ADVANCED REACTOR SAFEGUARDS

Process monitoring for MC&A: Optical spectroscopy

PRESENTED BY

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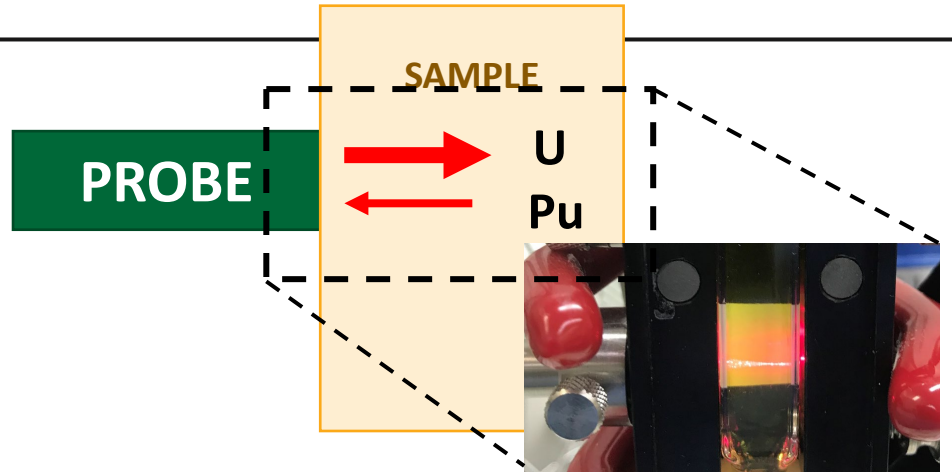
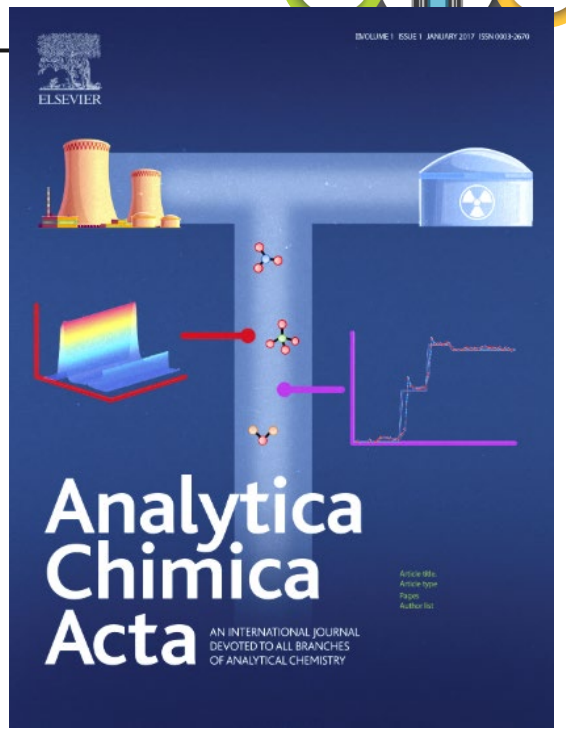
PNNL-SA-191977

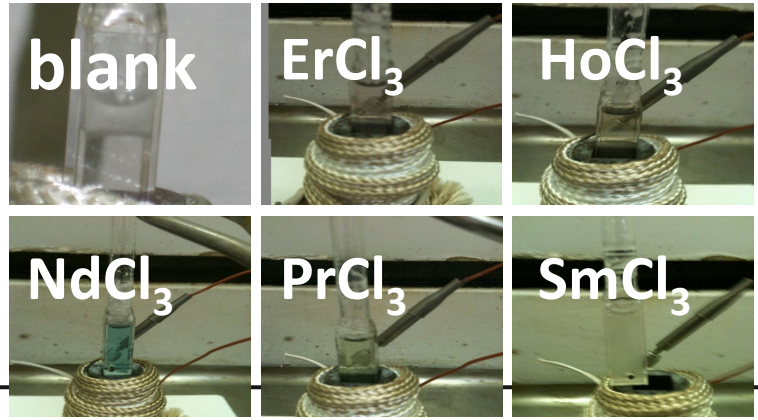
Sandia National Laboratories | U.S. DEPARTMENT OF ENERGY

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



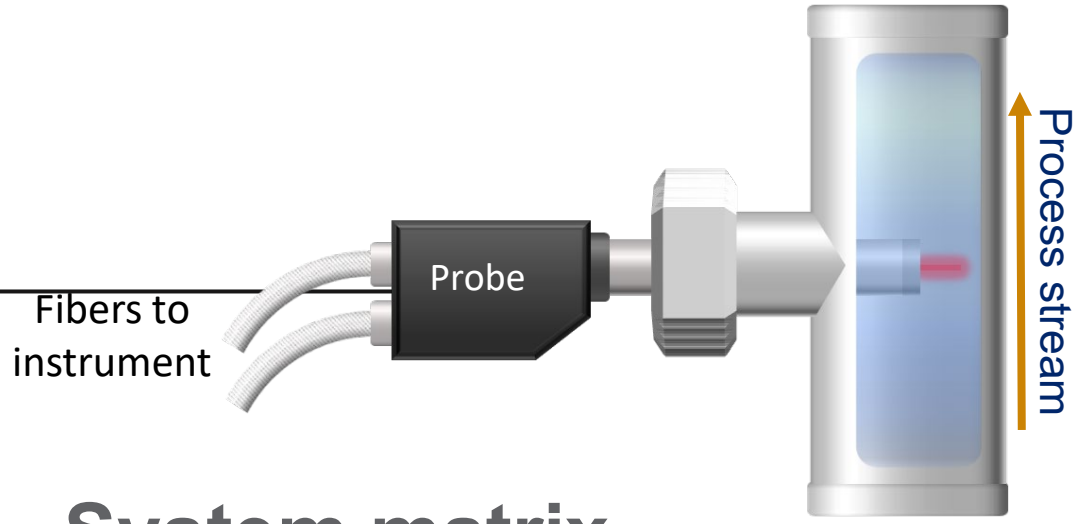




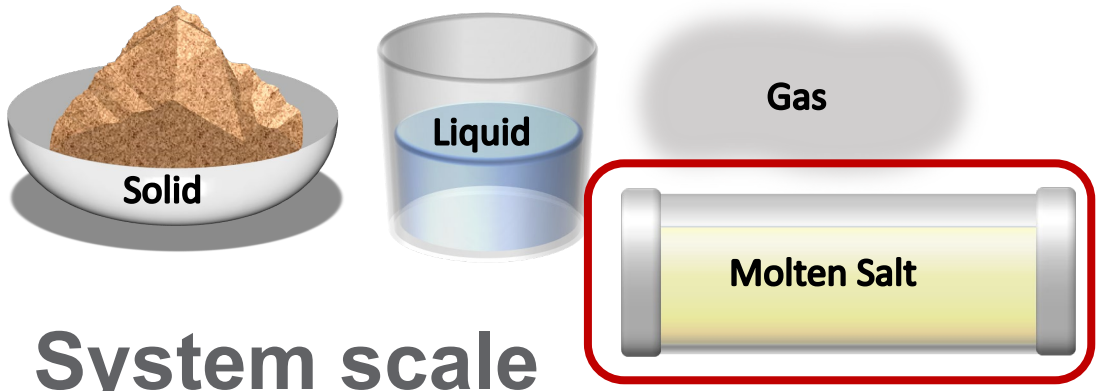
Tse, P., N.P. Bessen, S.A. Bryan, A. M. Lines, J.C. Shafer. "Review of On-line and Near Real Time Spectroscopic Monitoring of Processes Relevant to Nuclear Material Management" ***Analytica Chimica Acta***, 2020, 1107:1-13,

Chemical characterization: Optical spectroscopy

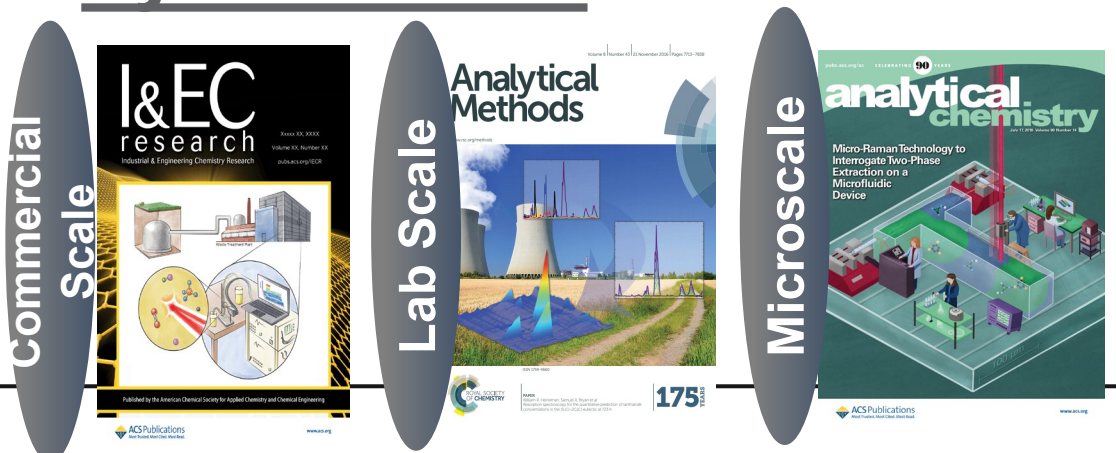
- Provides chemical information
  - Identification and quantification
  - Oxidation State
    - Essential information for control of systems
  - Molecular and elemental species
    - Essential information to control general system behavior (e.g., precipitation, species interaction)
- Highly mature technology
- Simplistic integration
- Versatile
- **Real time insight into complex chemistry**



System matrix

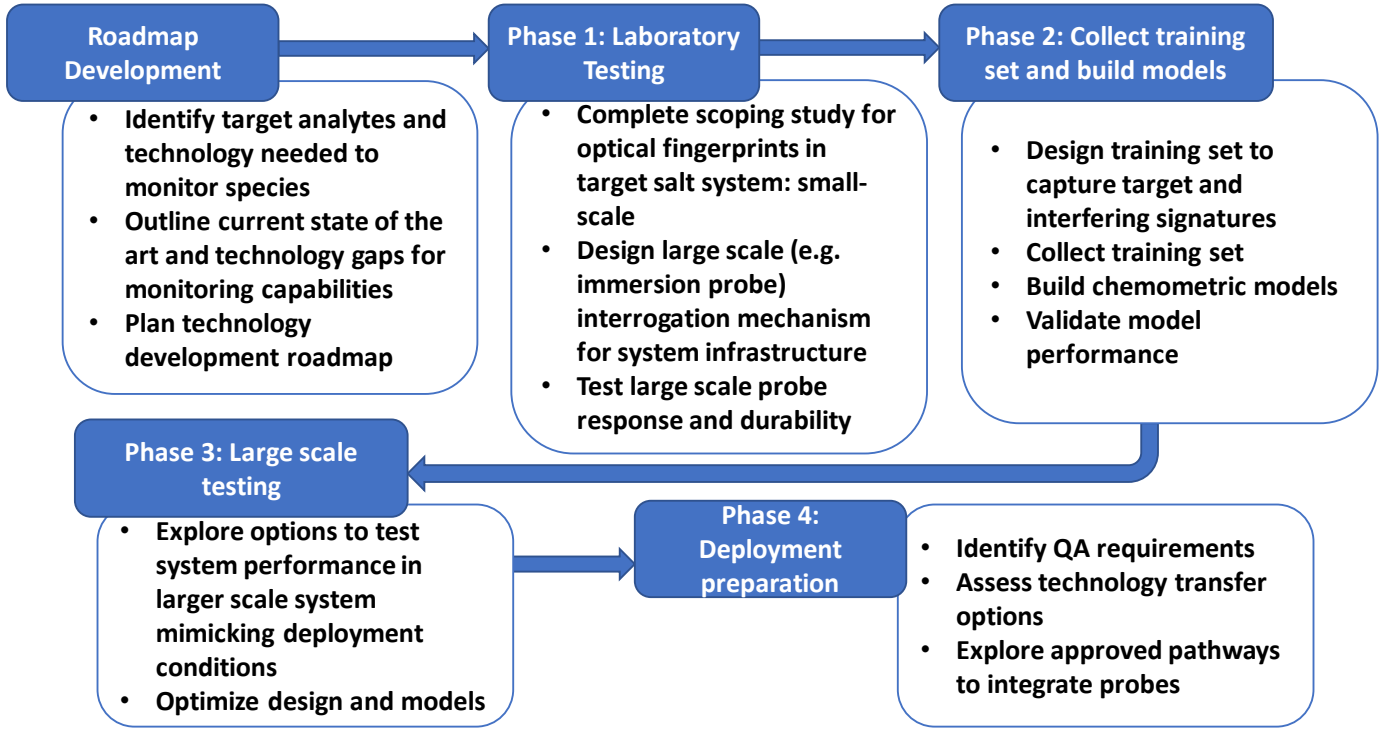


System scale

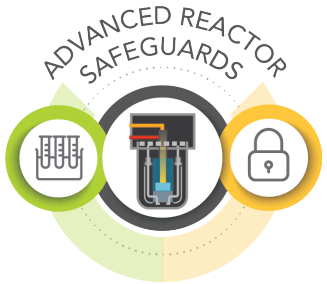


Needed area of development

- 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



FY23 Activities and milestones



- Collaborating with other national lab partners (e.g. LANL) to demonstrate proof of principle chemometric analysis of gamma count data
- Collaborate with TerraPower to design and build optical sensor flow cell for integration into microloop
- Test application of optical techniques to advanced salt systems

Milestone	Description	Due date	Date completed
M3RS-23PN0401053	Memo on completion of design of flow cell for microloop	31 Mar 2023	23 Mar 2023
M4RS-23PN0401054	Letter report to NTD highlighting progress on advanced testing of optical systems	30 Sept 2023	15 Sept 2023
M4RS-23PN0401051	Letter report on application of chemometric approaches to gamma data	30 Sept 2023	30 Aug 2023

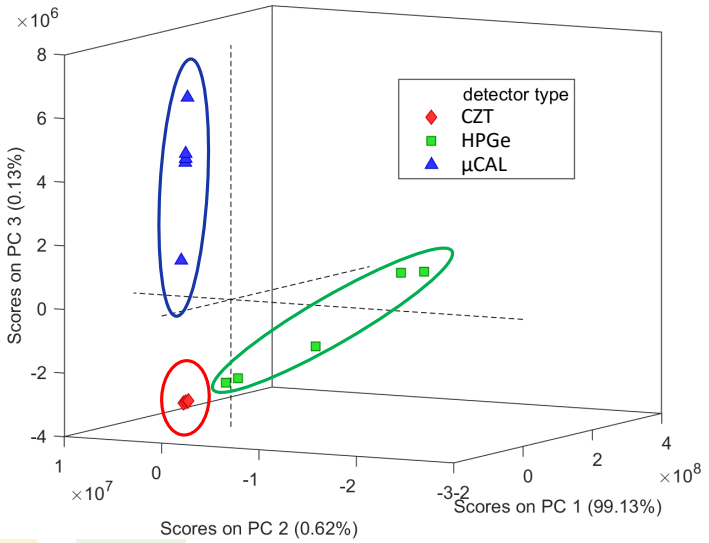
Application of chemometric modeling to gamma spectroscopy

- 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

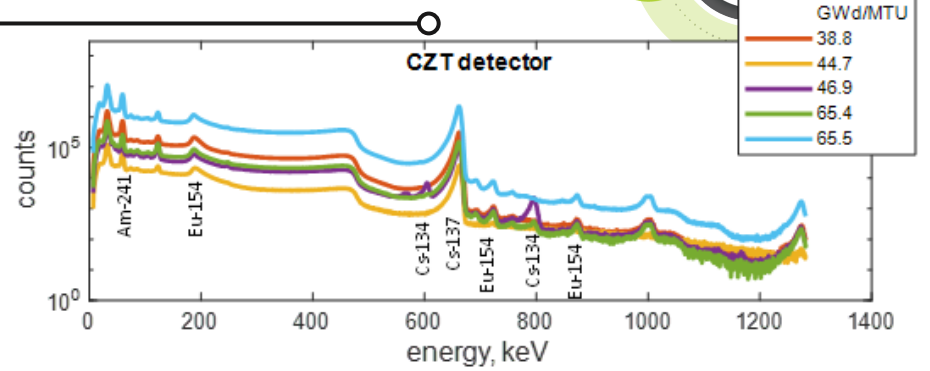
Radiometric data used for PCA

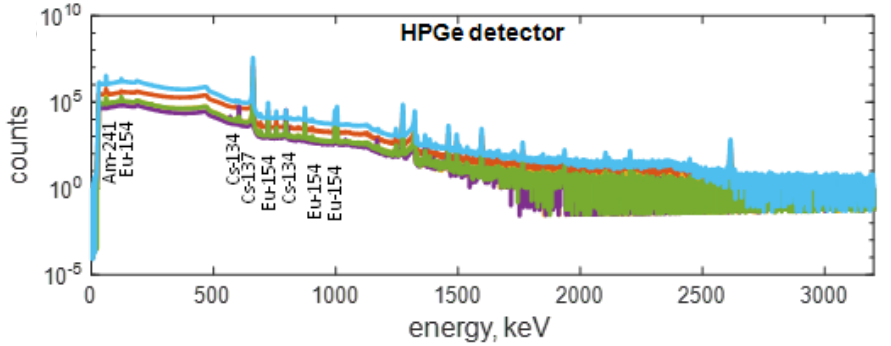
- Gamma spectra of fission product sample
  - shared by Mark Croce (LANL)
- Acquired simultaneously with three detectors
  - microcal (up to 300 keV),
  - planar HPGE (up to 1.2 MeV)
  - detector X (up to 8 MeV)

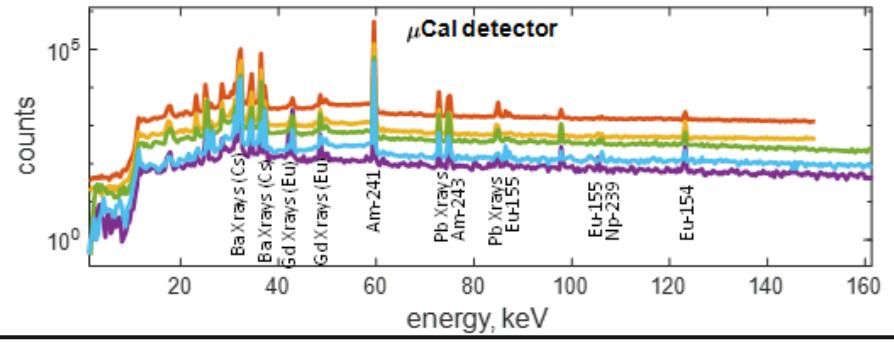
- Three measurement dates for each detector
- These can be analyzed by PCA
  - discriminate by detector type
  - discriminate by measurement time



*5 samples







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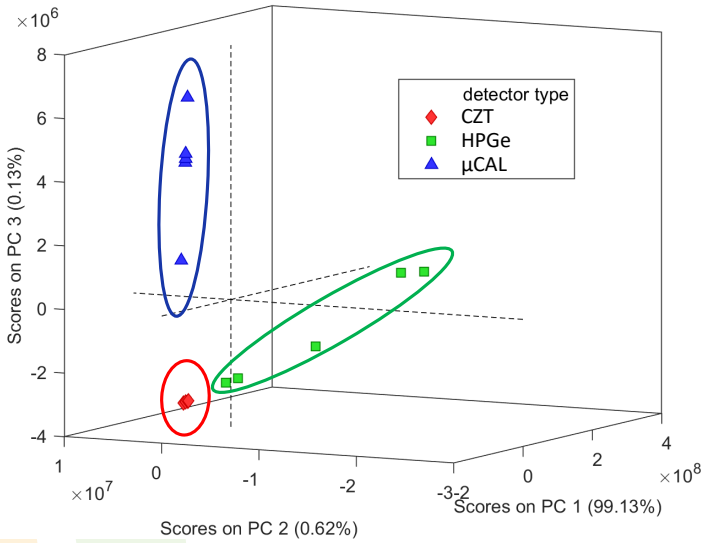
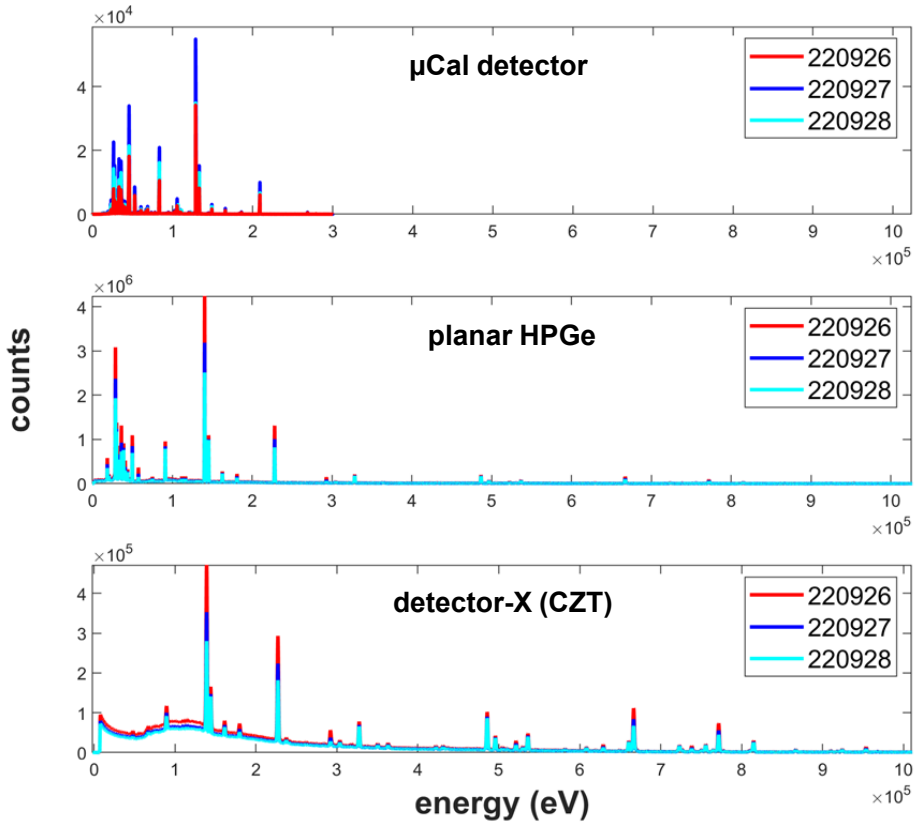
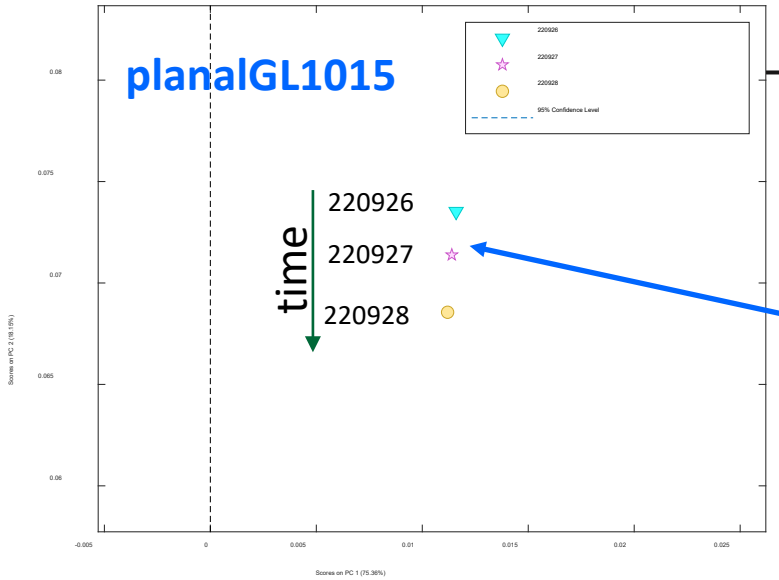
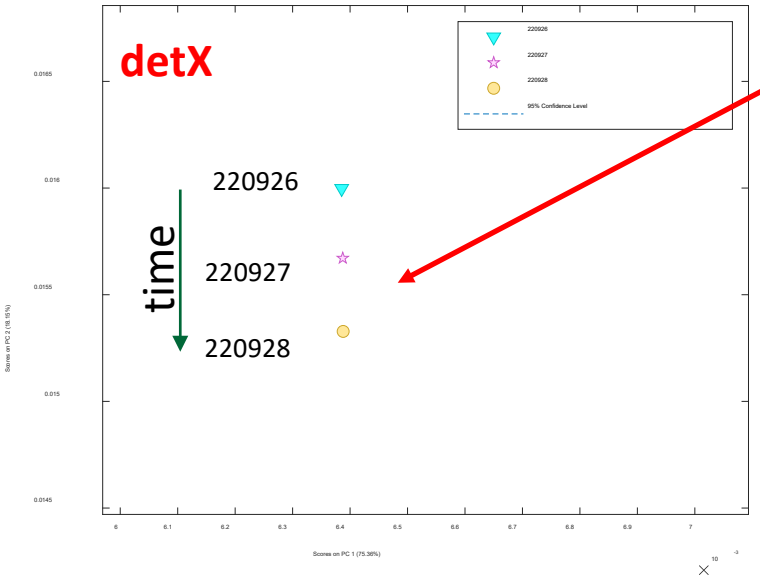


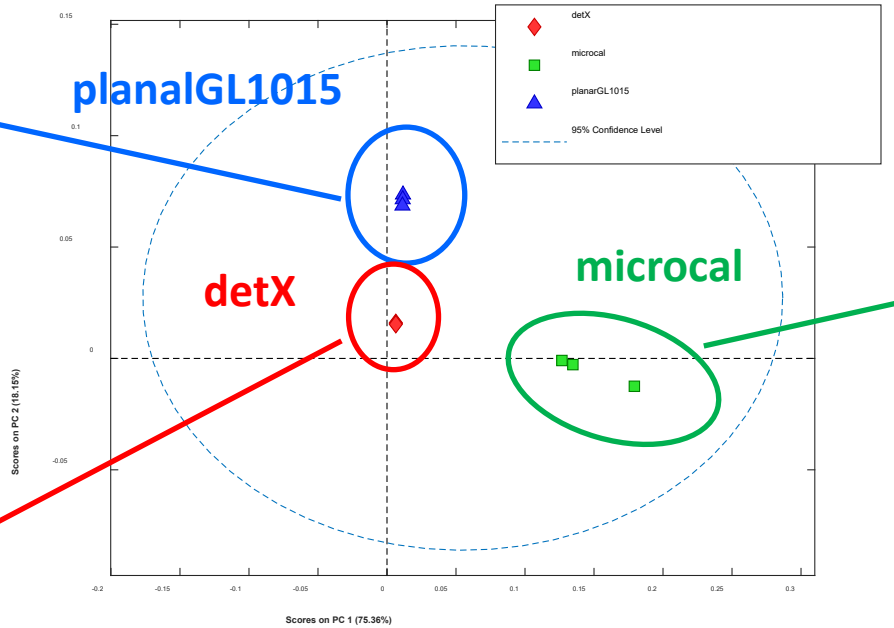
*single sample

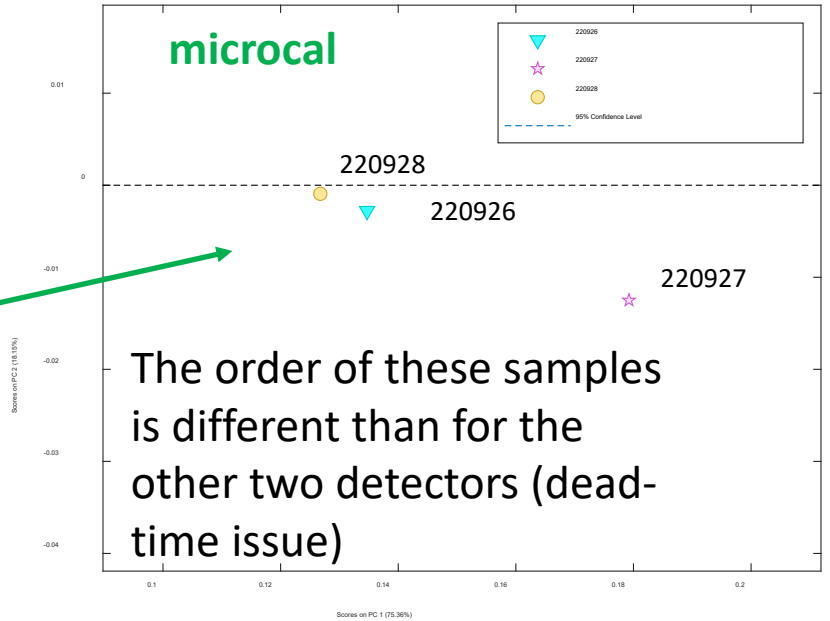


Radiometric analysis







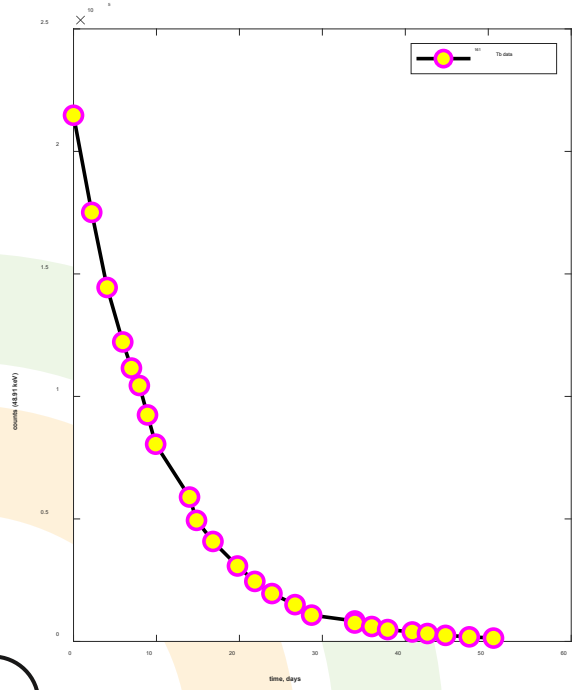


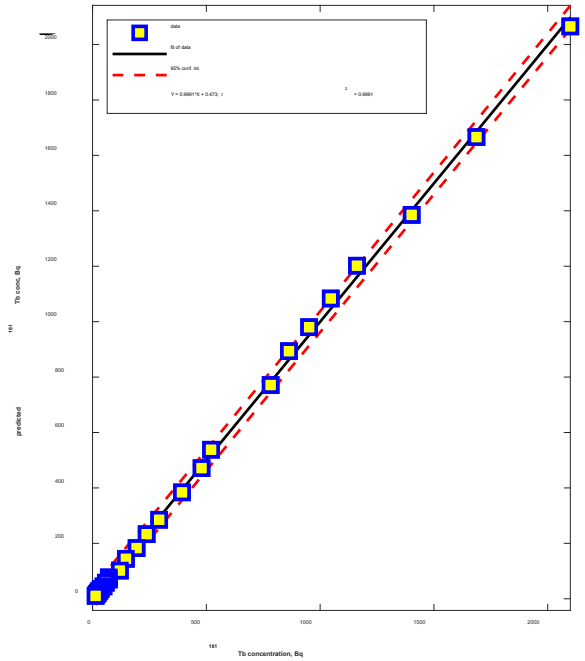
The order of these samples is different than for the other two detectors (dead-time issue)

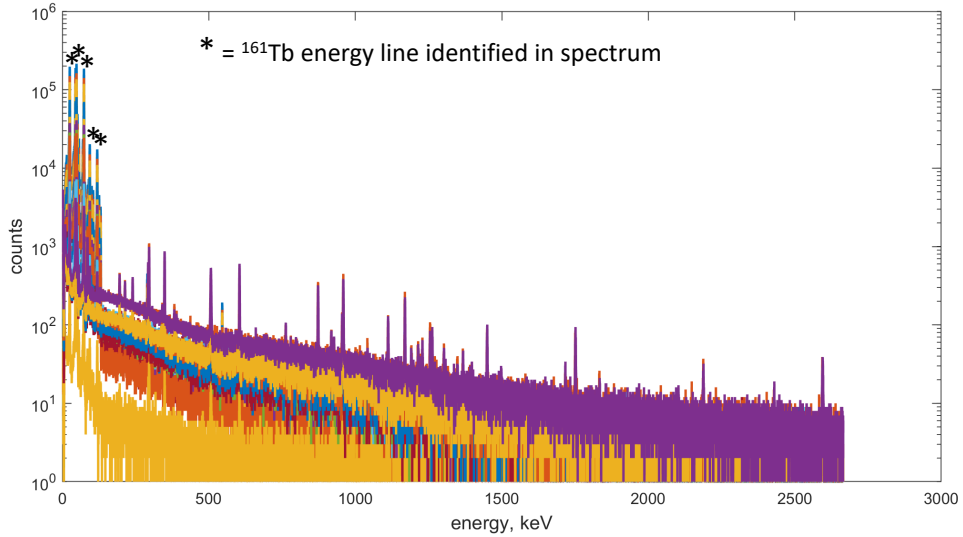
- Even with time out of sequence, measurements are still grouped by detector type
- Within groupings, can determine concentration of radioisotope
- This is indicator of time sequence that we can follow change in concentration (dig into with more specific dataset on next slide)

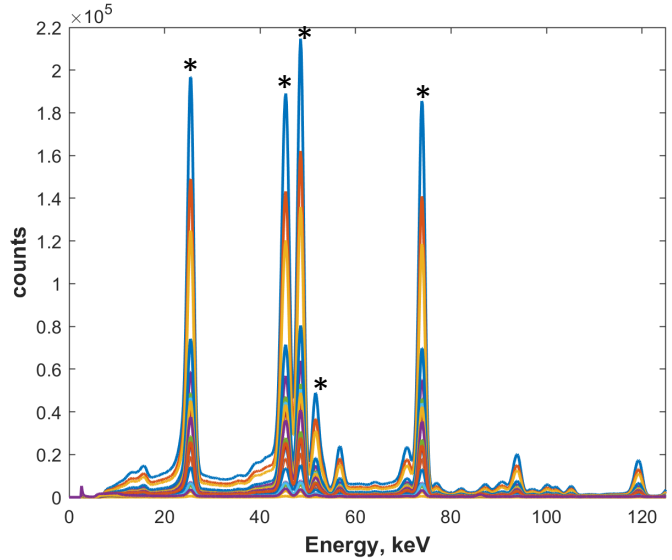
PCR Regression of single component data set

- Data shared by Mark Croce and Bruce Pierson
- Tb-161 sample on planar HPGe detector over 51 days



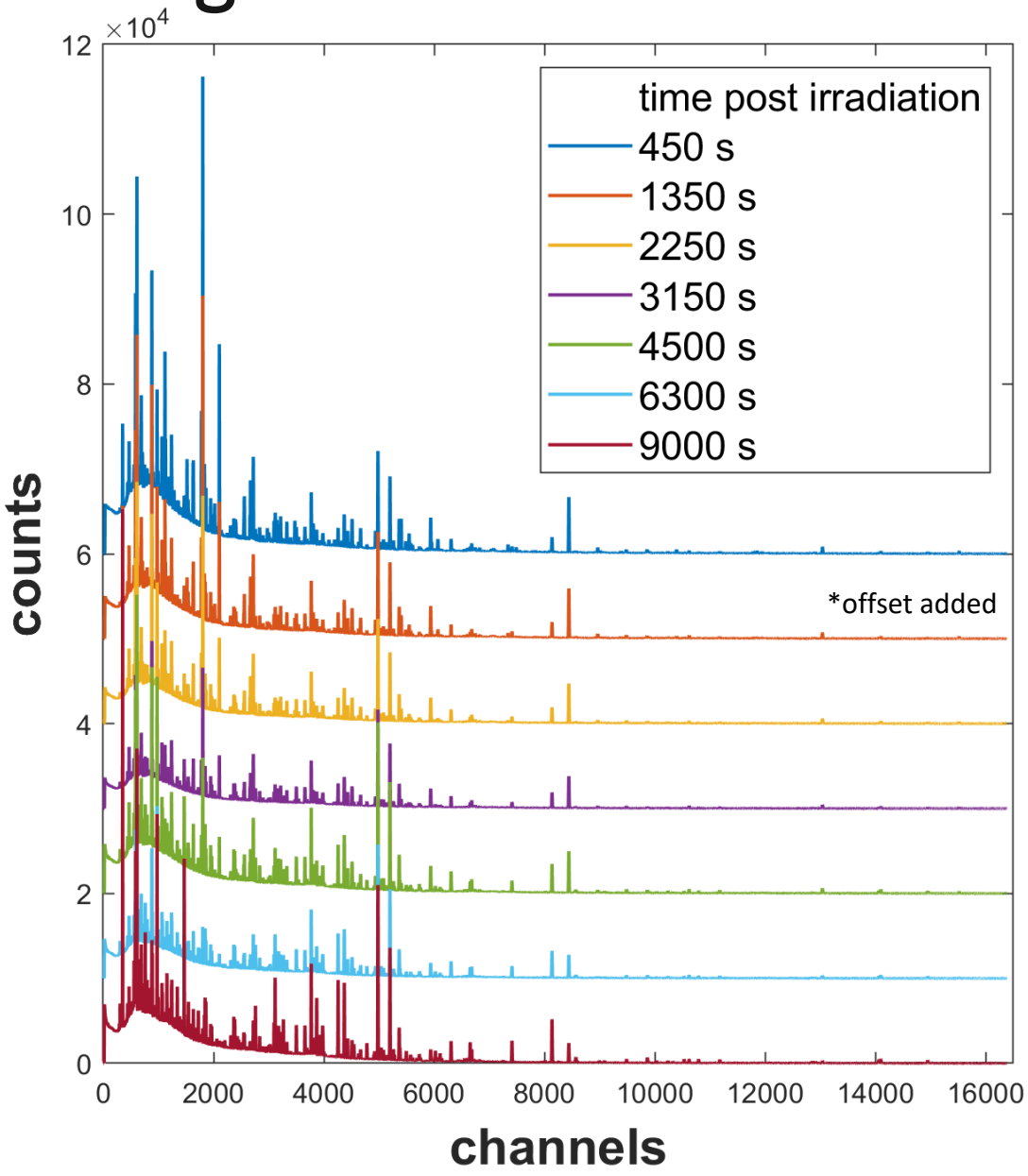






Application of chemometric modeling to multi-component data set

- Mixed fission products of Pu-239 activation measured on HGPe detector over 3 hours
- Data shared by Mark Croce and Bruce Pierson
- Spectra show high complexity and overlap of many signals



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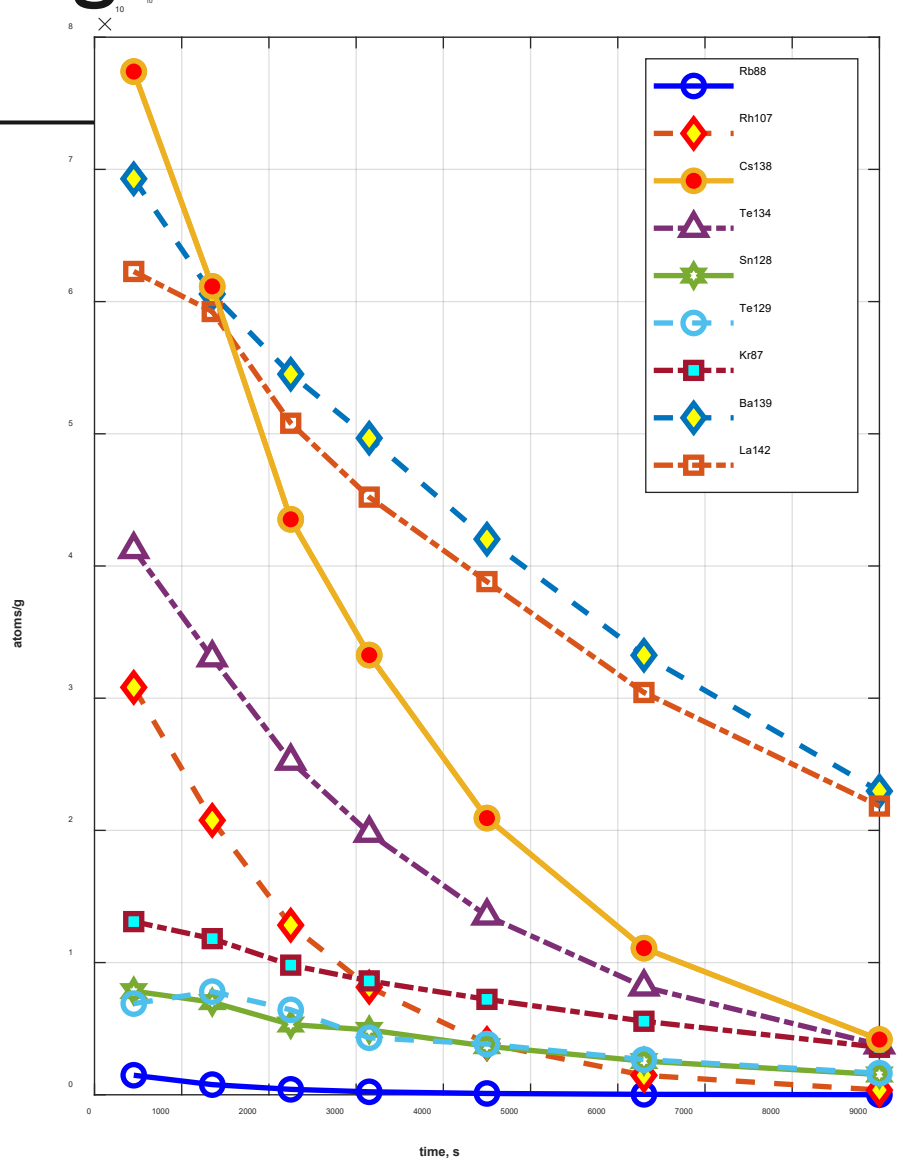
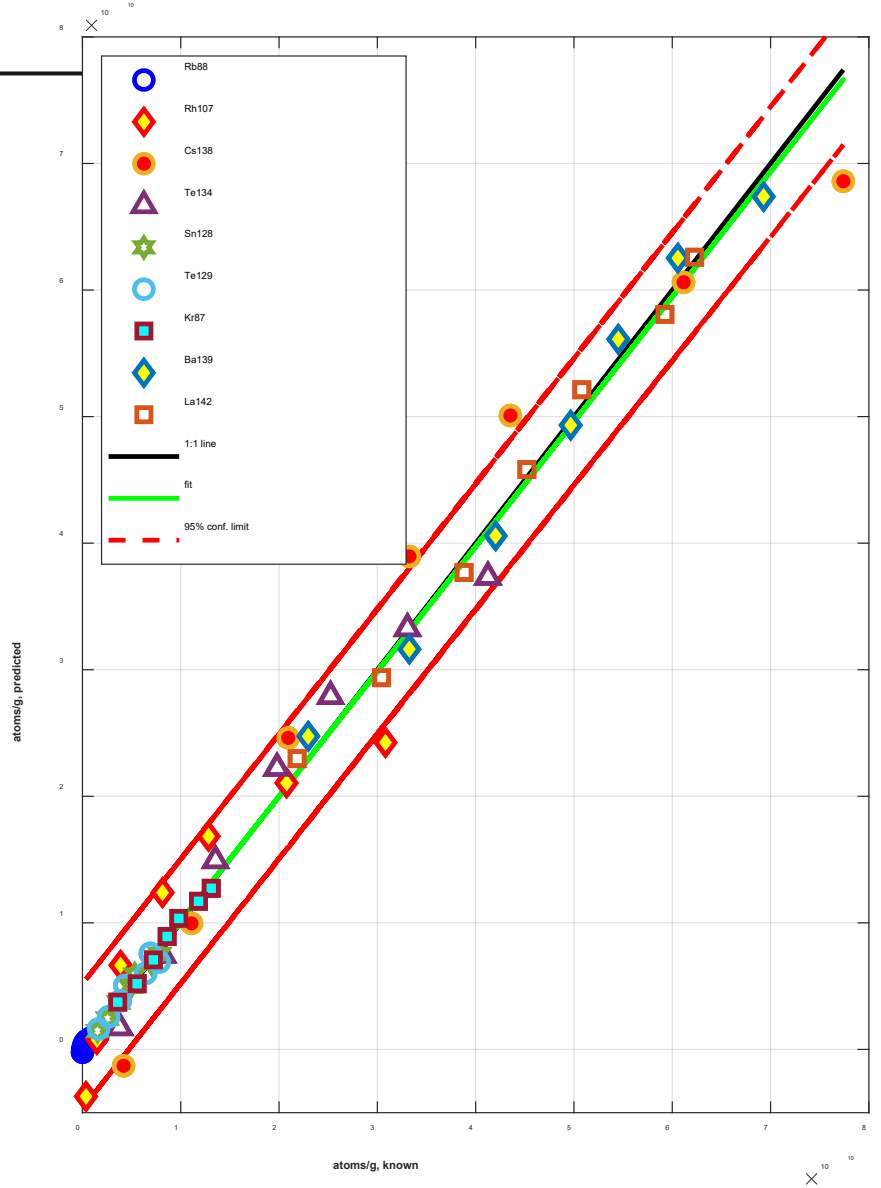


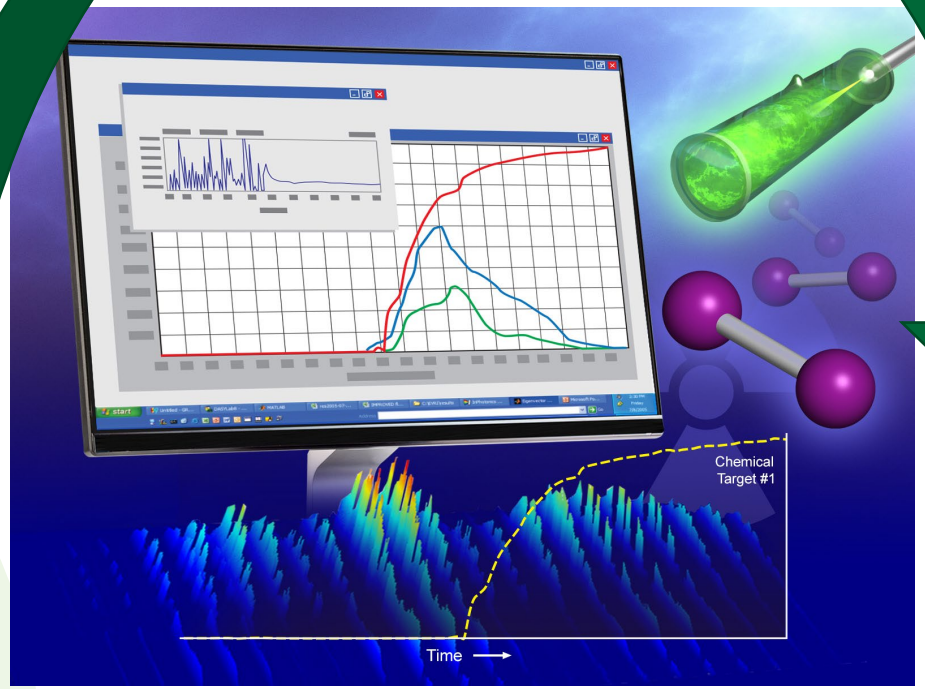
Application of chemometric modeling to multi-component data set

- Principal component regression (PCR) model of 9 fission products
- Next steps:
  - Adding in all fission products to regression model
- Involves building out Y blocks of concentrations or ratios of isotopes within measured samples
- Publication in progress
- **We are always excited to get additional data sets if folks are willing to share!**



Chemometric Model Building

Data

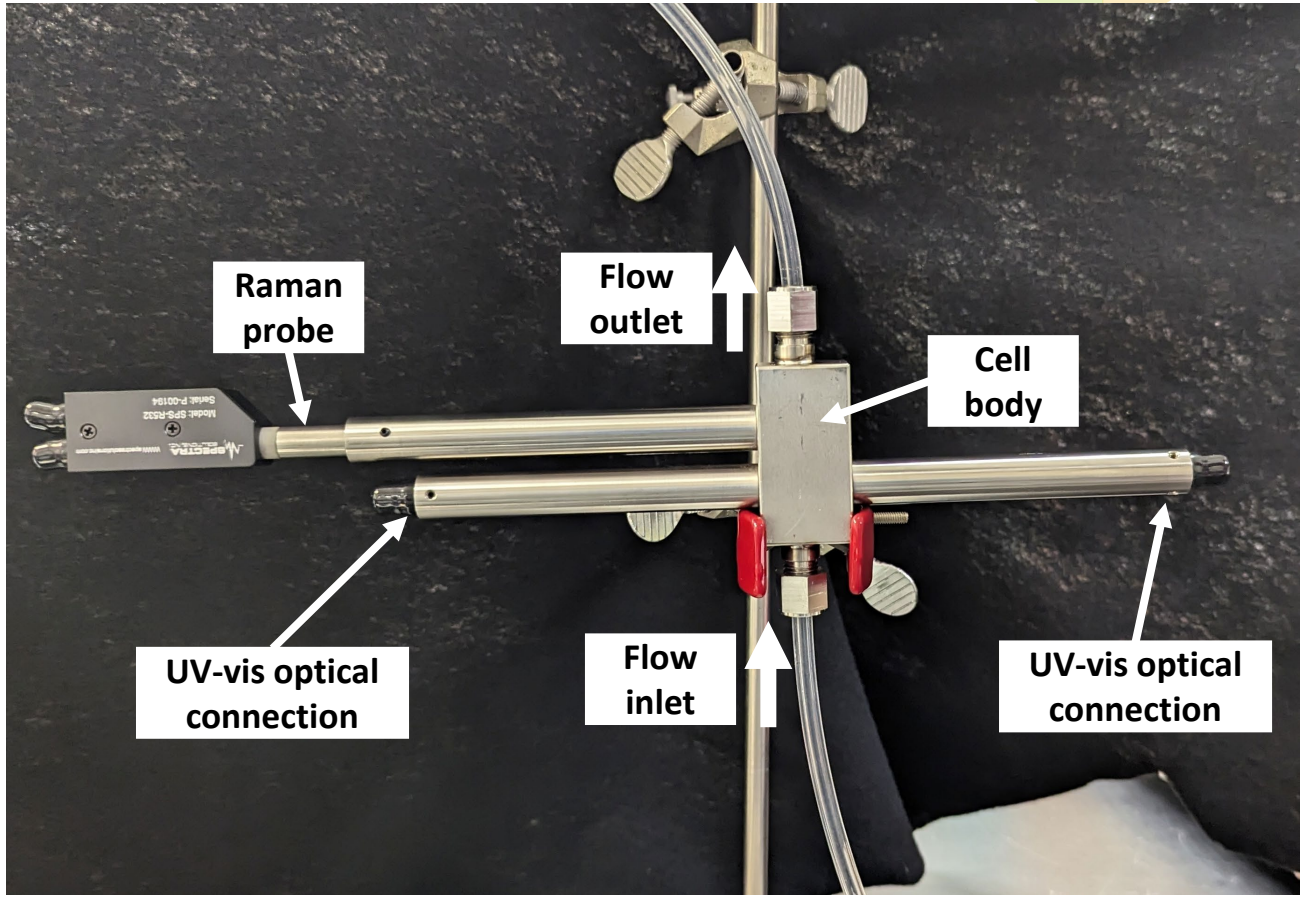


Information

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

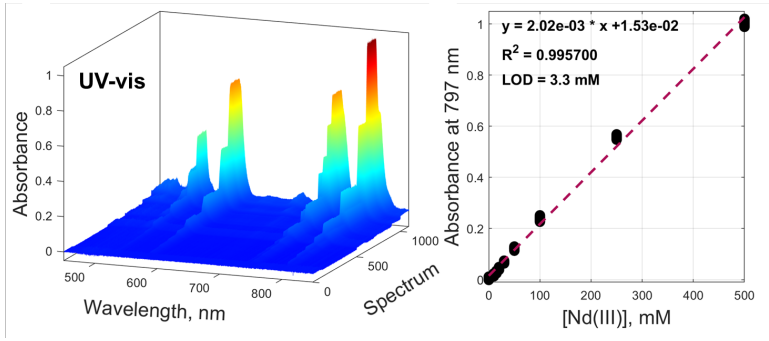
Sensor cell for flowing system integration

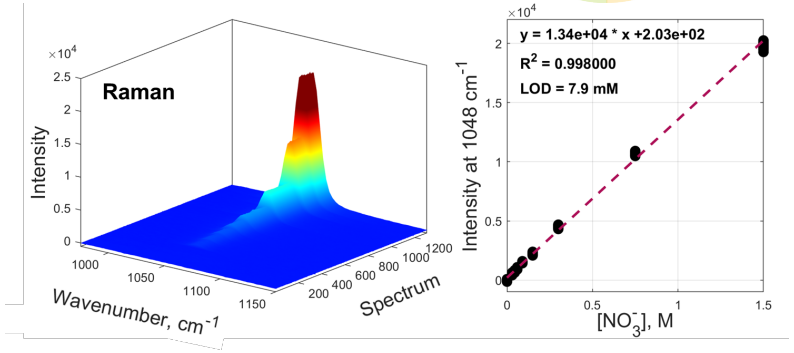
- Sensor flow cell developed to explore the integration of probes into flowing salt systems and gain insight into process signatures
- Mechanisms of integration (materials, seals, welding) can be modified to fit ANY system
- Initial testing of cell completed in aqueous solutions with non-rad surrogates
- Milestone M3RS-23PN0401053 completed 3/23/23

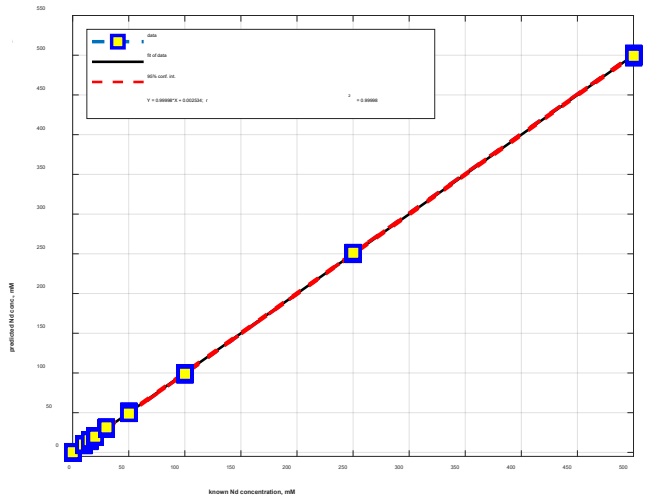


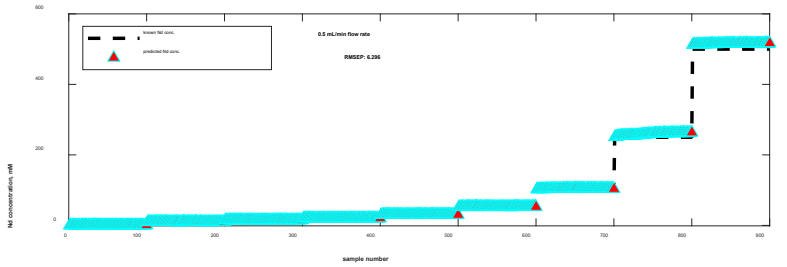
Sensor testing and modeling

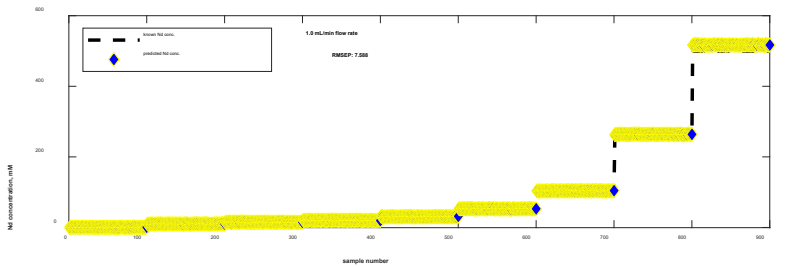
- Proof-of-concept testing on Nd(III) in water
- Consistent performance of flow cell
- Chemometric model for the prediction of Nd(III) at various flow rates





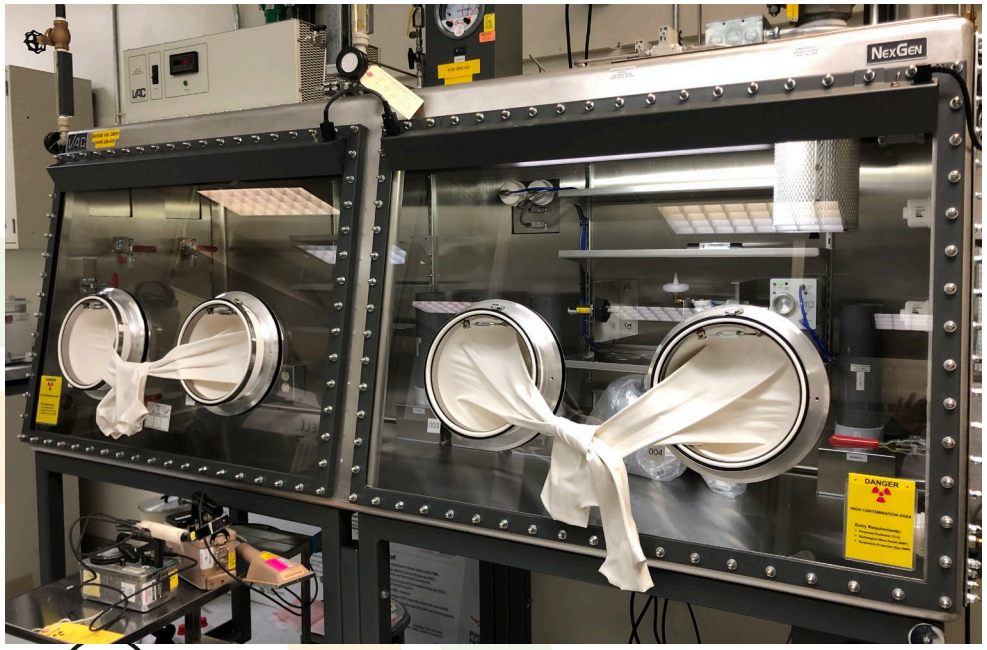


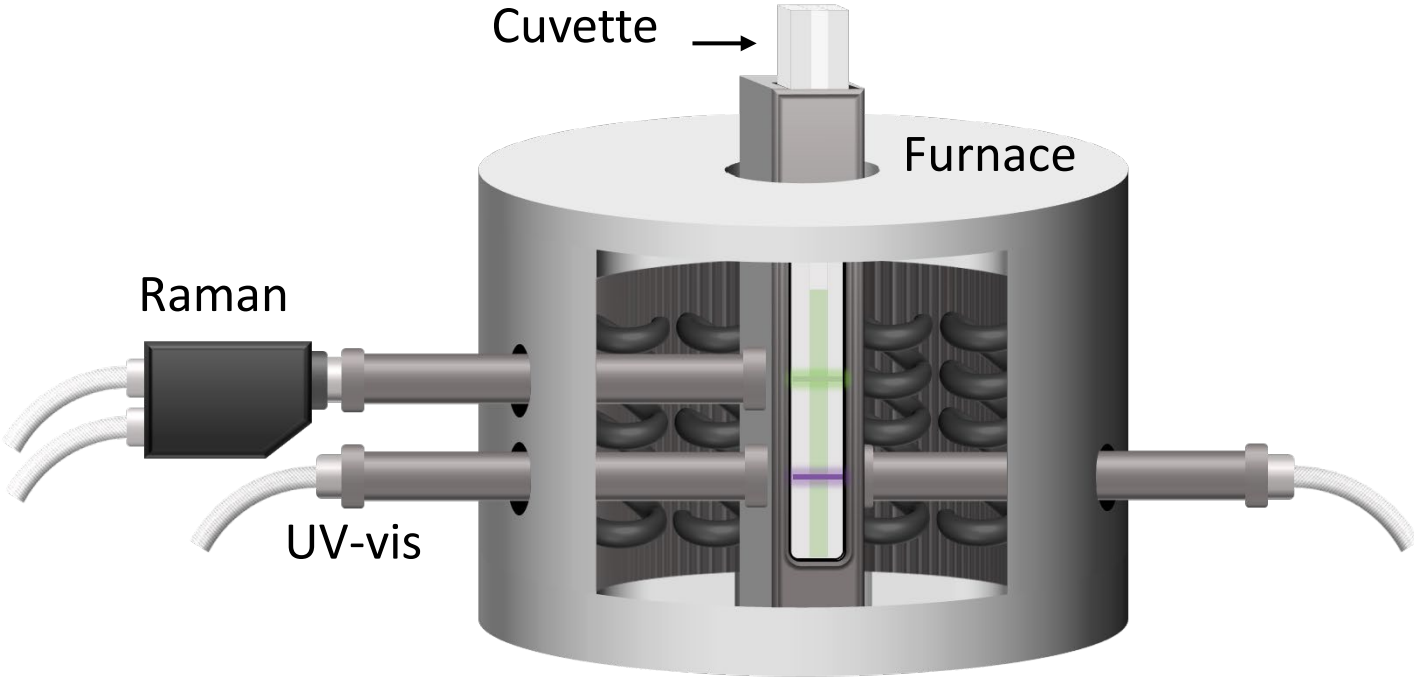




Installation of glove box for advanced process streams

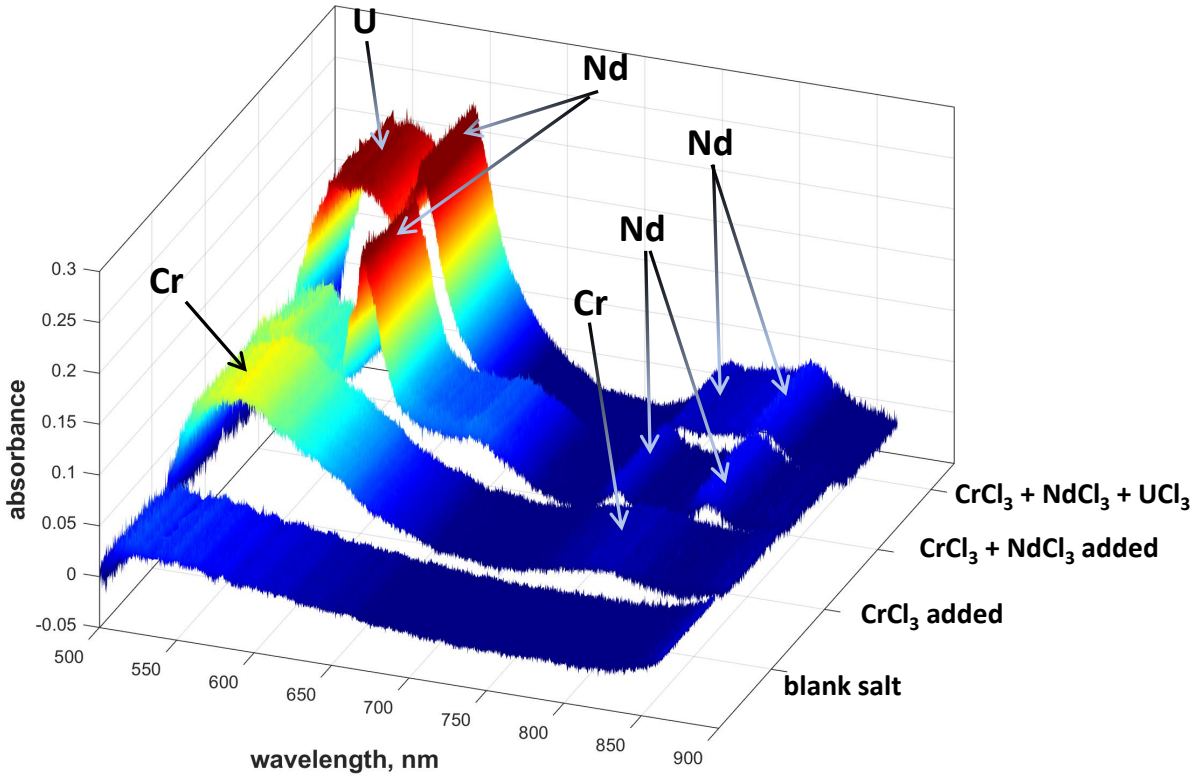
- Molten salt interrogation setup and salts were moved to a new inert enclosure
  - Significant effort in planning and execution
  - More modern atmospheric control and monitoring
  - Installed small scale furnace design





Initial testing in new glovebox

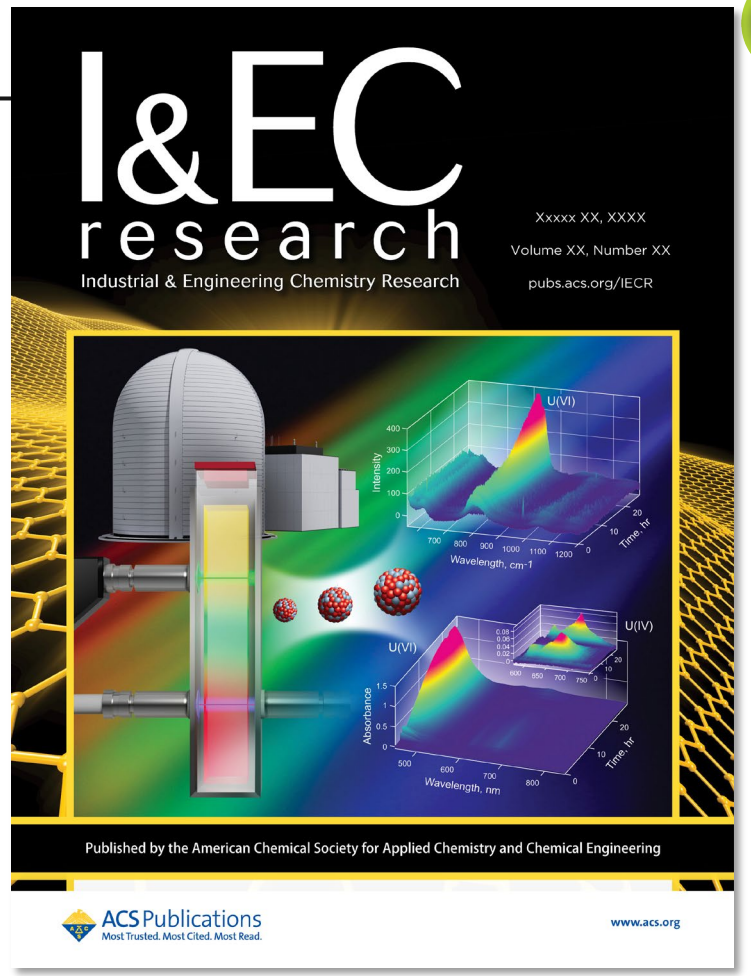
- Stable uranium speciation observed in new box
- Many species in reactor environment overlap with species of interest



Accomplishments and path forward

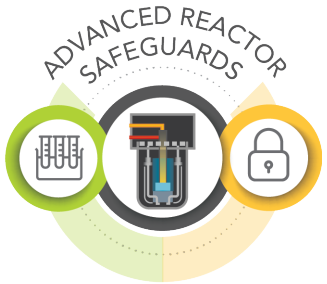
- Continue exploration of chemometrics application to radiometric data
  - Includes expanding sets (if folks are willing to share!) and building regression models

- Expansion of optical data sets and testing/building more advanced chemometric models
  - Exploring more robust optical materials for more accurate data sets
  - Increasing chemical complexity (e.g. fission products, corrosion products, TRU species)



Branch, Shirmir; Felmy, Heather; Schafer Medina, Adan; Bryan, Samuel; Lines, Amanda Exploring the complex chemistry of Uranium within molten chloride salts" ***Industrial & Engineering Chemistry Research***, 2023, 62, 37, 14901–14909. https://doi.org/10.1021/acs.iecr.3c02005, **featured on cover**

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 national lab partners (e.g. LANL) to demonstrate proof of principle chemometric analysis of gamma count data

- M3RS-24PN0401063: Letter report to NTD highlighting progress on optical testing and TRU measurement (due 09/30/2024)
- M4RS-24PN0401061: Letter report to NTD on application of chemometric approaches to gamma data (due 09/30/2024)

Acknowledgements

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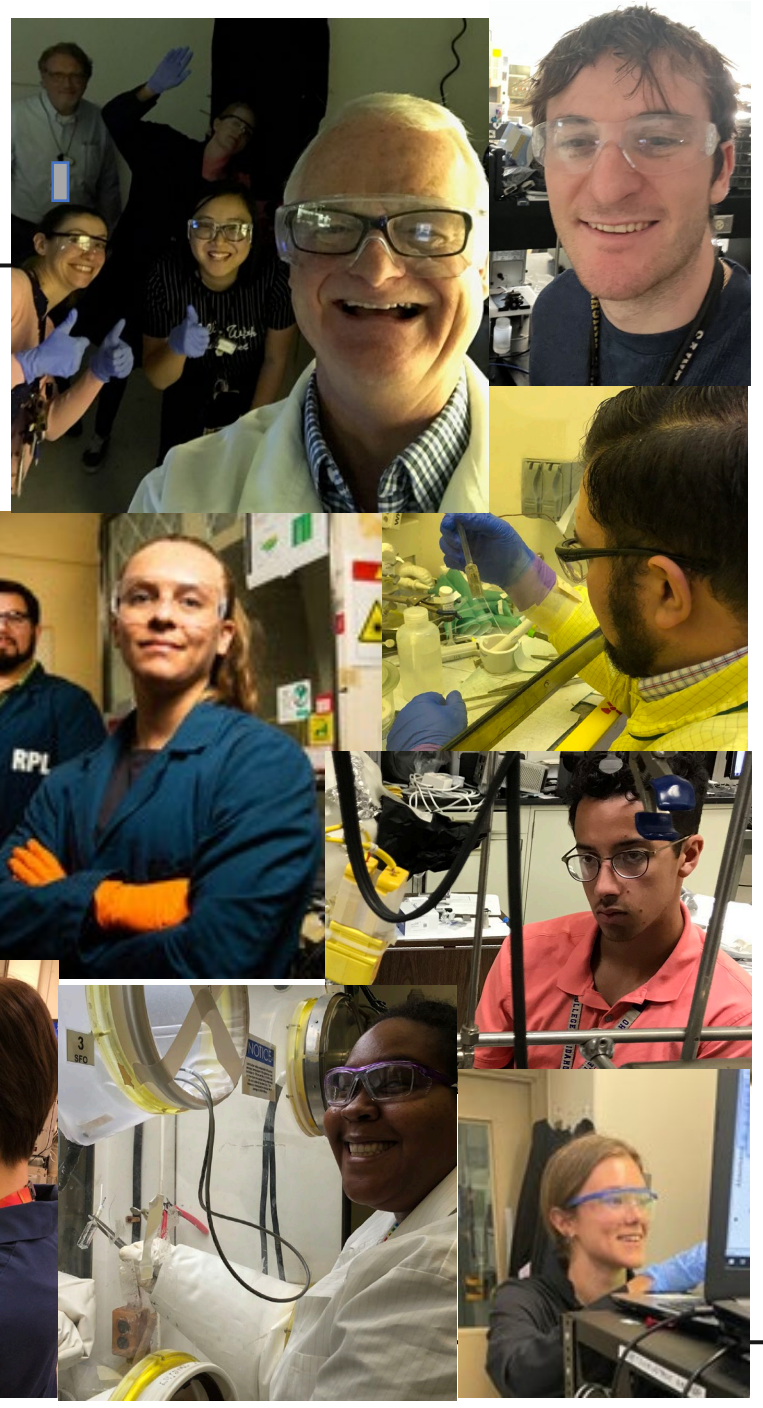
Nicole Hege (CSM)
Molly Vitale-Sullivan (SULI)
Andrew Clifford
Alyssa Espley

U.S. DOE NE, ARSS campaign



Thank you