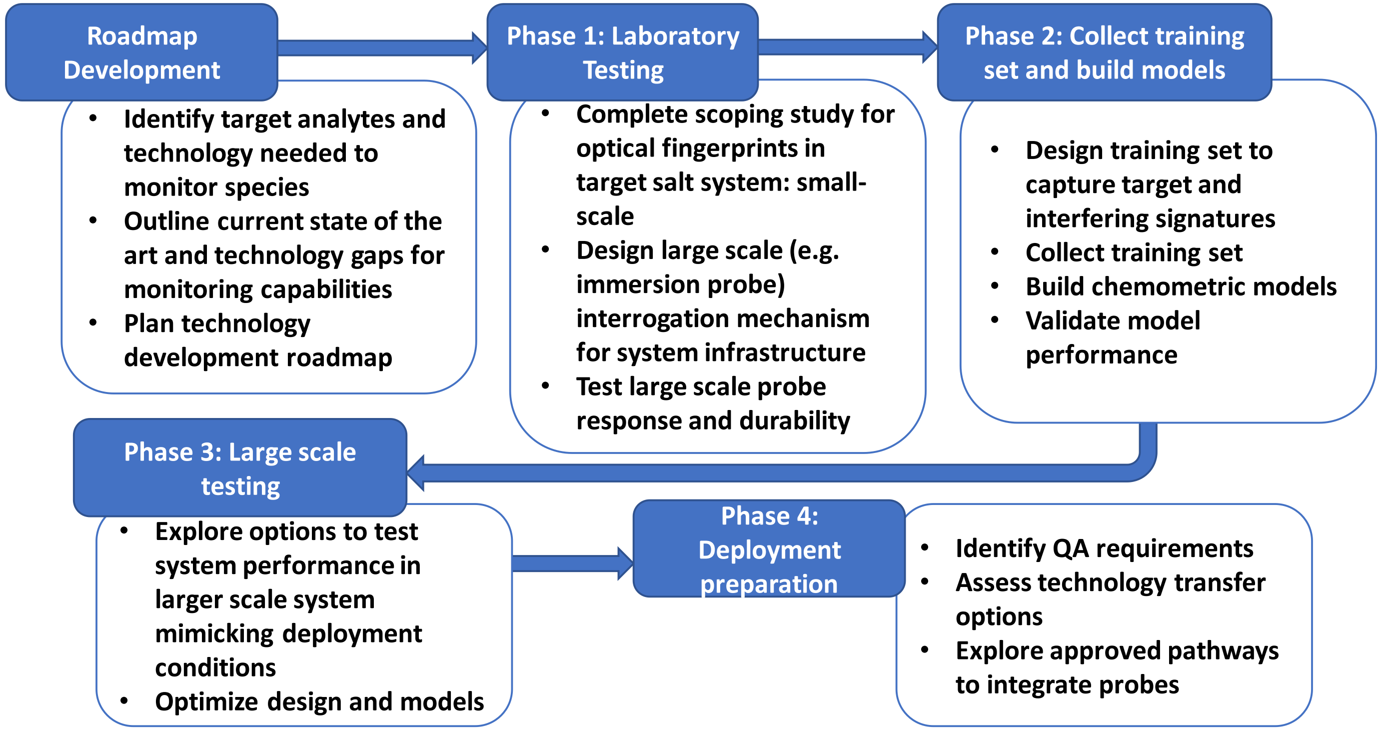
S. Branch, H. Felmy, A. Schafer Medina, S. Bryan, A. Lines. *Industrial & Engineering Chemistry Research* 2023 62 (37), 14901-14909 DOI: 10.1021/acs.iecr.3c02005

Needed area of development

- Demonstrate ability to provide needed information and measurement uncertainty for actinides and other key targets without placing undue burden on the MSR system

- Develop probes that can be leveraged in various deployment scenarios

- Roadmap is used as guide; current path is advancing beyond



FY24 Activities and milestones

- Modification of current PNNL small-scale setup to more effectively test optical sensor materials
- Proof-of-principle demonstration of TRU measurement (e.g. Pu)
- Collaborating with other gamma spectroscopists to apply chemometric analysis of complex gamma count datasets

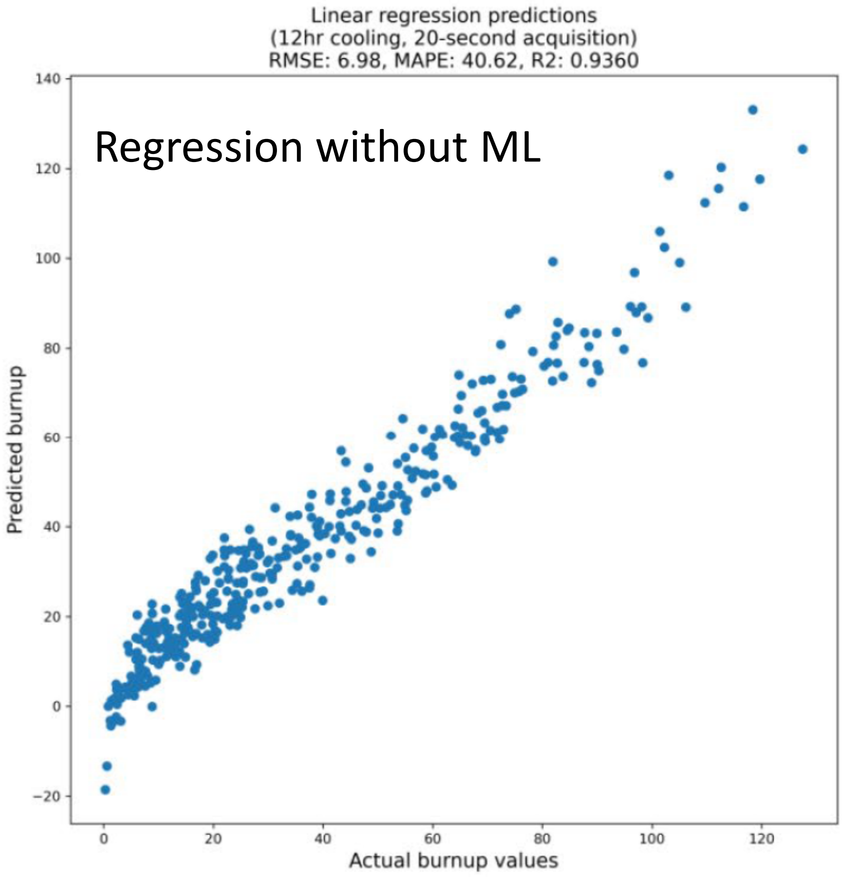
Milestone	Description	Due date
M4RS-24PN0401061	Letter report to NTD on application of chemometric approaches to gamma data	30 Sept 2024
M3RS-24PN0401063	Letter report to NTD highlighting progress on optical testing and TRU measurement	30 Sept 2024
M3RS-24PN0401064	Memo to NTD highlighting progress on advance testing of TRU target	30 Sept 2024

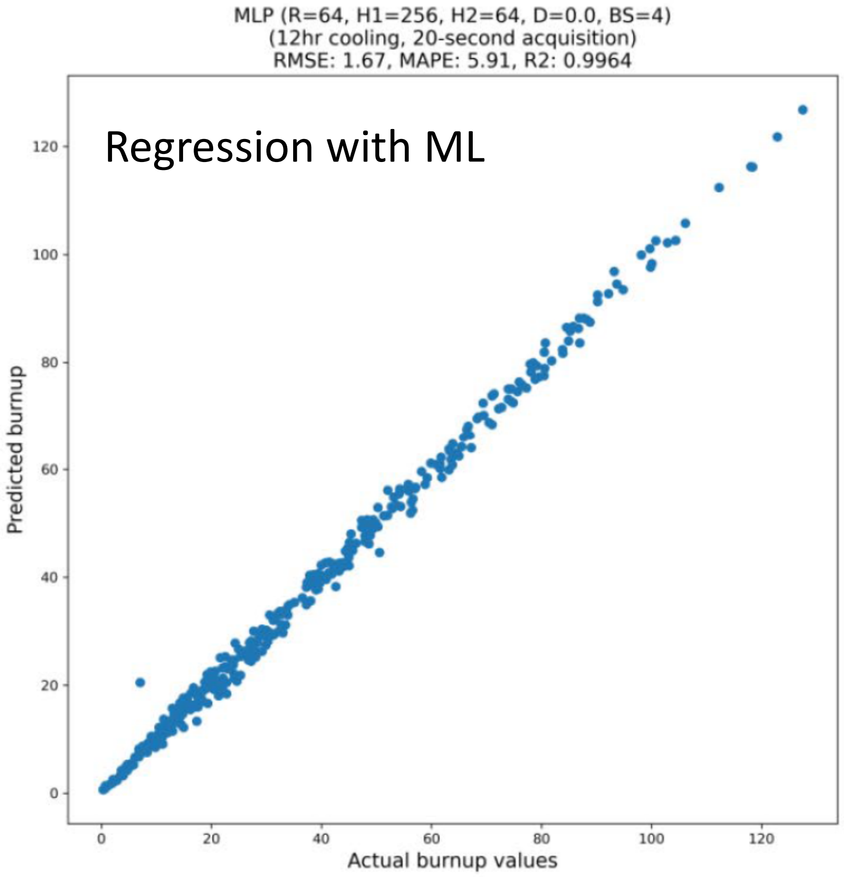
Application of chemometric modeling to gamma spectroscopy

- Overview: Chemometrics allows us to add an autonomous component to data analysis while also improving flexibility to accurately handle and analyze highly complex data exhibiting multiple interfering signals.
- Goal: Explore applicability of chemometric analysis to complex radiometric data sets
  - Utilize multivariate techniques
    - Principal Component Analysis (PCA) pattern recognition and group classification
    - Principal Component Regression (PCR) for quantitative prediction
  - Opportunity to collaborate with other PNNL ventures and other national lab partners

Precedence of machine learning (ML) application to gamma spectroscopy (Cui et al, 2021)

- Gamma spectroscopy has been used for estimation of burnup measurement
  - Machine learning approaches used to lower the uncertainty of the burnup estimate for short-cooled pebbles

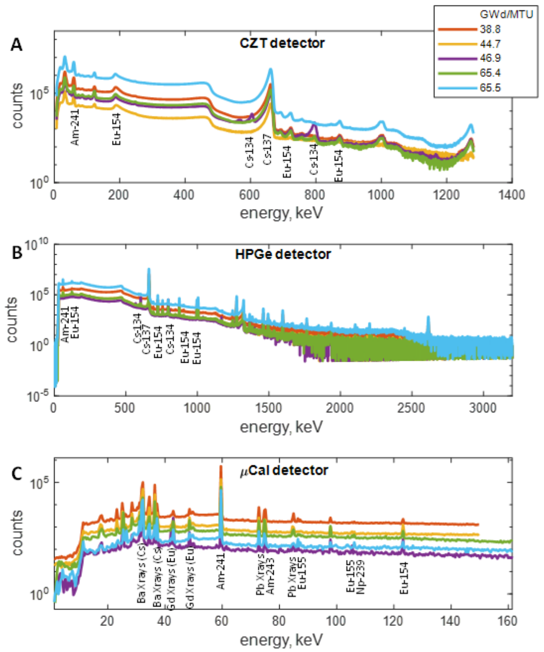




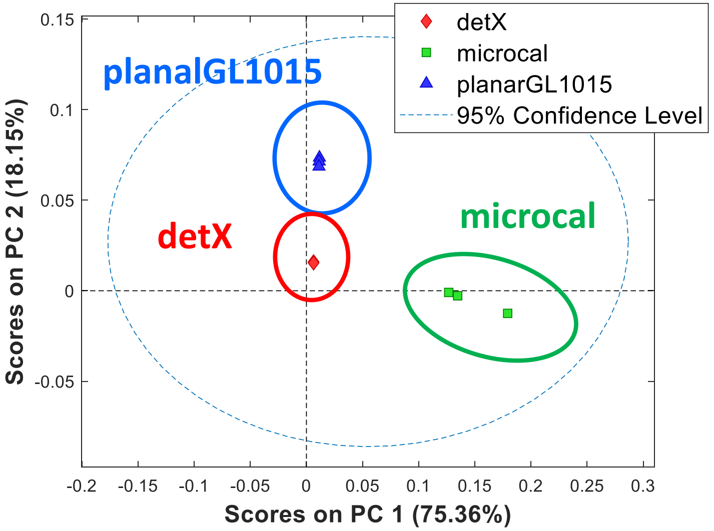
Y. Cui et al, “Use Machine Learning to Improve Burnup Measurement in Pebble Bed Reactors,” BNL-222200-2021-FORE, Brookhaven National Laboratory (September 2021).

Summary of FY23 application of chemometric analysis to gamma spectroscopy

- Demonstrated ability to use PCA to differentiate between
  - Detector type
  - Detection time
  - Decay of single isotope sample
- PCR to 9 short-lived activation products
  - Mixed activation products of Pu-239 activation measured on HGPe detector over 3 hours
- Regression analysis of decay of single sample with limited analytes



PCA



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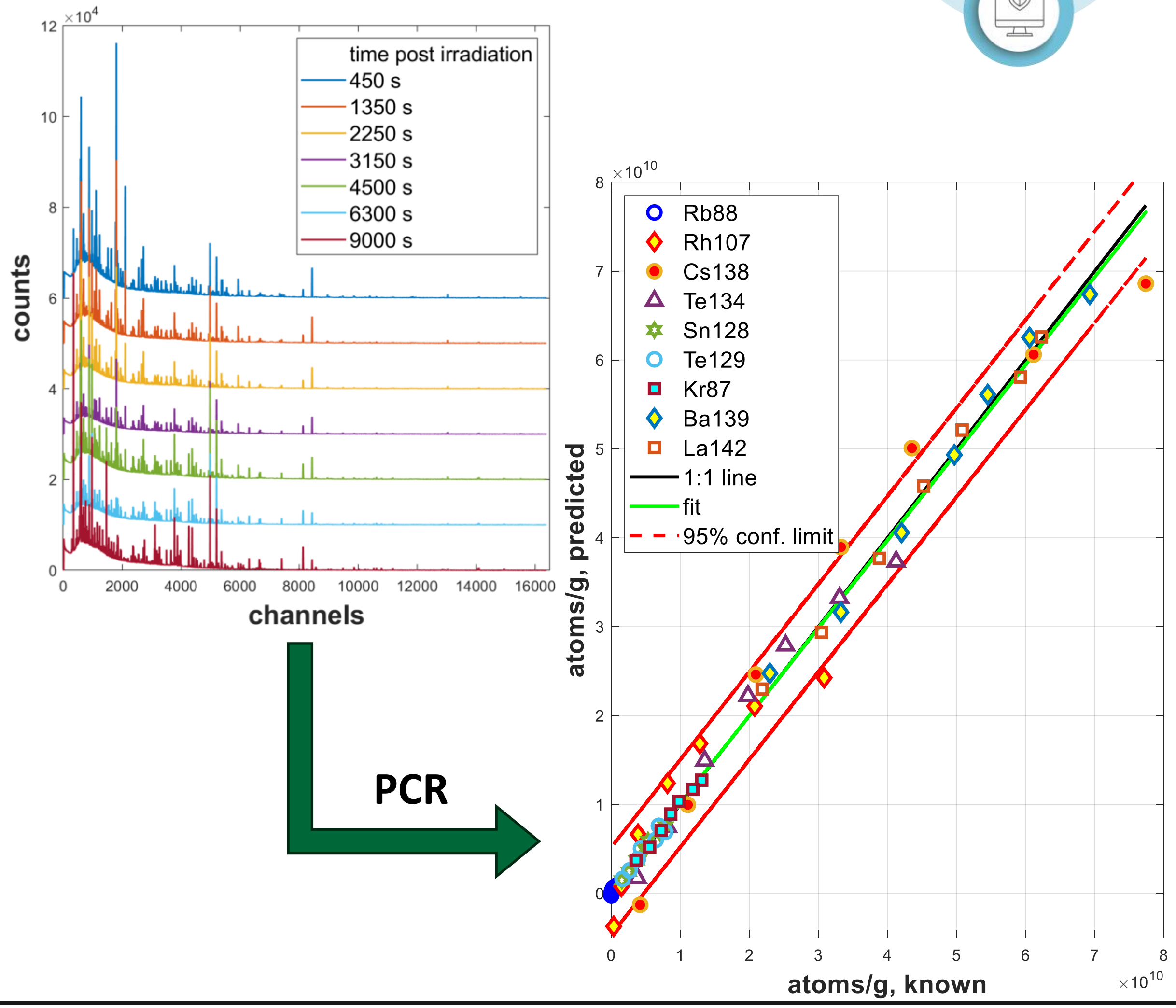
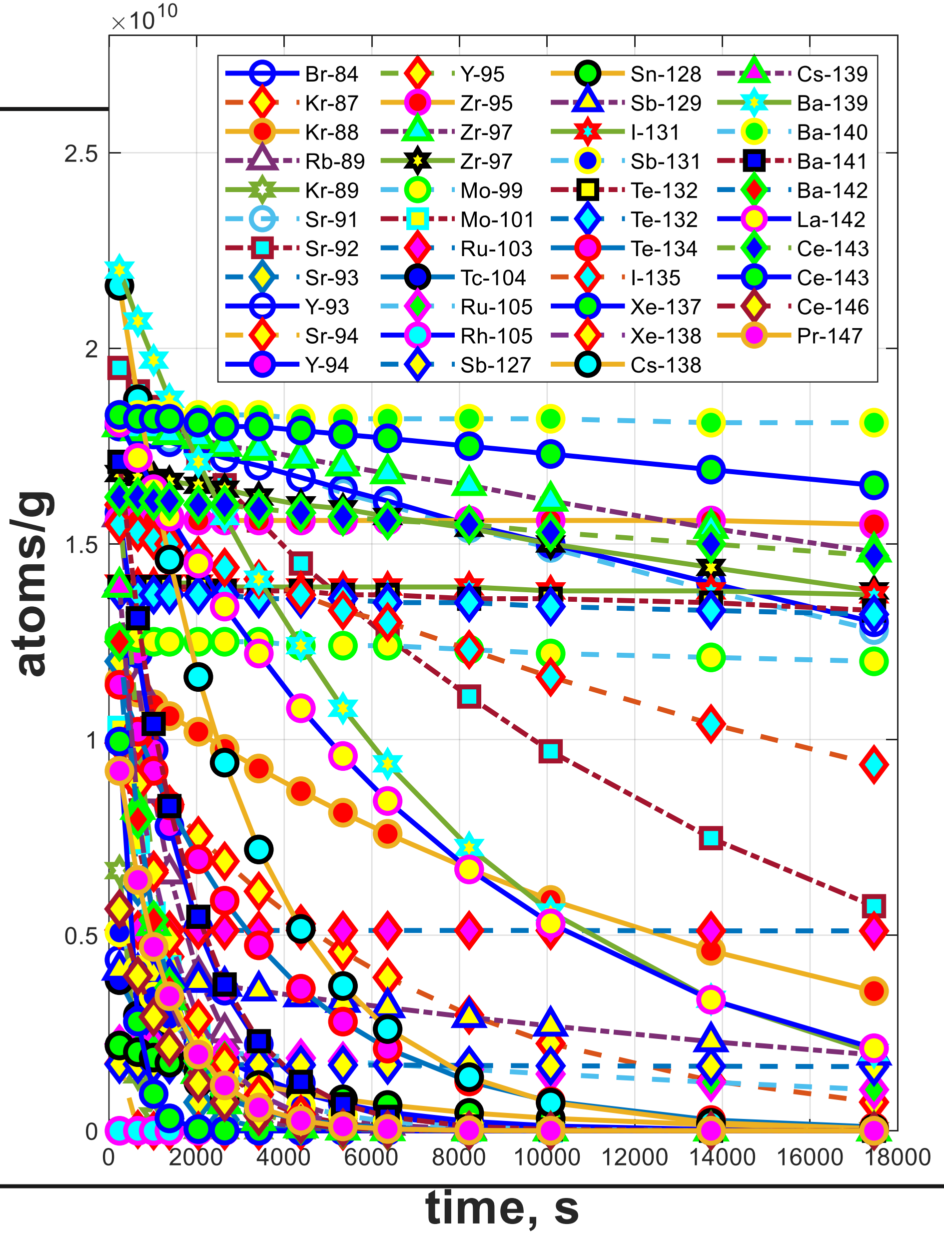


Application of chemometric modeling to extended data set: FY24 progress

- Milestone M4RS-24PN0401061: ON TRACK
- Data set has increased complexity from FY23 data
  - Neutron pulse of U-233 sample
  - Increased number of decay analytes
- Involves building out Y blocks of concentrations or ratios of isotopes within measured samples
- Special thanks to Bruce Pierson, Dana Arbova and Erin Morrison, and Erin Good (PNNL) for dataset[1]



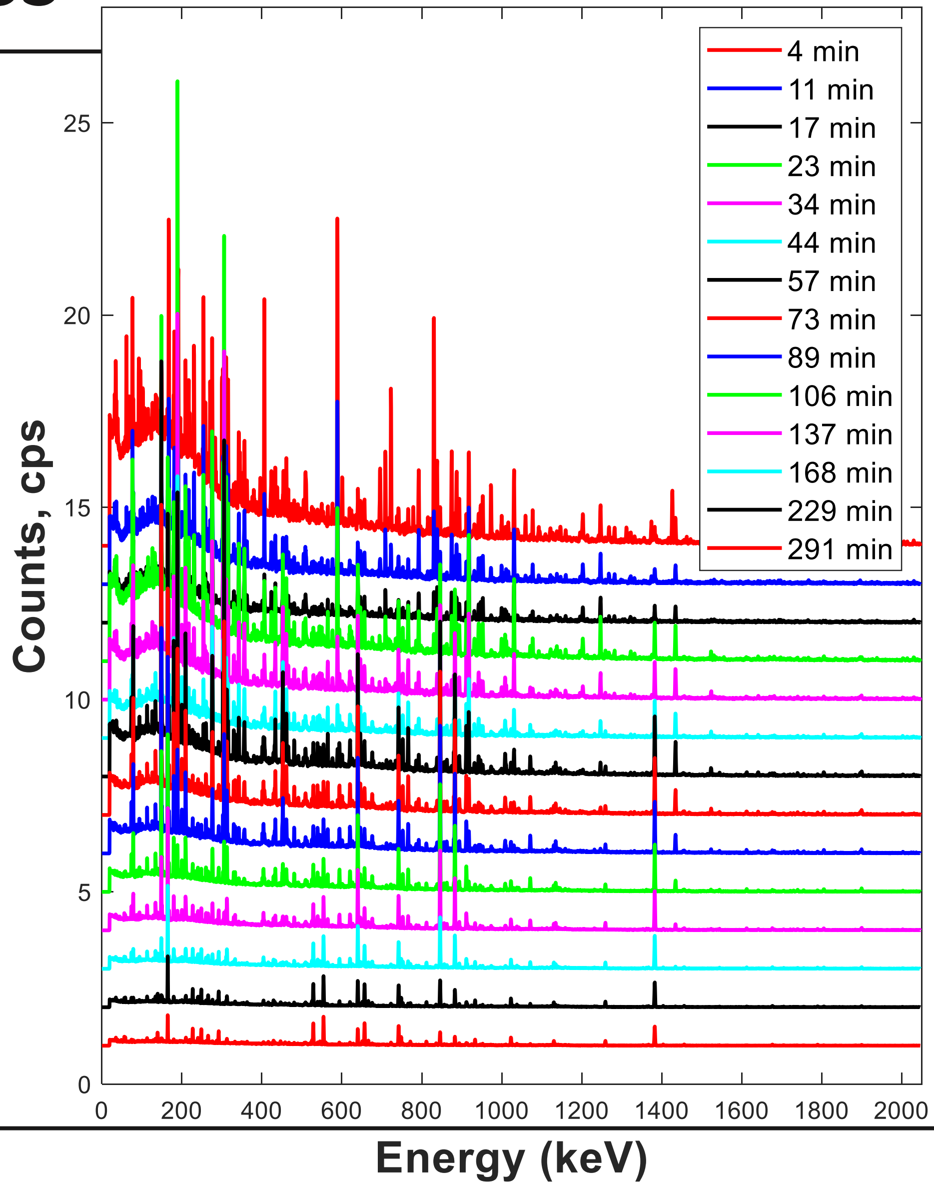
1. *J Radioanal Nucl Chem* **(2015)** 306:79–91 Cumulative fission yields of short-lived isotopes under natural abundance-boron-carbide-moderated neutron spectrum

Application of chemometric modeling to extended data set: FY24 progress

- Fission products of U-233 neutron pulse activation
  - Data from *J. Radioanal. Nucl. Chem* (2015) database[1]

- Spectra show high complexity and overlap of many signals

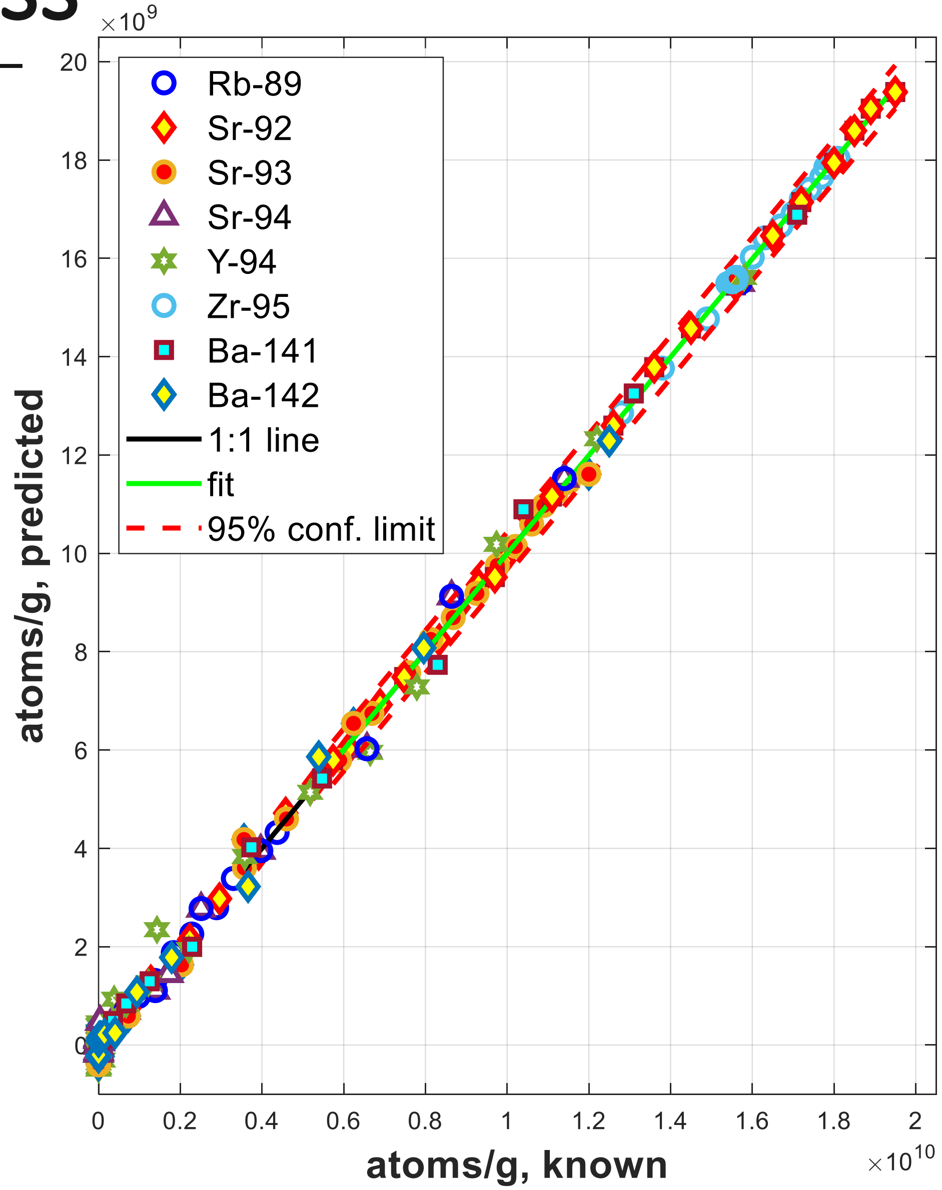
- Spectra paired with concentration (atoms/g) of known fission products can be used as a basis for regression models



1. *J Radioanal Nucl Chem* **(2015)** 306:79–91. Cumulative fission yields of short-lived isotopes under natural abundance-boron-carbide-moderated neutron spectrum

Application of chemometric modeling to extended data set: FY24 progress

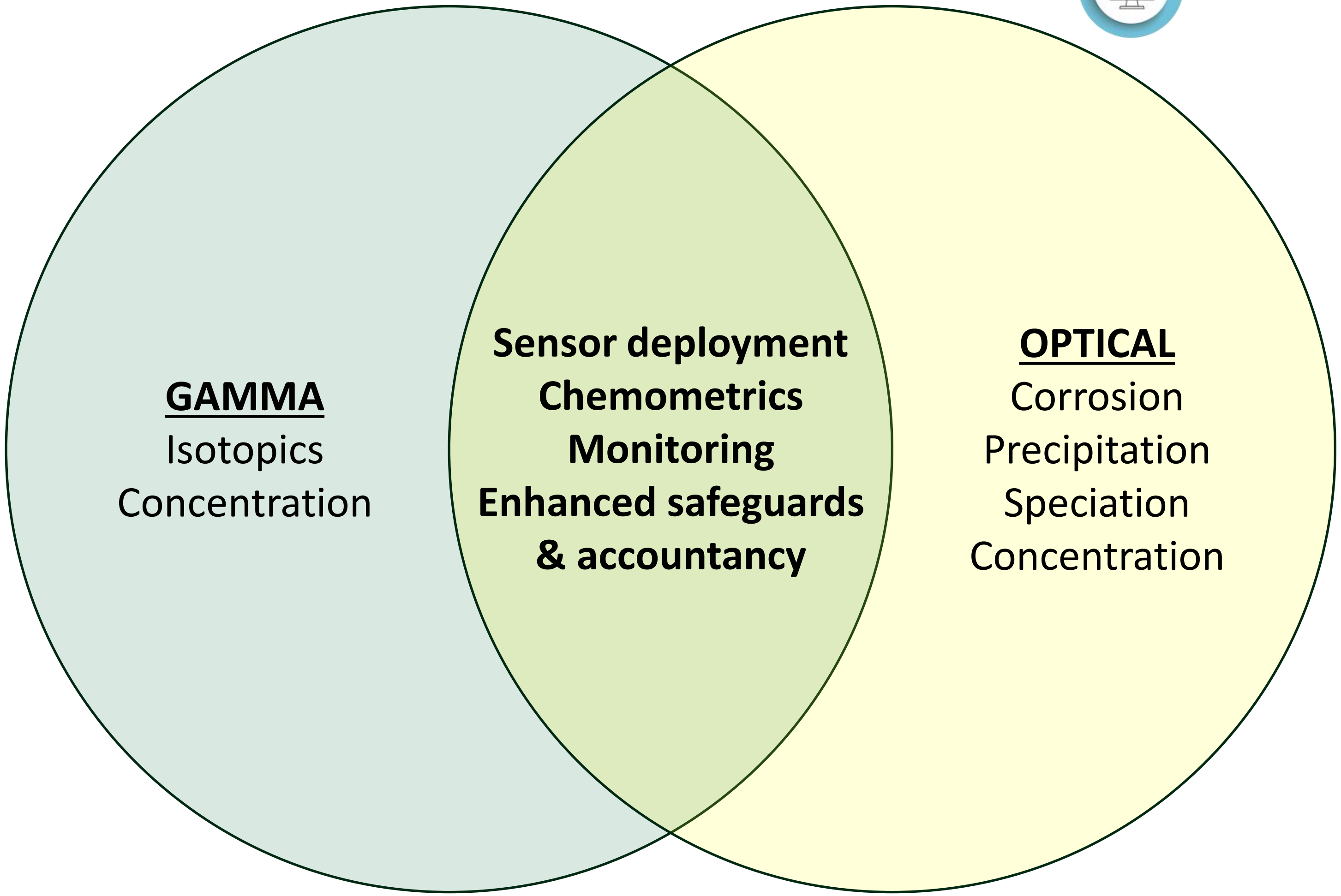
- Principal component regression (PCR) model of 8 fission products of U-233 activation
- Next steps:
  - Adding in all fission products to regression model
  - Involves building out Y blocks of concentrations or ratios of isotopes within measured samples
- Currently working on additional datasets:
  - U-235
  - U-238
  - Np-237
  - Pu-239
- Manuscript in progress



Combining worlds

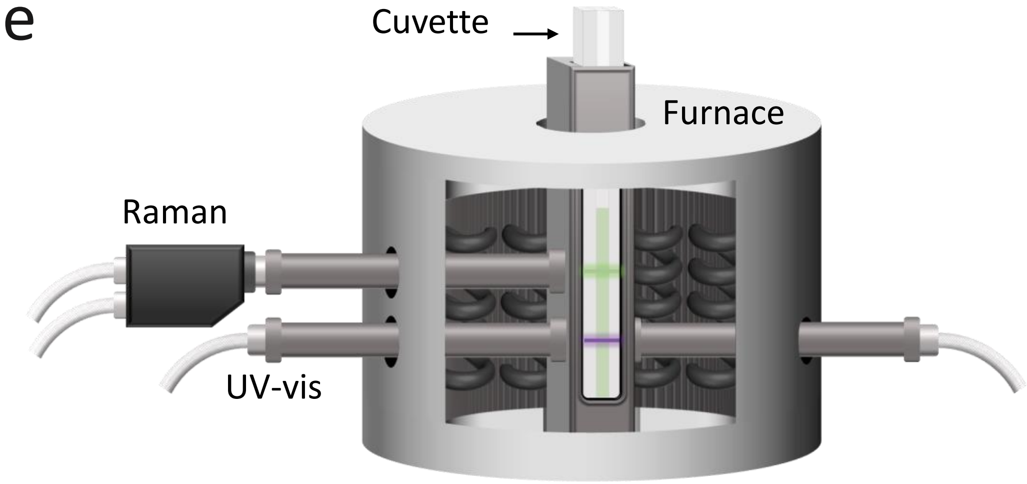
- Opportunities to combine optical measurement with gamma spectroscopy
  - Leverage sensors and data fusion

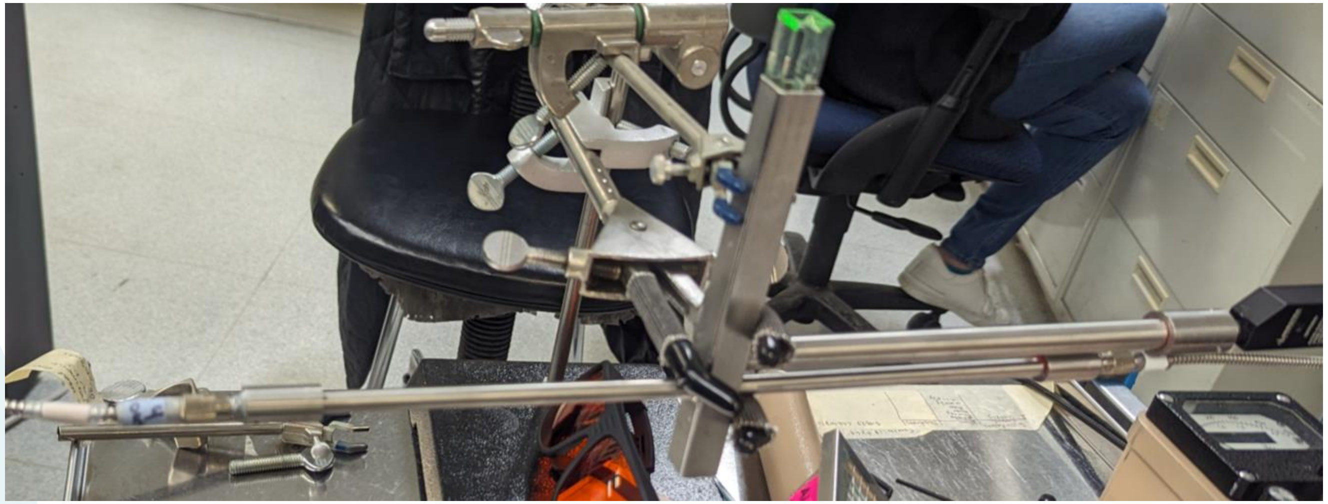
- Combining both can provide comprehensive insight into the chemical and isotopics of MSR behavior



Advancement of optical testing

- Updated small-scale furnace components
  - Focal length of cell holder components
  - Modified probe body for modularity
  - Received new material cuvette
- **Expansion into actinides**





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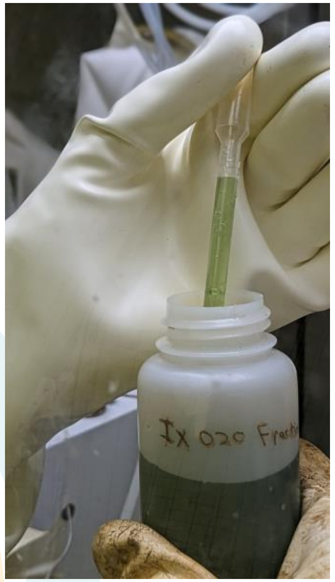
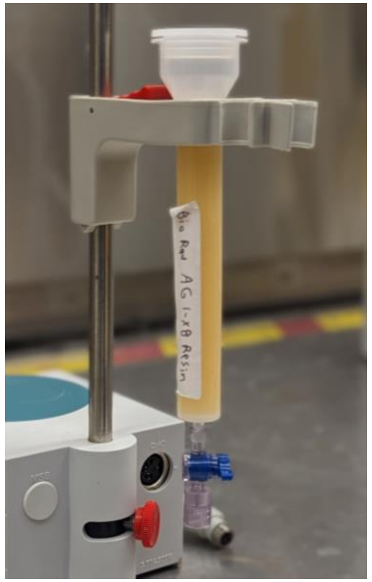
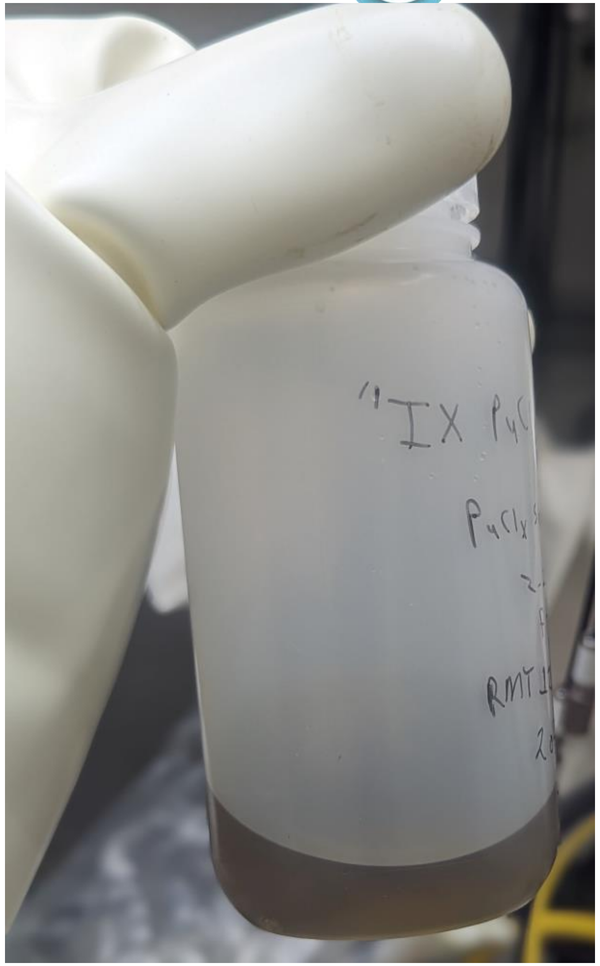
TRU target: Pu chloride preparation

- Received as a ~1 g Pu in HNO_3
    - ~94% Pu(IV) and ~6% Pu(VI)
- Adjusted to Pu(IV) w/ H_2O_2 and $Na(NO_2)_2$
- Ion exchange to convert chloride form
    - ~5 BV elution with 2 M HCl

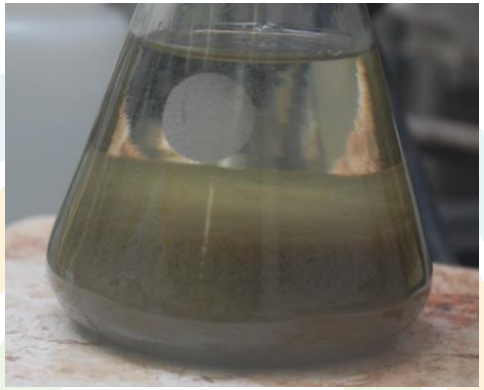


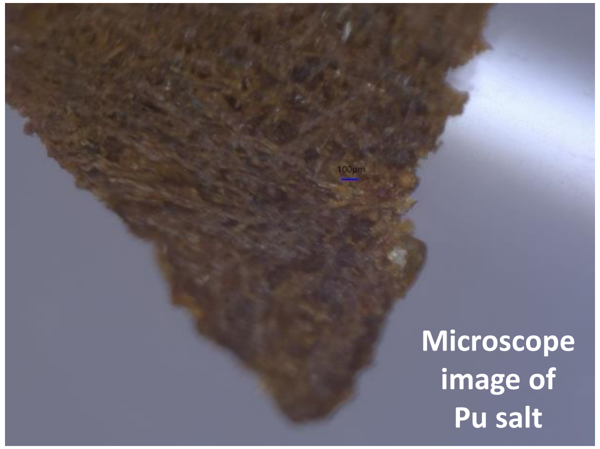




Pu chloride preparation

- Converted to $Pu(OH)_4$ with NaOH
- Co-precipitation with NaCl followed by drying on hot plate with distillation trap
- Recovered light brown solids consistent with Pu(IV)
  - Spectroscopy confirmed 15-20% Pu(III) and 80-85% Pu(IV)

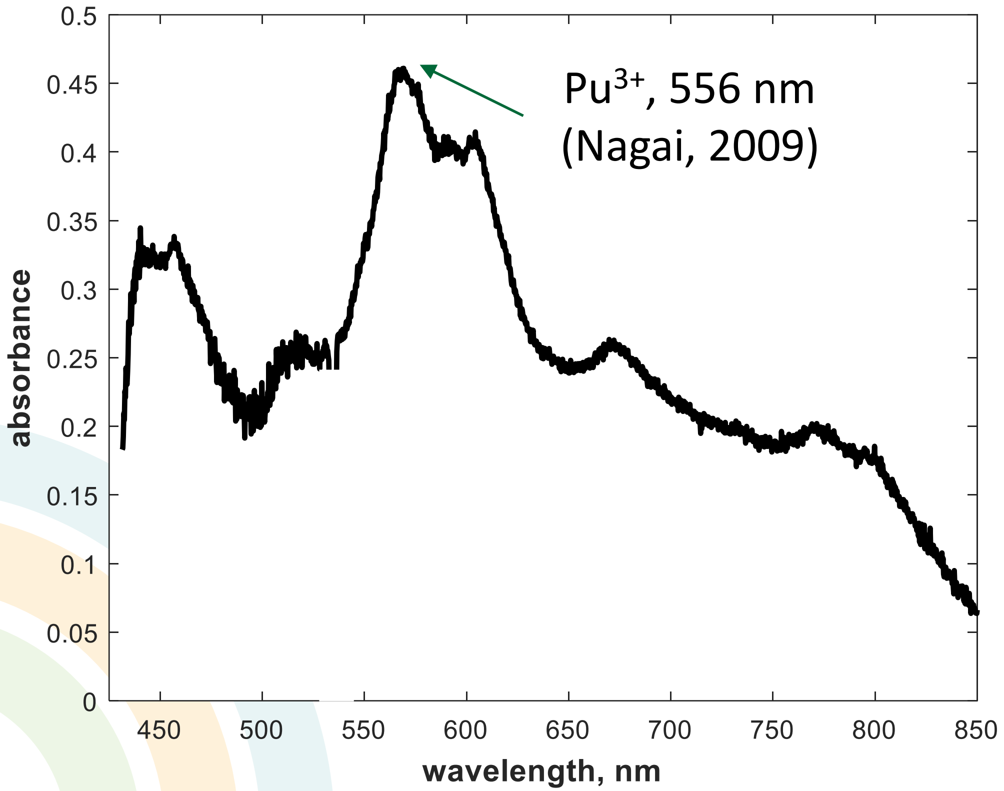


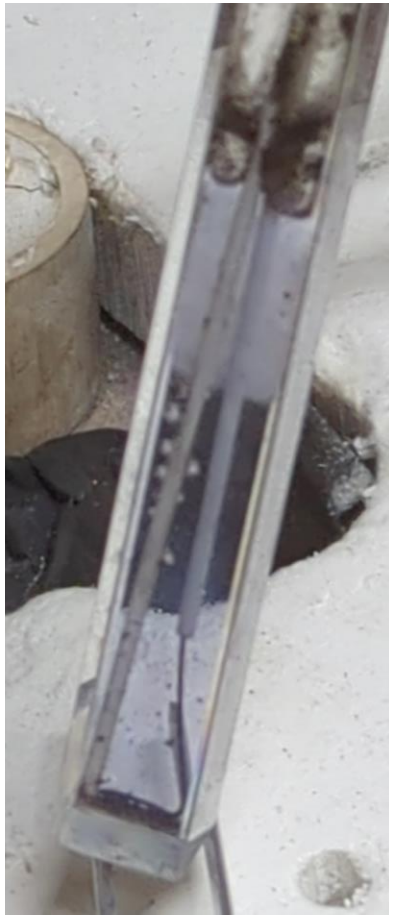


Microscope image of Pu salt

Initial Pu characterization

- Pu in NaCl-$MgCl_2$, 550 °C





Pu melt with mixed analytes

- Pu + other analytes in NaCl-$MgCl_2$, 550 °C
- Observed suspended precipitates

Analyte	Max wt%
Pu	0.448
U	0.352
Nd	0.256
Co	0.164

Pu

Pu + U

Pu + U + Nd

Pu + U + Nd + Co

FY24 Accomplishments

- Continue exploration of chemometrics application to radiometric data
  - Includes expanding sets into multi-analyte systems and building regression models
  - Milestone M4RS-24PN0401061: ON TRACK

- Advancement of optical testing system
  - Testing robust optical interrogation hardware for more accurate data sets
  - Milestone M3RS-24PN0401063: ON TRACK

- Expansion of optical data sets and testing/building more advanced chemometric models
  - Increasing chemical complexity (e.g. fission products, corrosion products, TRU species)
  - Milestone M3RS-24PN0401064: ON TRACK

Path forward

1. Continue building optical libraries, expansion of complex chemometric models, and advancement of instrumentation
   a. High-resolution fingerprints of target species (Xe arc lamp)
   b. Extend beyond UV-vis (e.g. NIR)
   c. Expand into other eutectic salts of industrial interest

2. Sensor fusion of optical and gamma spectra allows for the ability to provide comprehensive insight into radioactive decay/chemical composition through chemometric analysis

Acknowledgements

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Nicole Hege (CSM)
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Andrew Clifford
Alyssa Espley

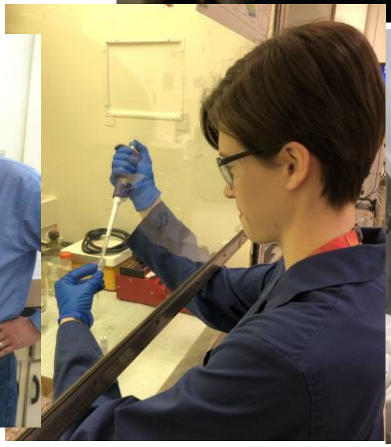
U.S. DOE NE, ARSS campaign











Thank you