U.S. DEPARTMENT OF ENERGY | Office of NUCLEAR ENERGY

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# Optical on-line monitoring within harsh environments

PNNL-SA-182532

Amanda Lines

# In- or On-line Monitoring

- Sensors directly in or on the process
- In situ and real-time analysis of a given process or system

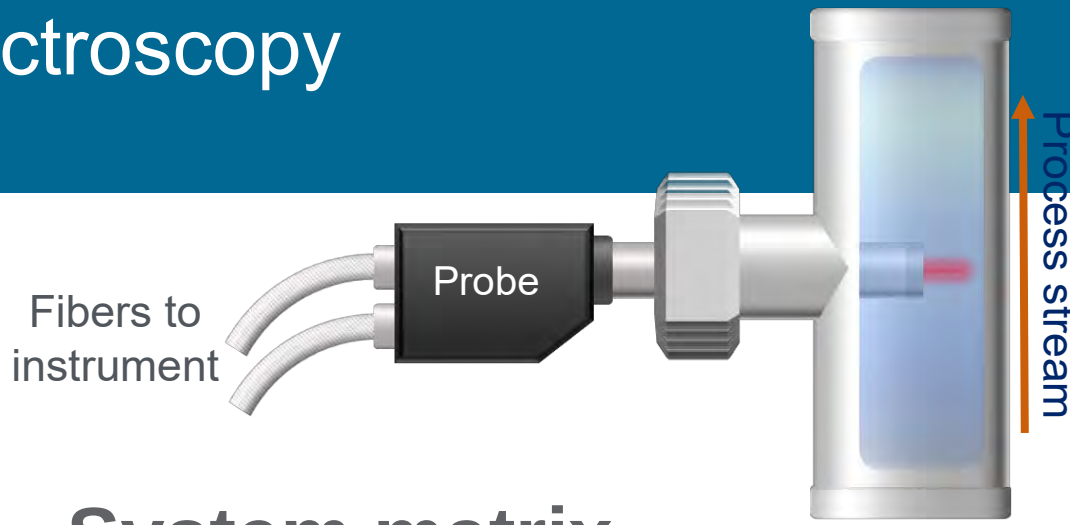

Fundamental characterization

Efficient process design

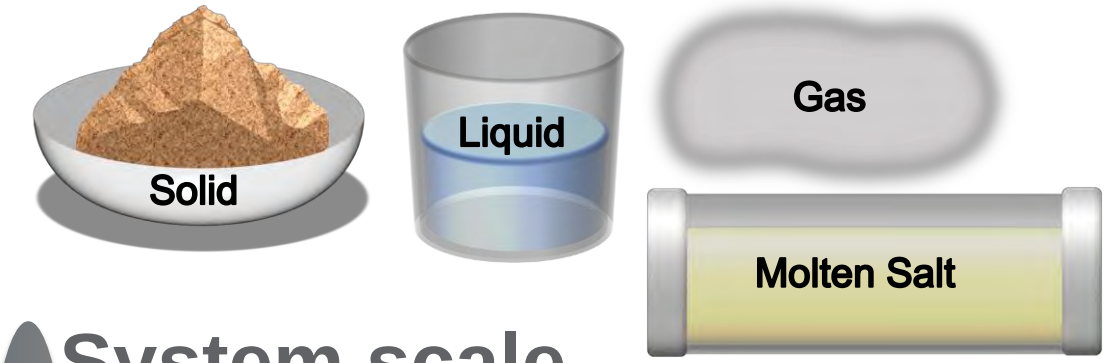
Safe and cost-effective deployment

# Chemical Characterization: Optical Spectroscopy

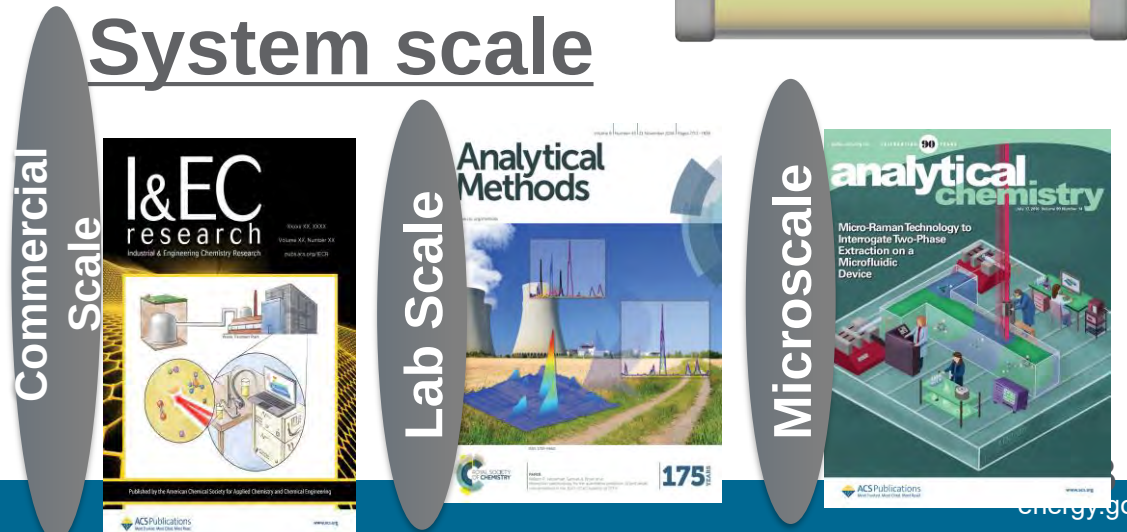
- Provides chemical information
  - Identification and quantification
  - Oxidation State
    - Essential information for control of systems
  - Molecular and elemental species
    - Essential information to control general system behavior
- Highly mature technology
- Simplistic integration
- Versatile




## System matrix

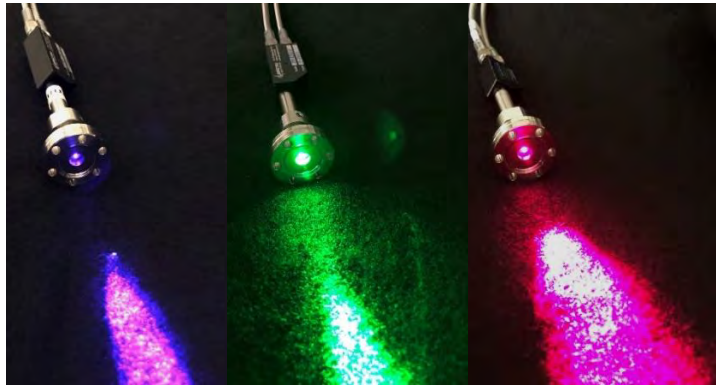



## System scale

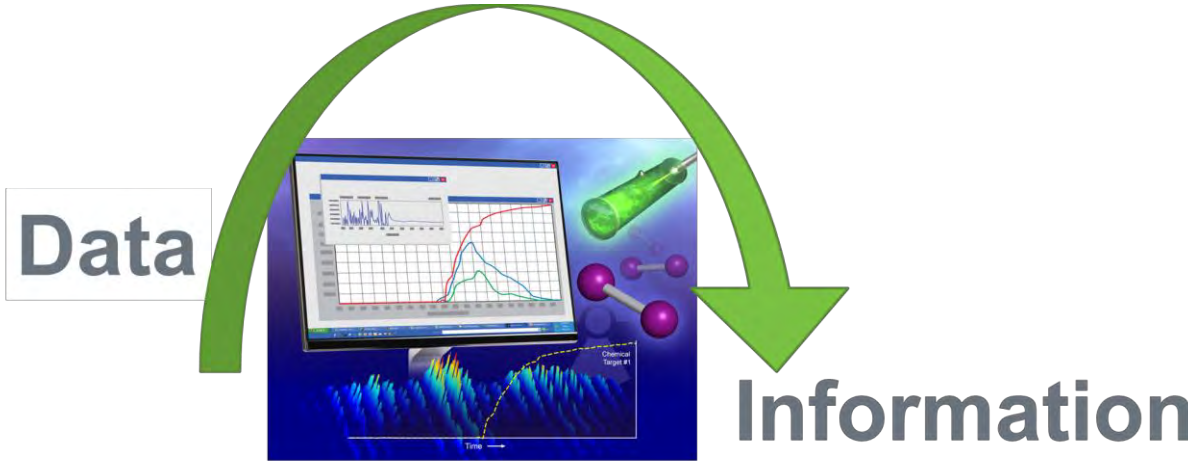


# The Two-Pronged Challenge of Monitoring Harsh and Complex Chemical Systems

- Probe development
  - Overcoming COTS limitations to build sensors that can survive:
    - Highly corrosive systems (HF gas, molten salts)
    - High temperature systems (molten salts)
    - Radiation
- Making smart sensors
  - Building autonomous tool kits that can parse interfering fingerprints and accurately identify and quantify chemical targets

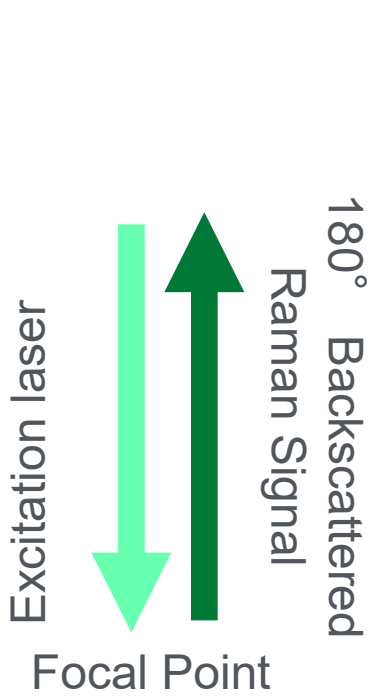


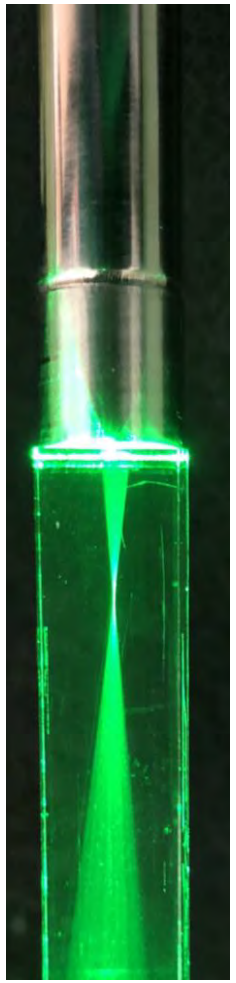
405 nm 532 nm 671 nm



# Optical Probe Basics

- Instrumentation setup
  - Remote monitoring
  - Detector/light sources (electronics) connected to probes via fiber optic cables
- Probe components
  - Optics (lenses, windows, etc) and housing (typically metal body)
- Specs
  - Dependent on spectroscopy type and application conditions

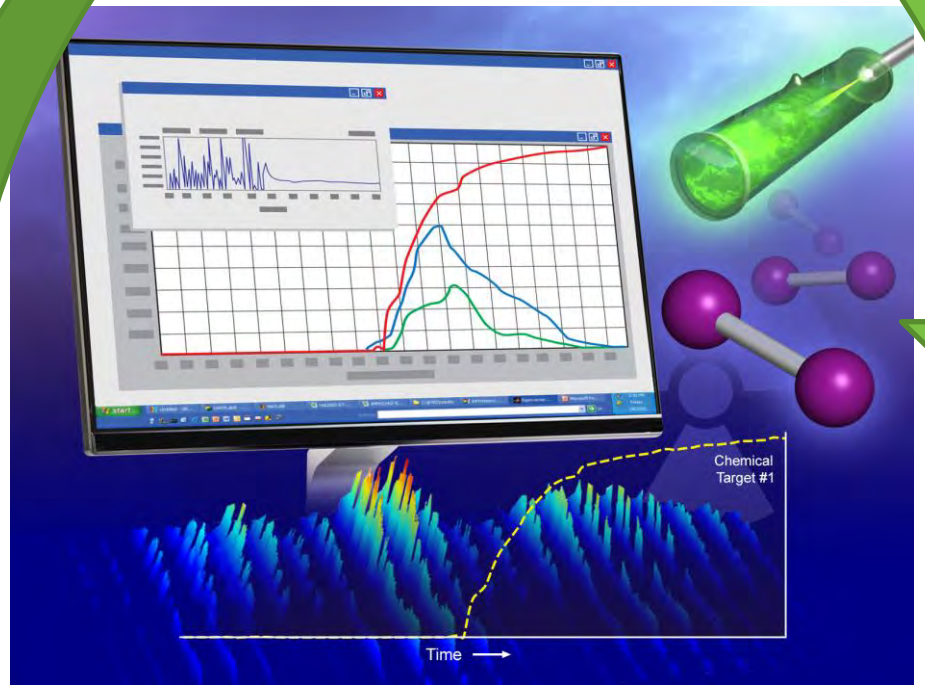


# Making Sensors Smart

Molten Salt Reactor PROGRAM

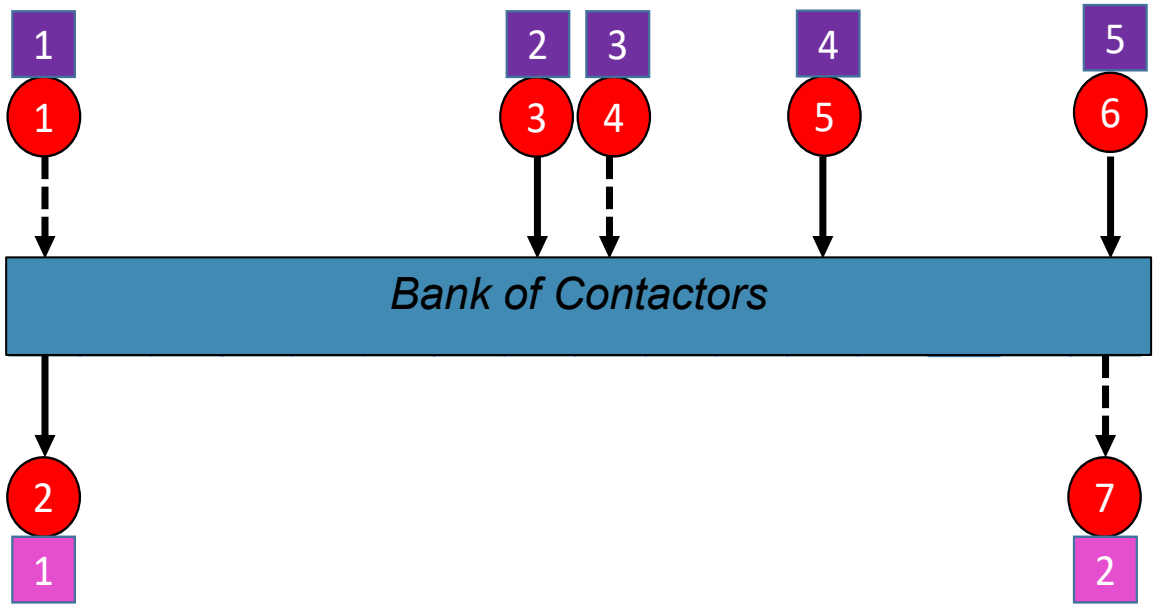
**Data**




**Information**

**Any sensor is only as valuable as the information you get out of it**

# UNF Fuel Recycle




Aqueous stream

Organic stream

Spectroscopic measurement: U, Pu, and HNO3

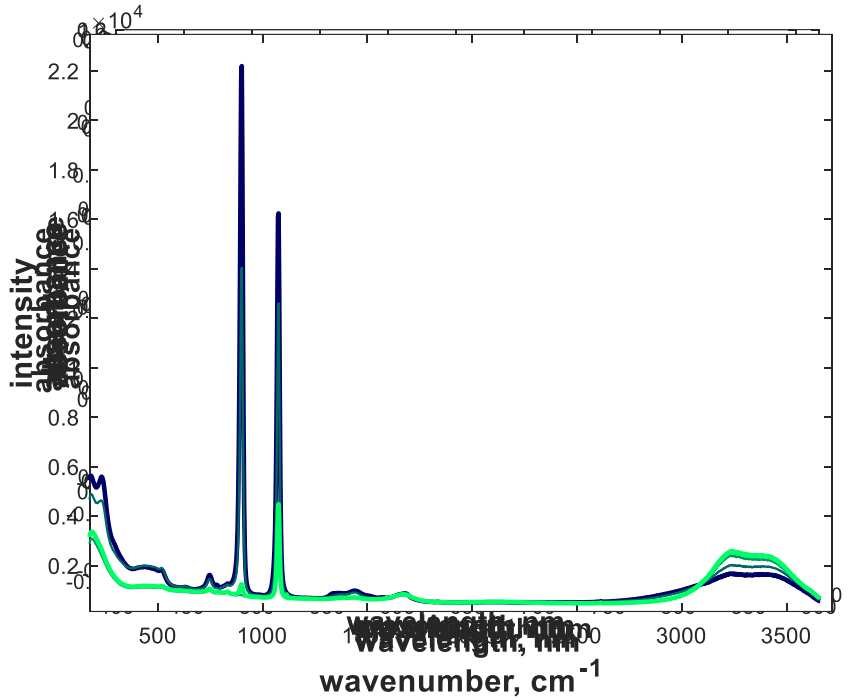
Flowrate/density measurement, Coriolis meter

Flowrate/mass measurement, time collection and scales

Lumetta, G. J.; Allred, J. R.; Bryan, S. A.; Hall, G. B.; Levitskaia, T. G.; Lines, A. M.; Sinkov, S. I., Simulant testing of a co-decontamination (CoDCon) flowsheet for a product with a controlled uranium-to-plutonium ratio. Separ Sci Technol 2019, 54 (12), 1977-1984

# CoDCon On-line Monitoring System Design

## Raman




Fission products

Pu: 3+, 4+, 6+
U: 4+

Np: 4+, 5+, 6+

Uranyl
HNO3

UV-vis absorbance

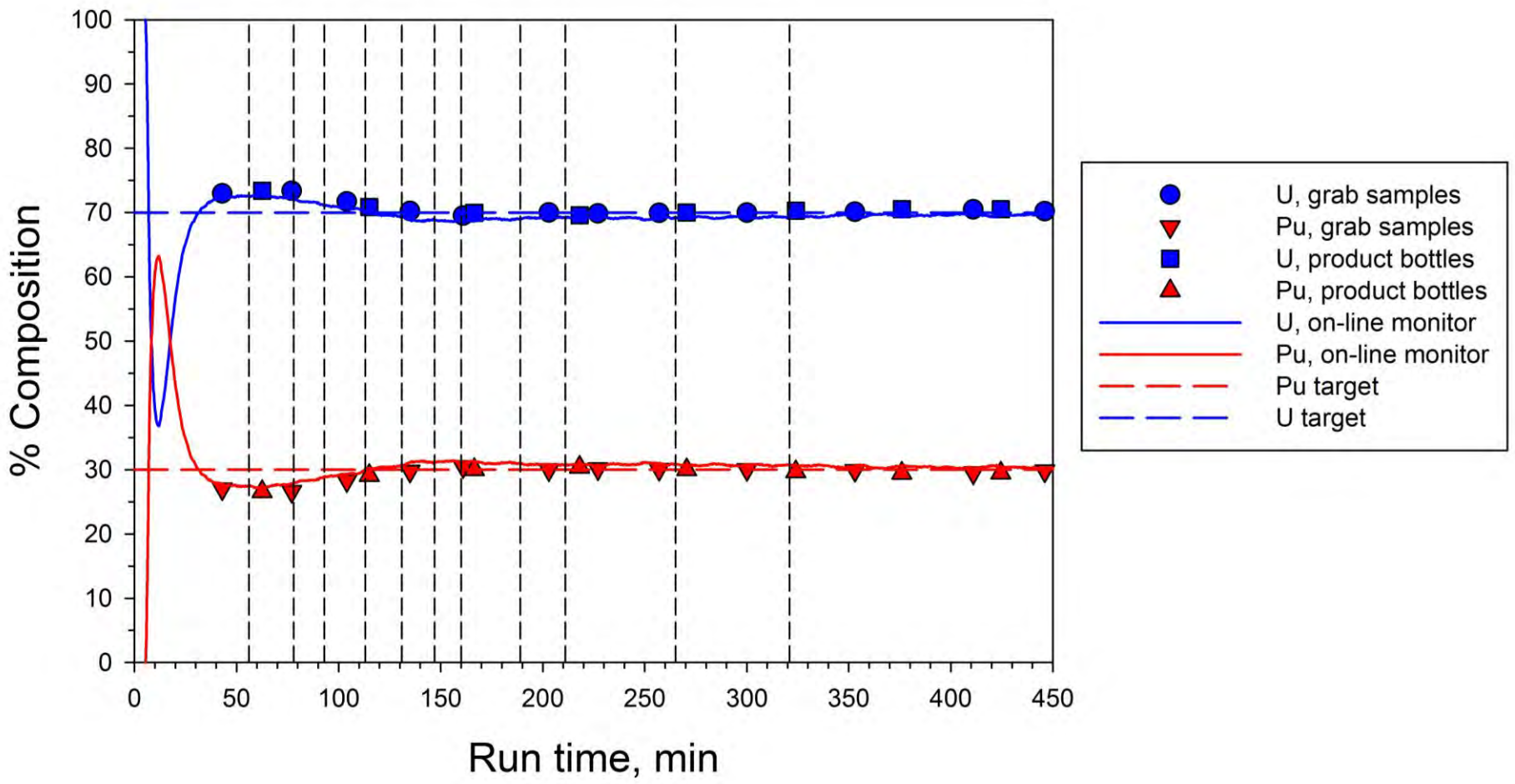
NIR absorbance

Raman

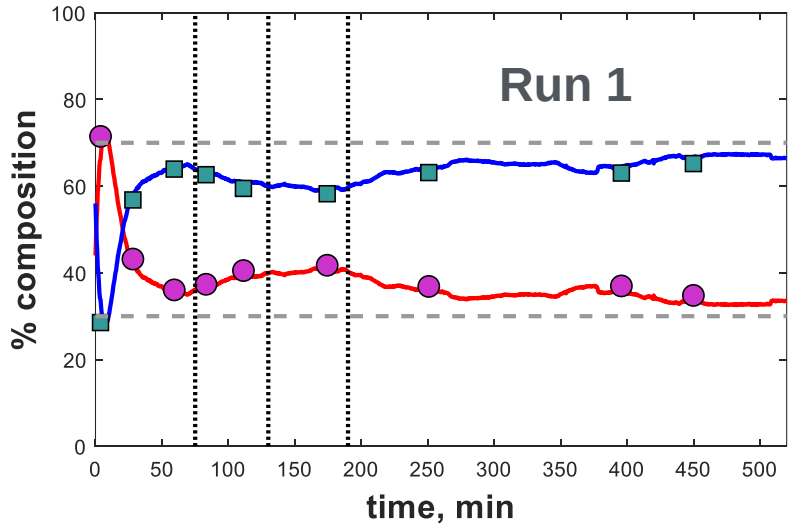
Flow cell installed on all inlets and outlets

Lines, A. M.; Hall, G. B.; Asmussen, S.; Allred, J.; Sinkov, S.; Heller, F.; Gallagher, N.; Lumetta, G. J.; Bryan, S. A., Sensor Fusion: Comprehensive Real-Time, On-Line Monitoring for Process Control via Visible, Near-Infrared, and Raman Spectroscopy. *Acs Sensors* **2020,** *5* (8), 2467-2475.

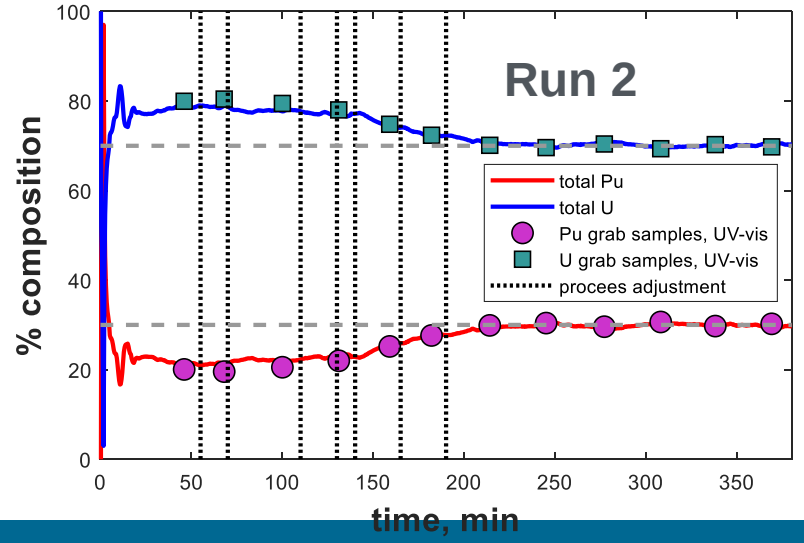
# Validation in process: CoDCon

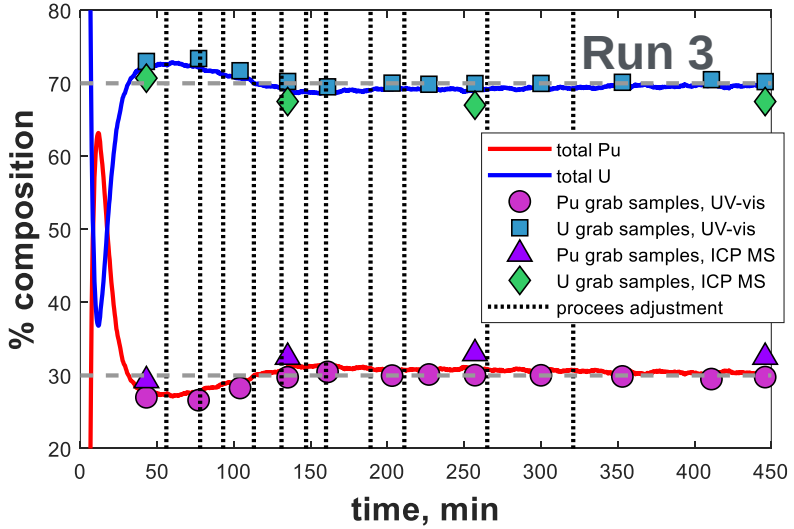


# Benefits observed over multiple CoDCon Runs

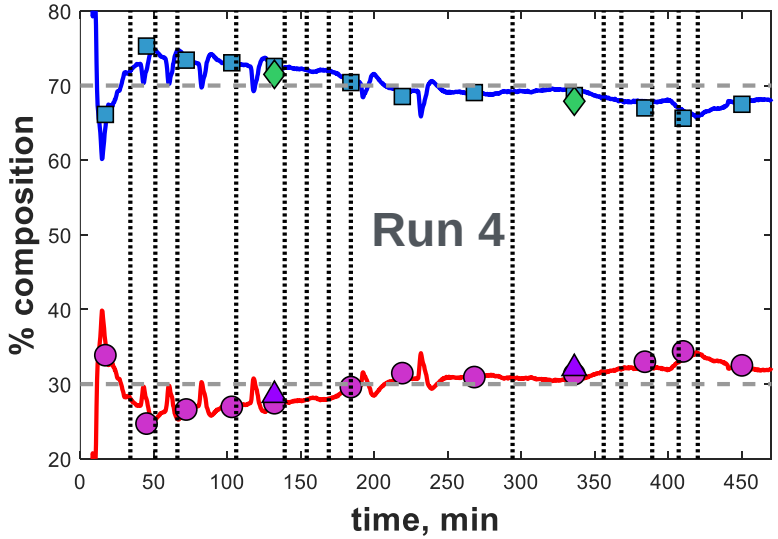



Identification of failing pump




Capture of short-lived aberrant behavior



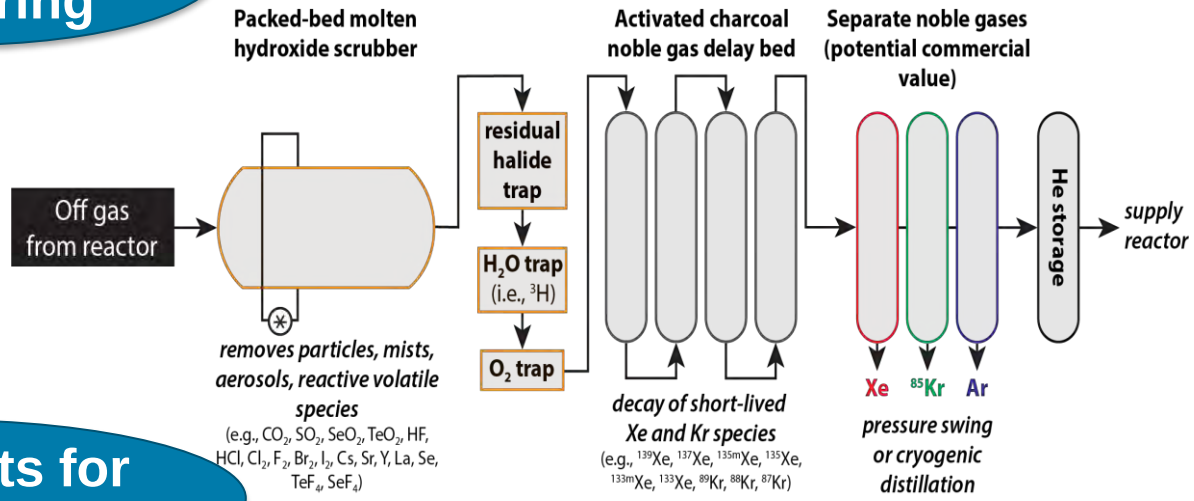

Lines, A.M.; J.B. Hall; S. Asmussen; J. Allred; S. Sinkov; F. Heller; N. Gallagher; G.J. Lumetta; S.A. Bryan, "Sensor fusion: comprehensive real-time, online monitoring for process control via visible, NIR, and Raman spectroscopy", submitted, 2020.

# Examples Within the Molten Salt Realm: MSR Off-gas

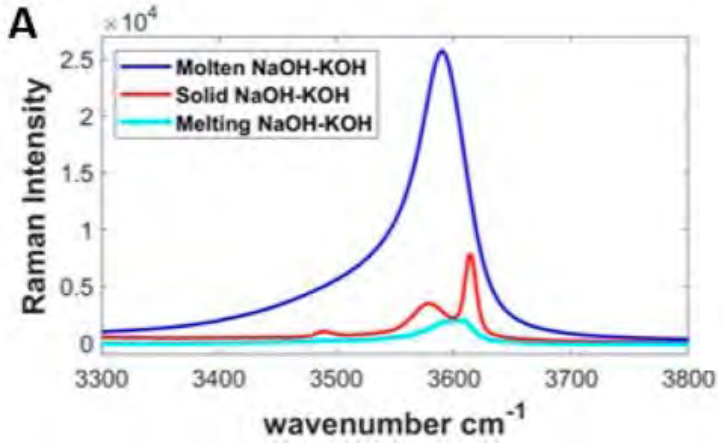
- Building tools that enable **safe**, **cost effective**, and **near-term deployment** of MSRs
- OLM to support:
  - More timely development and demonstration of processes
  - Process control and monitoring of deployed systems

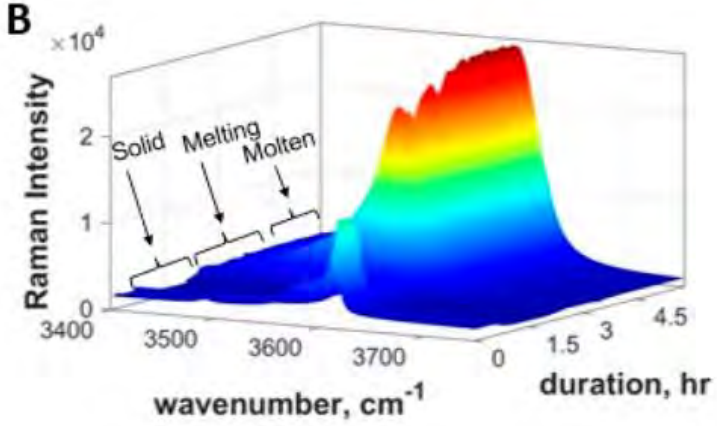
**Off-gas monitoring**

Mcfarlane, J.; Ezell, N.; Del Cul, G.; Holcomb, D. E.; Myhre, K.; Chapel, A.; Lines, A.; Bryan, S.; Felmy, H. M.; Riley, B. *Fission Product Volatility and Off-Gas Systems for Molten Salt Reactors*; Oak Ridge National Lab.(ORNL), Oak Ridge, TN (United States): 2019.

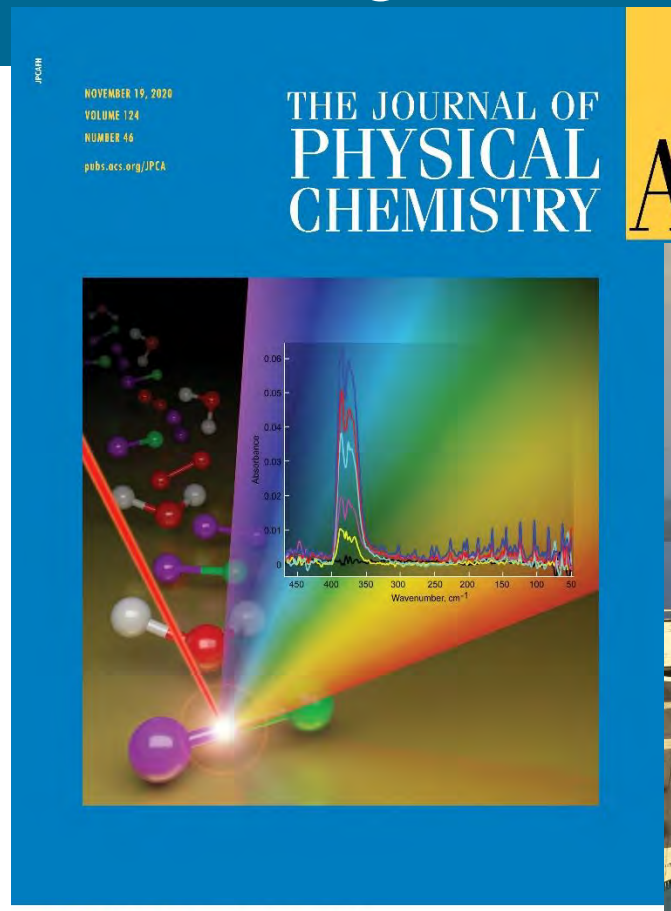



**Molten salts for gas treatment**

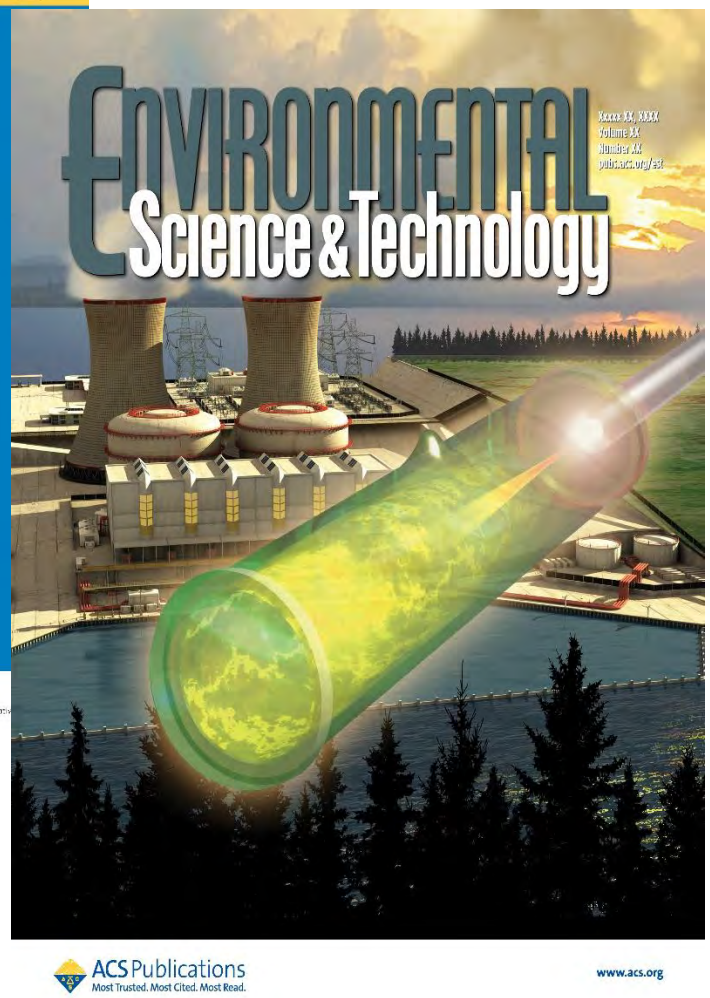


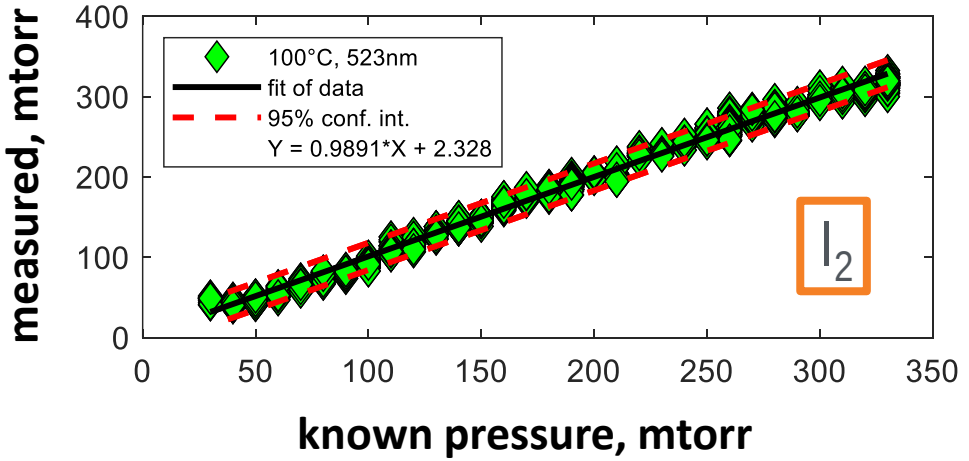
# Monitoring Iodine Species

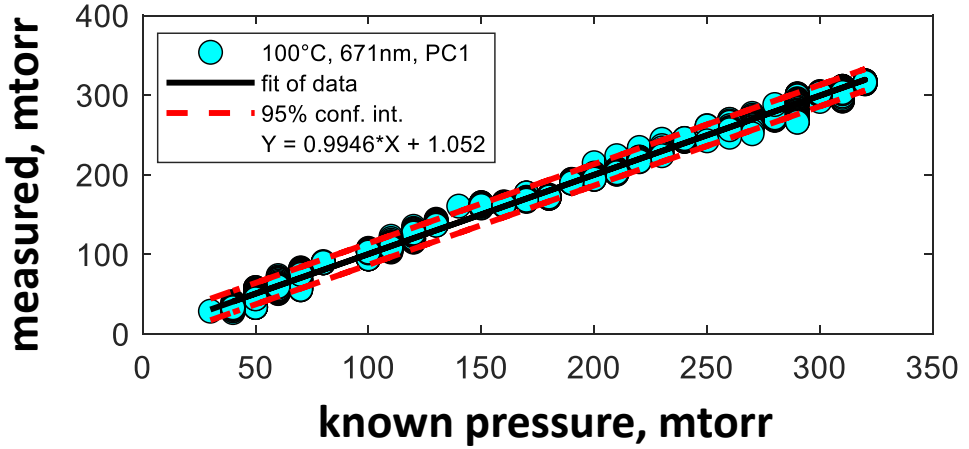


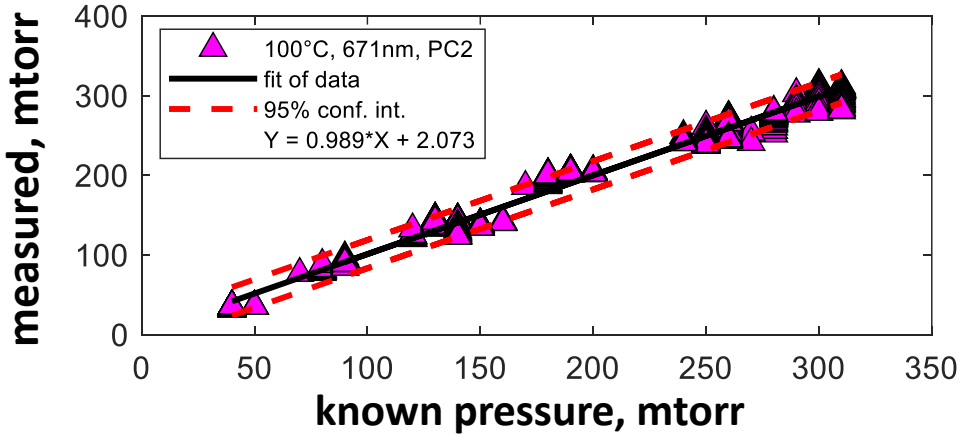

Hughey, K. D.; Bradley, A. M.; Tonkyn, R. G.; Felmy, H. M.; Blake, T. A.; Bryan, S. A.; Johnson, T. J.; Lines, A. M., Absolute Band Intensity of the Iodine Monochloride Fundamental Mode for Infrared Sensing and Quantitative Analysis. ***J Phys Chem A*** *2020, 124* (46), 9578-9588.




Felmy, H. M.; Clifford, A. J.; Medina, A. S.; Cox, R. M.; Wilson, J. M.; Lines, A. M.; Bryan, S. A., On-Line Monitoring of Gas-Phase Molecular Iodine Using Raman and Fluorescence Spectroscopy Paired with Chemometric Analysis. ***Environ Sci Technol*** *2021, 55, 6, 3898–3908.*



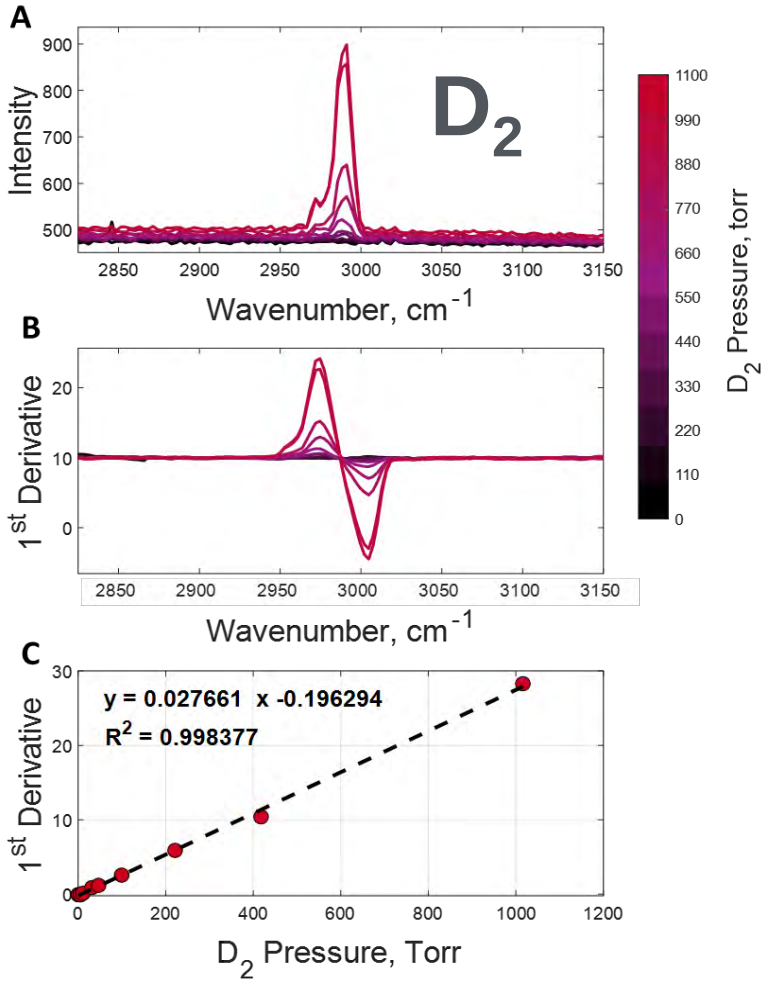
# Dual Phase Monitoring and H Isotopes

## Dual phase gas-NaOH melt monitoring

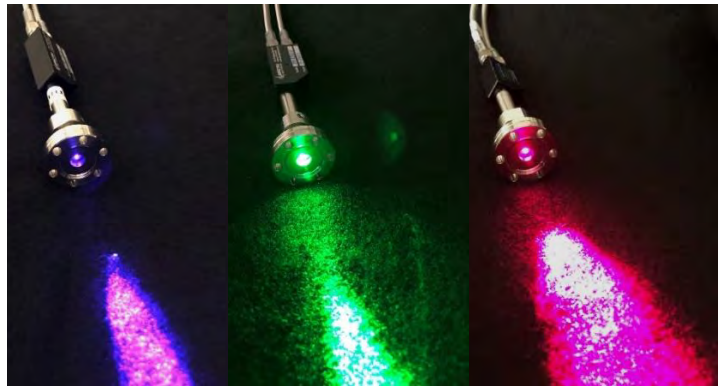


Adan Schafer Medina, Heather M. Felmy, Molly E. Vitale-Sullivan, Hope E. Lackey, Shirmir D. Branch, Samuel A. Bryan, and Amanda M. Lines
*ACS Omega* **2022** *7* (44), 40456-40465
DOI: 10.1021/acsomega.2c05522

## Integration of probes into systems for H isotope analysis

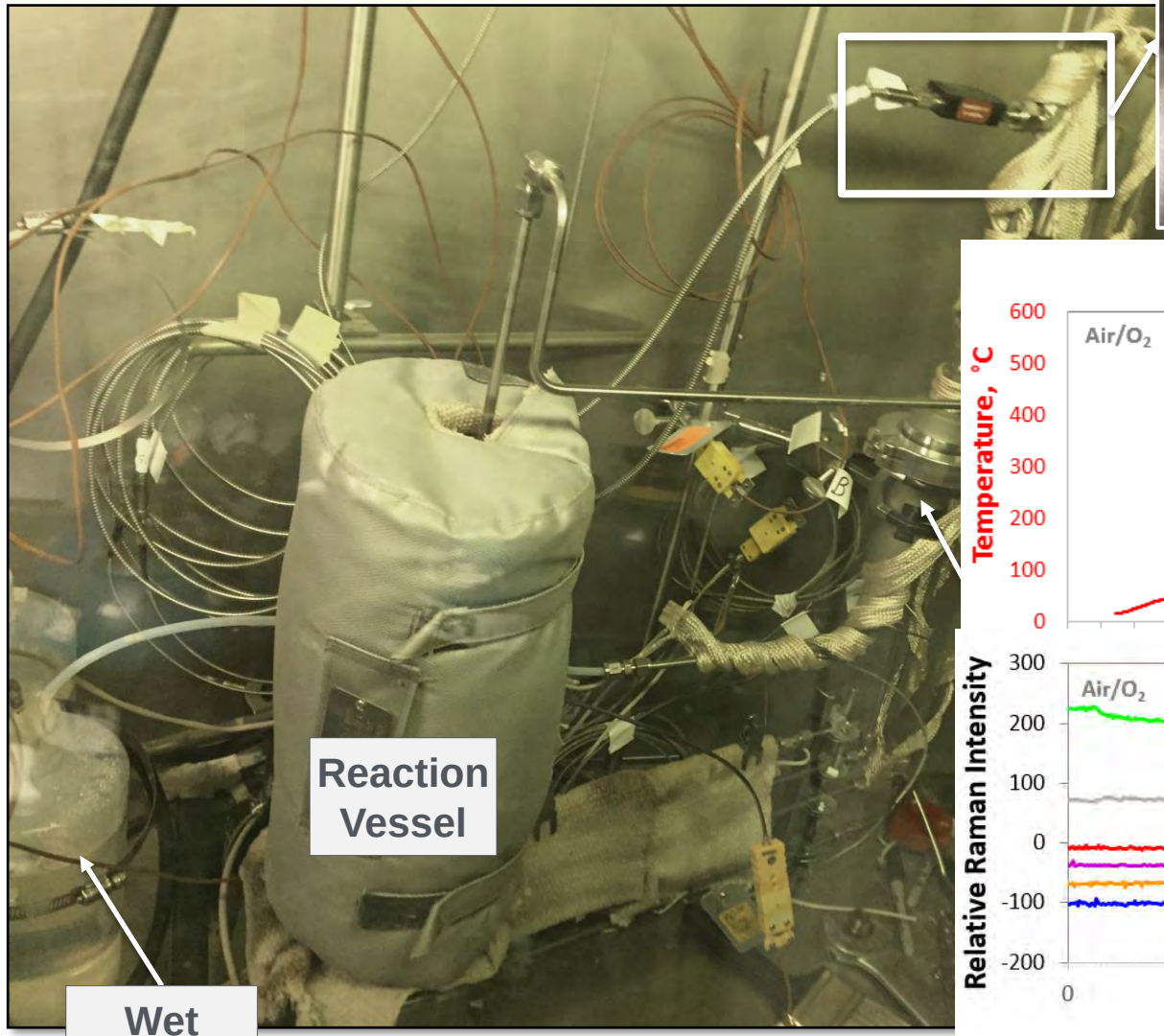




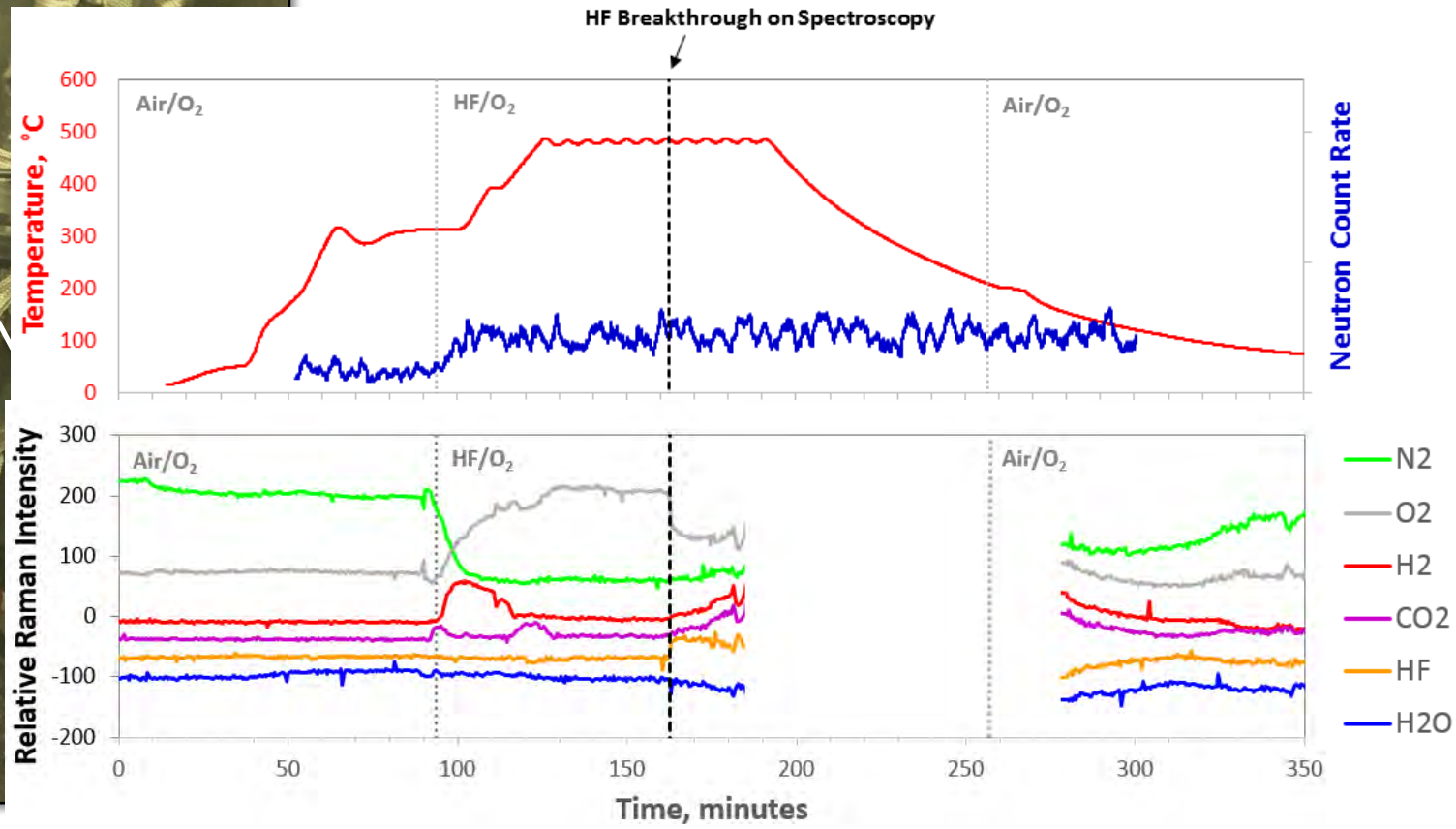


405 nm 532 nm 671 nm

# Other Gas Phase Work




Casella A.J., J.C. Carter, A.M. Lines, J.M. Bello, S.A. Bryan, R.A. Clark, and J.F. Corbey, et al. "In Stream Monitoring of Off-Gasses from Plutonium Fluorination." *Actinide Research Quarterly* Second Quarter 2019, no. 1:31-35, 2019



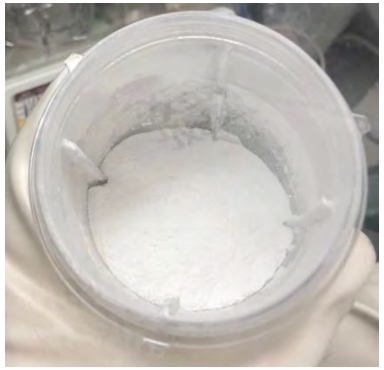
# Examples Within the Molten Salt Realm: Actinides within Molten Chloride Salts

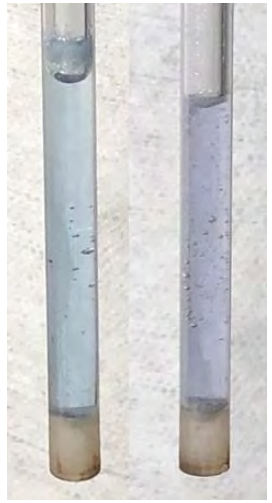
- Building tools that enable **MC&A** of MSRs
- OLM to support:
  - In Situ and Real-time accounting of nuclear material
  - Enabling vendors to find workable solutions to accountancy challenges in liquid fueled reactors

**Accountancy of U**

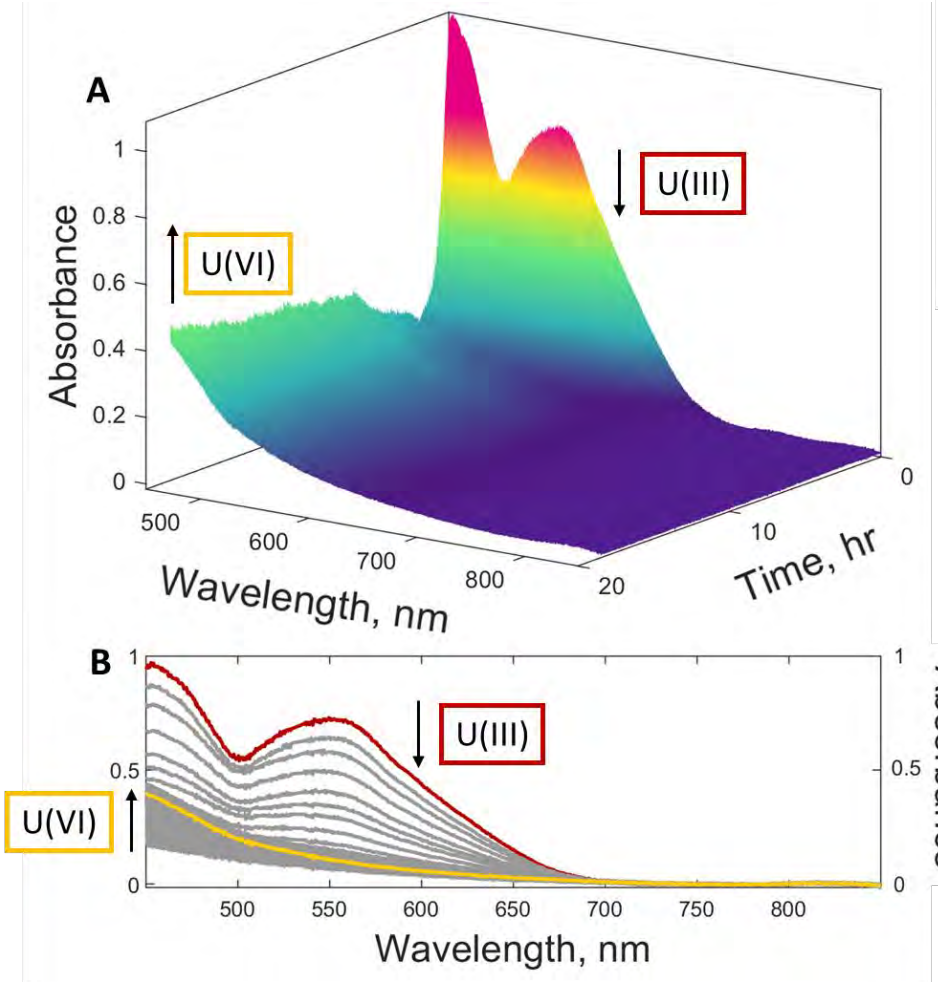


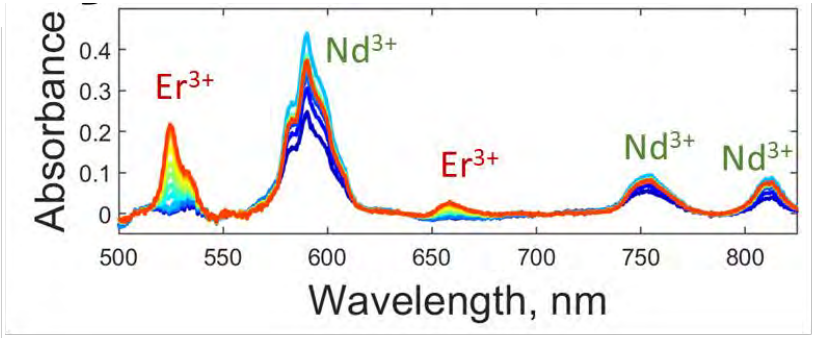
**Collaboration with Industry**

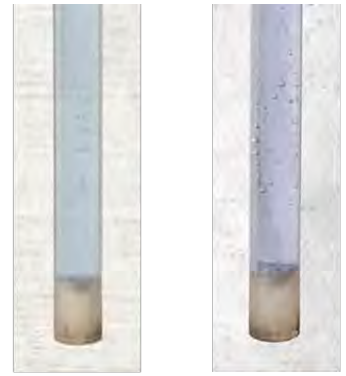


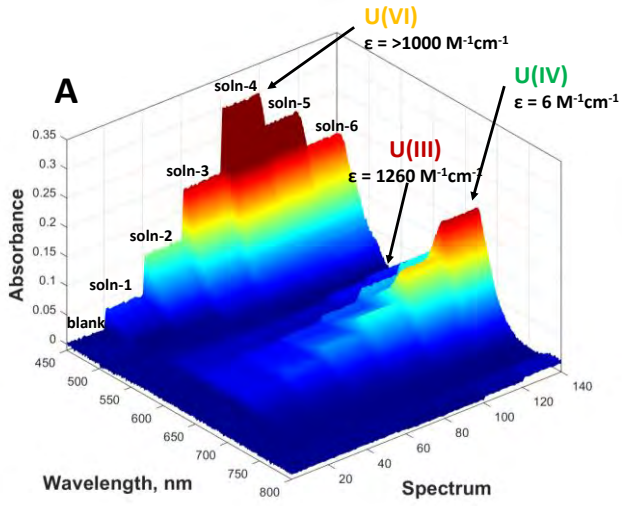



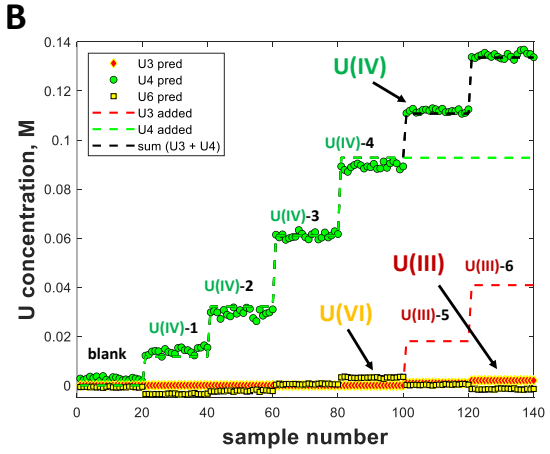
# Other MSR Enabling Technologies:
## In salt melt characterization of f elements, ARS Campaign



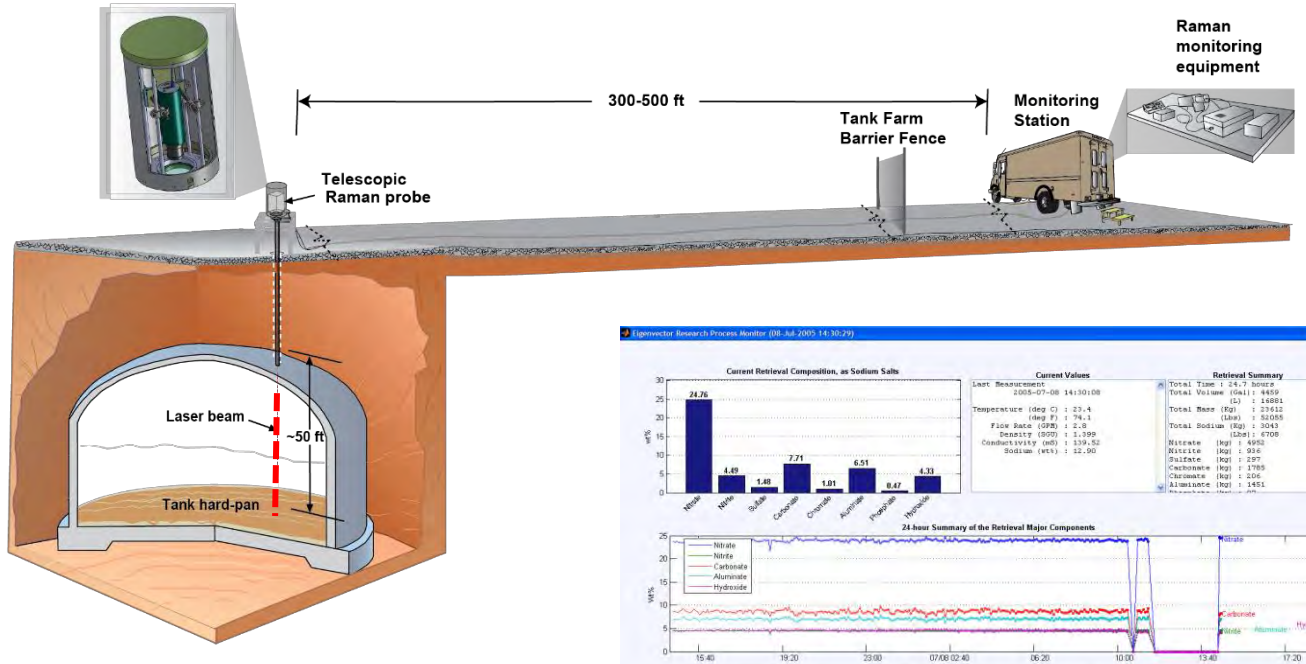



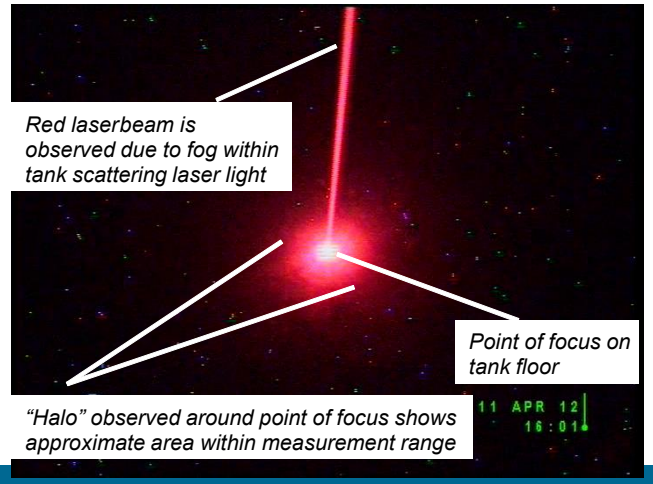





# Legacy Wastes Clean up and Processing: Hanford tanks and hard pans



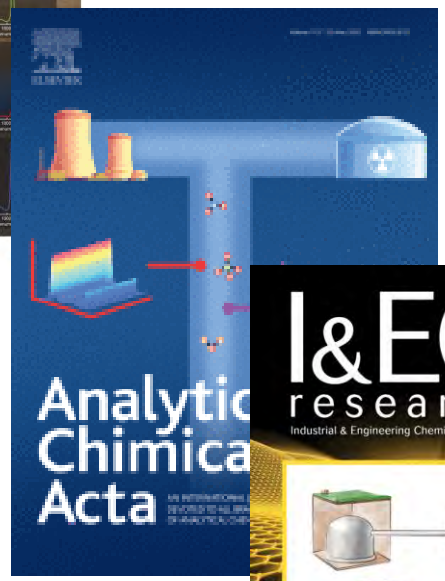




- Telescopic Raman to characterize tank hardpan
- Probe placed at top of riser; Laser focused on hard pan ~50' below

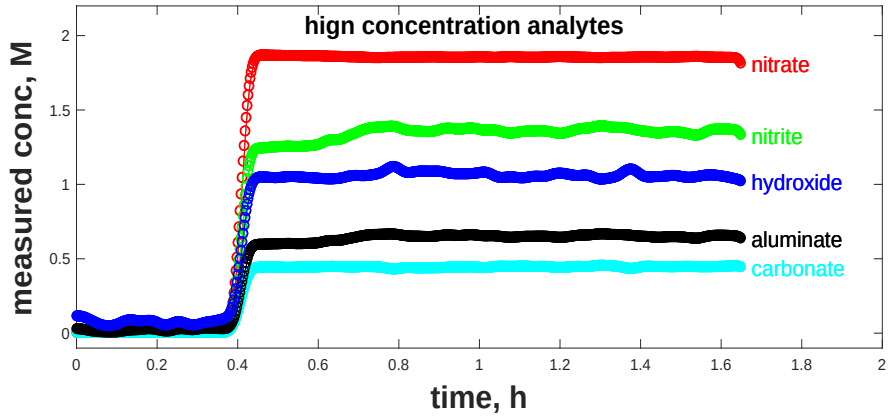
# Legacy Wastes Clean up and Processing: Hanford tanks and hard pans

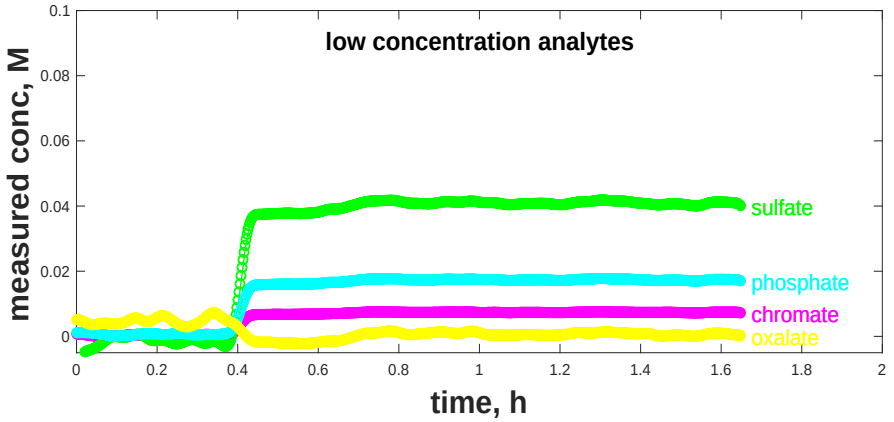

Felmy, Heather; Lackey, Hope; Schafer Medina, Adan; Minette, Michael; Bryan, Samuel; Lines, Amanda, "Leveraging multiple Raman excitation wavelength systems for process monitoring of nuclear waste streams", accepted, February 11, 2022, ***ACS ES&T Water***. DOI: 10.1021/acsestwater.1c00408




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


Lines, A.M., P. Tse, H.M. Felmy, J.D. Wilson, J. Shafer, K. Denslow, A.N. Still, C.K. King, S.A. Bryan. "On-line, real-time analysis of highly complex processing streams: Quantification of analytes in Hanford tank sample", ***Ind. Eng. Chem. Res.***, 2019, 58, 47, 21194-21200.




Analysis of real Hanford samples from tanks:

- AP-105
- AY-102

And simulants

- AP-101
- S-109
- AP-105
- AY-102

# Conclusions

- Optical sensors offer a powerful route to characterize the chemical composition of process streams and samples
- Application within the nuclear field requires adaptation of sensors and probes to withstand harsh environments
  - Optimizing/developing window materials to enhance performance/reduce corrosion/darkening
  - Radiation hardening/testing
- Application also requires development of analytical tool kits
  - Making smart sensors

# Acknowledgements

U.S. DOE NE

**PNNL Team:**

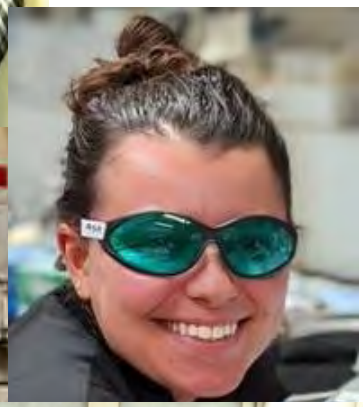
Amanda Lines
Sam Bryan
Heather Felmy
Shirmir Branch
Adan Schafer Medina
Richard Cox
Bethany Kersten
Brian Riley

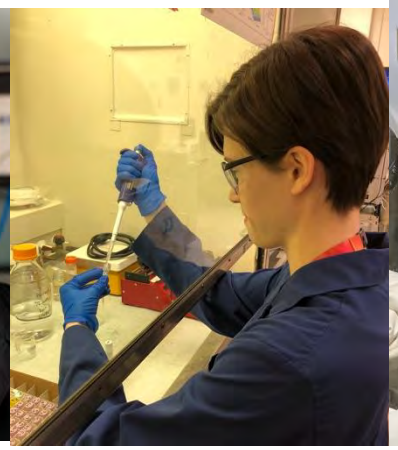
**ORNL Team:**

Joanna Mcfarlane
Hunter Andrews
Kevin Robb

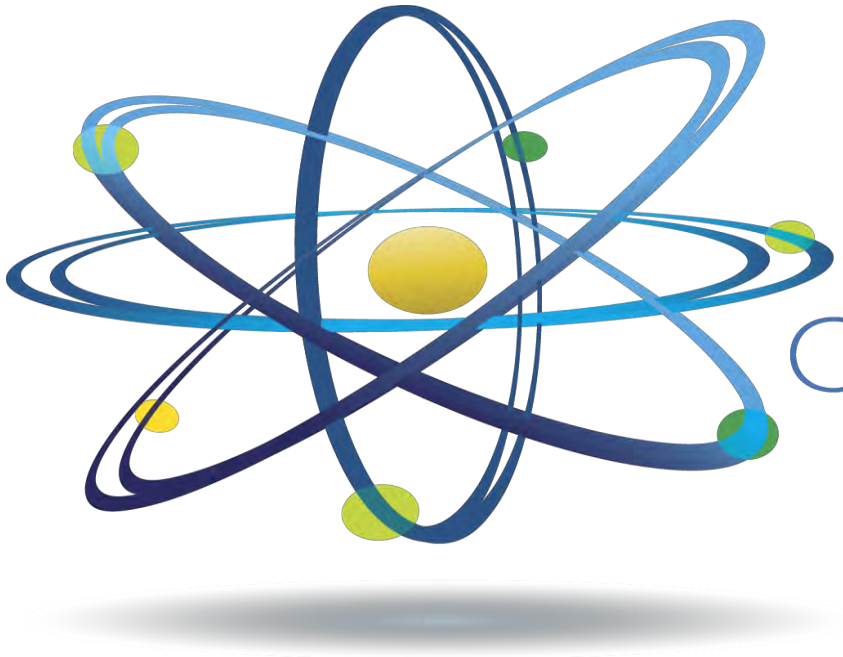
**Students/visiting faculty/guests:**

Prof. Gilbert Nelson (C. Idaho)
Job Bello (Spectra Solutions Inc.)
Hope Lackey (WSU)
Molly Vitale-Sullivan (SULI)
Andrew Clifford
Bethany Kersten



# Questions



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Molten Salt Reactor
PROGRAM