ADVANCED REACTOR SAFEGUARDS & SECURITY

Process monitoring for MC&A: Optical spectroscopy

FY26 ART-MSR Program Review

PRESENTED BY

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On-line or In-line Measurement for Real-time, Continuous Salt Analysis

- MSRs are receiving significant attention due to the potential benefits they offer in safety and efficiency
- MSR systems pose unique challenges to MC&A analysis
  - Due to complexity of the salt/reactor system
  - Particularly in the case of on-line conditioning or treatment of salts
- In situ and real-time analysis of salt chemistry is a potential game changer in terms of enabling operators to understand MC&A impacts

Continuous (On-line):
lower accuracy but unparallel insight into trends and notably improved relevance in statistical sampling

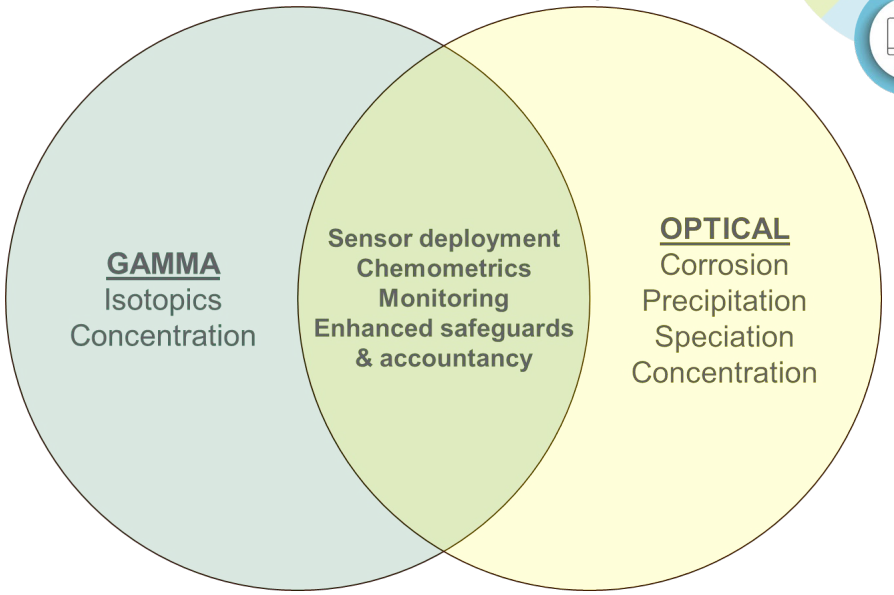
Vs

Periodic (Off-line):
higher accuracy but limited to no insight into trends and greater sensitivity to heterogeneous sampling

Combining for a comprehensive and accurate analysis

Selecting Impactful Tools for On-line Monitoring of MSRs

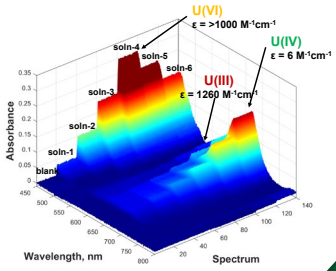
- Ultimately multiple on- or in-line monitoring tools will be needed to provide the full picture
- Two key tools for chemical/isotopic analysis include Raman and gamma spectroscopy
- **Goal: provide needed information and measurement uncertainty for actinides and other key targets without placing undue burden on the MSR system**



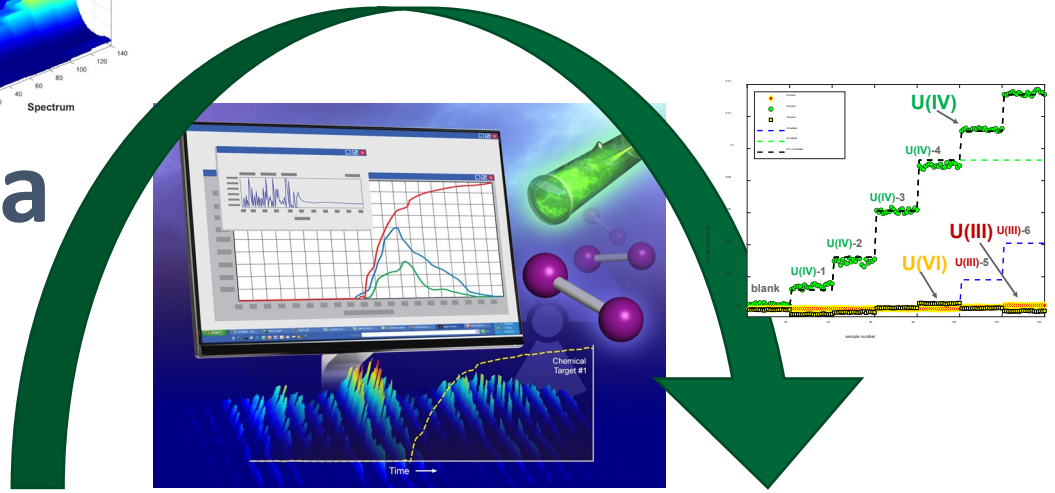
- Combination of multiple analytical techniques builds a more complete description of complex chemical information
  - Optical (vis-NIR, Raman) = oxidation state, precipitation, speciation, etc.
  - Gamma = isotopic information
- Application of chemometrics to data analysis to improve accuracy and flexibility in analyzing highly complex data exhibiting multiple interfering signals

Sensor Impact is Solidified by Partnering with Robust and Automated Data Analysis

- Sensor data will be complex. To realize benefits of on-line monitoring, automated data analysis is essential
- Furthermore, fusing or combining data from multiple sensors to support analysis builds a more robust tool that can handle salt variability and properly highlight potential heterogeneity
- **Real time insight into complex chemistry**



Data

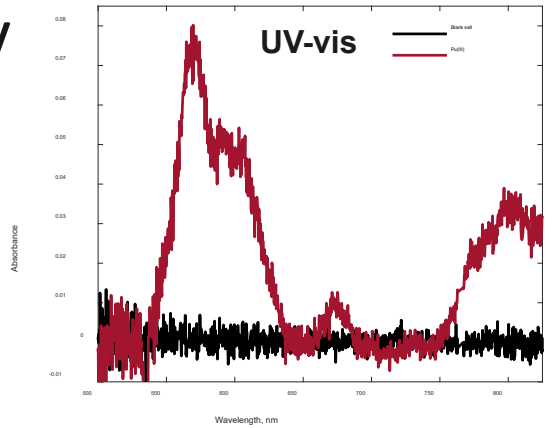


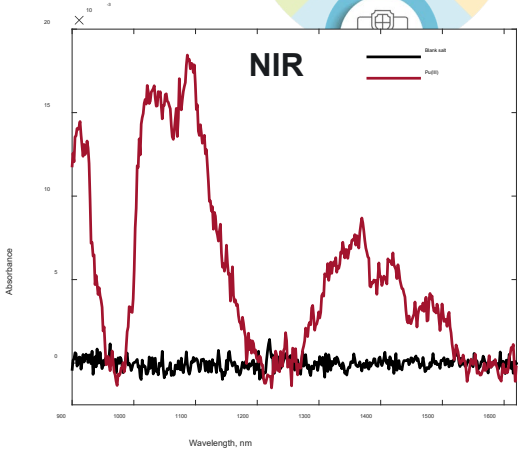
Information

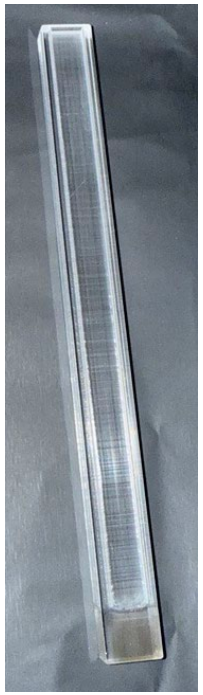
Enabling researchers and operators to understand complex processes with *in situ* and real-time feedback on process conditions

Considerations for Online Monitoring

- Target optimal quantification uncertainty for various analytical techniques
- Variable experimental scale
  - Calibration transfer
- Discernment between operation/safeguards effects
  - Temperature, corrosion, etc.
- Modeling techniques
- Monitoring hardware/tools for deployment







*developed under other efforts

Fundamental characterization: **Chemometrics**

Tools for interrogation: **Hardware**

On-line monitoring

Analyte accountancy

- Building widely applicable chemometric models and solidifying understanding of achievable uncertainties requires collection of a significant amount of data
- A select list of measurable chemical systems is shown here
- A sequential list of experiments and usability of data will be shown next

Analyte	Molar extinction coeff. (abs)	Chem. form(s) (experimental)	Observed challenges for optical measurement
U(IV)	6.46 $M^{-1}cm^{-1}$ (670 nm) 13 $M^{-1}cm^{-1}$ (1100 nm)	UCl_4	Low molar absorptivity
U(III)	1260 $M^{-1}cm^{-1}$ (480 nm) 17.5 $M^{-1}cm^{-1}$ (1100 nm)	UCl_3	Plating out in presence of some corrosion and FP surrogates
$[UO_2]^{2+}$	57.2 $M^{-1}cm^{-1}$ (450 nm)	UCl_3 (oxidation to U^{6+})	Indicates presence of oxygen in molten salt system
Pu(III)	20 $M^{-1}cm^{-1}$ (563 nm) 0.05 $M^{-1}cm^{-1}$ (1100 nm)	K_2PuCl_6 Na_2PuCl_6 $PuCl_3$	Low solubility at lower concentrations; optical fingerprint can overlap other actinide species
Nd(III)	10.7 $M^{-1}cm^{-1}$ (589 nm)	$NdCl_3$	Optical fingerprint can overlap actinide species
Eu(III)	420 $M^{-1}cm^{-1}$ (330 nm)	$EuCl_3$	Precipitation with corrosion products
Er(III)	9.2 $M^{-1}cm^{-1}$ (377 nm)	$ErCl_3$	Low molar absorptivity
Ho(III)	10.10 $M^{-1}cm^{-1}$ (450 nm)	$HoCl_3$	Low molar absorptivity
Dy(III)	0.233 $M^{-1}cm^{-1}$ (1111 nm)	$DyCl_3$	Low molar absorptivity; optical fingerprint can overlap actinide species
Cr(III)	46 $M^{-1}cm^{-1}$ (545 nm)	$CrCl_3$	Plating out in presence of other analytes
Co(II)	204 $M^{-1}cm^{-1}$ (609 nm)	$CoCl_2$	Plating out in presence of other analytes
Fe(III)	398 $M^{-1}cm^{-1}$ (295 nm)	$FeCl_3$	Optical fingerprint overlaps with actinides of interest
Ni(II)	63.8$M^{-1}cm^{-1}$ (628 nm)	$NiCl_2$	Plating out in presence of other analytes

Accountancy in mixed analyte systems

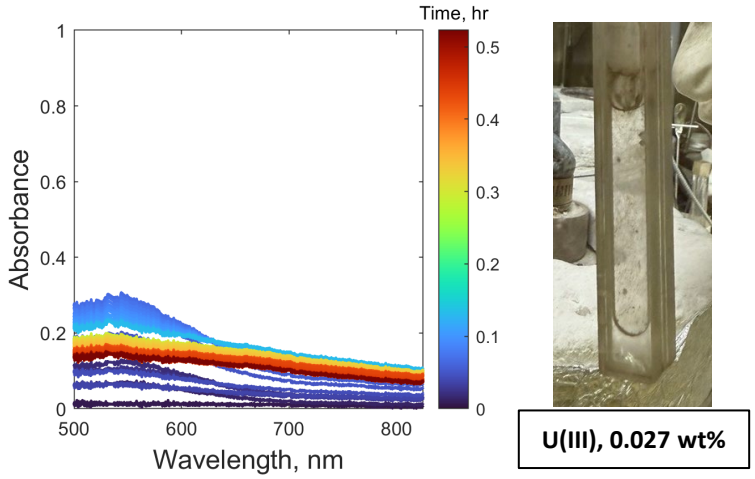
- Several variants of mixed salt systems were studied
- Three examples of experimental schemes are shown here
- Experimental approaches to mixed U/Pu systems precipitated, meaning data could not be leveraged for model building efforts

Experiment #1	Experiment #2	Experiment #3
1. Blank salt 2. Add U 3. Add Nd (precipitation)	1. Blank salt 2. Add Nd 3. Add Cr 4. Add U (precipitation)	1. Blank salt 2. Add Pu (precipitation) 3. Add Zr (dissolution) 4. Add Nd 5. Add U (precipitation) 6. Add Zr (no change)

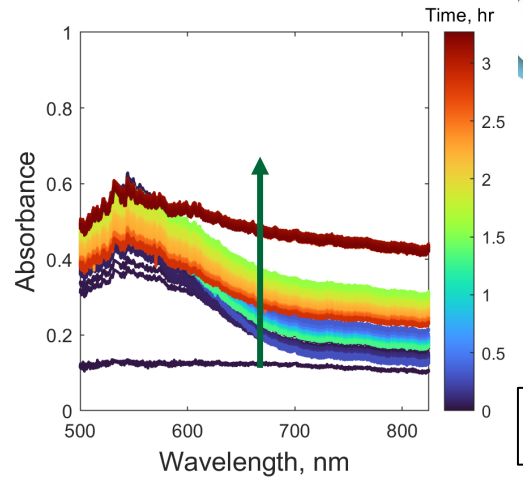
A review of the multiple mixed system attempts is detailed in PNNL-39142.

Precipitation can still be tracked

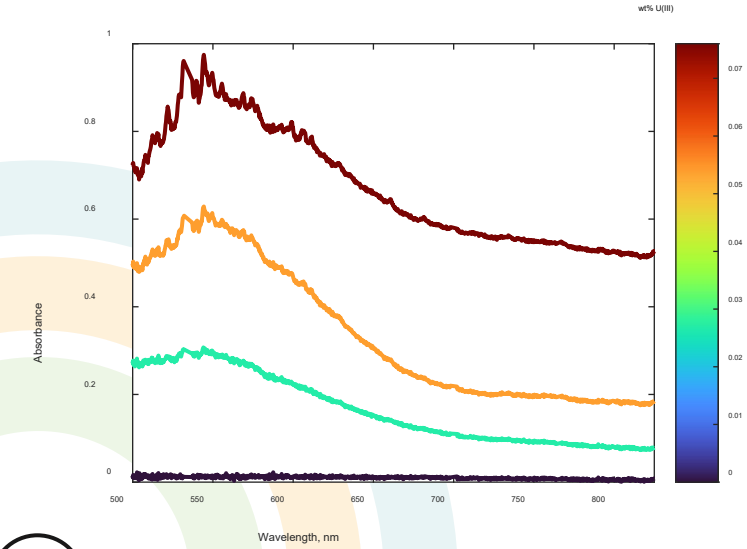
- Dissolved U species
- Oxidation and addition of Pu causes formation of precipitates
- Quantifiable U fingerprint still observable

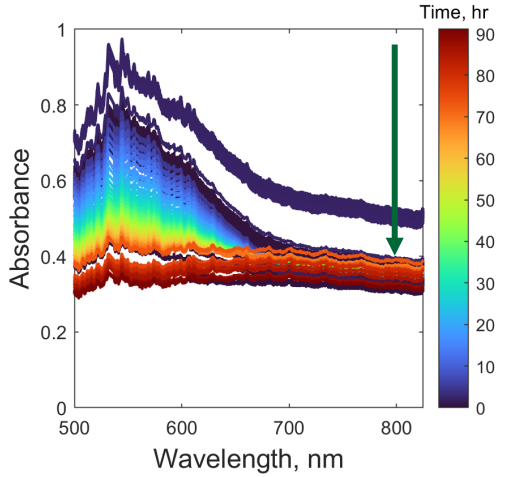


U(III), 0.027 wt%



U(III), 0.076 wt%
Zr(IV), 0.034 wt%



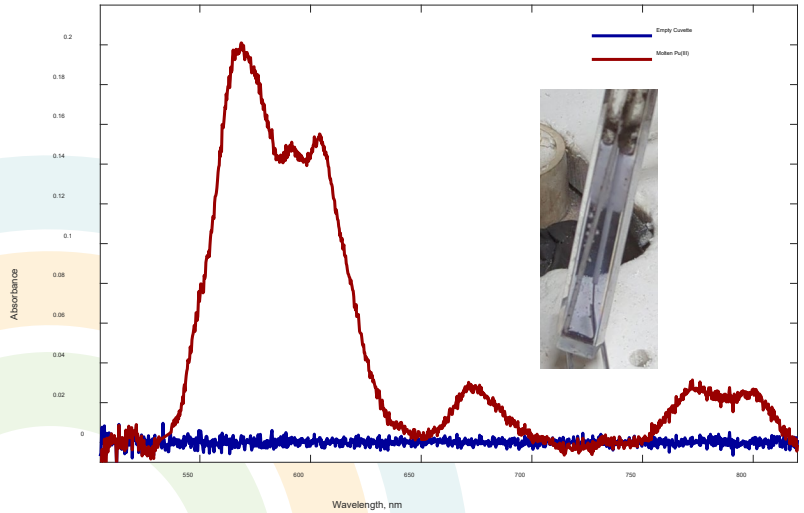


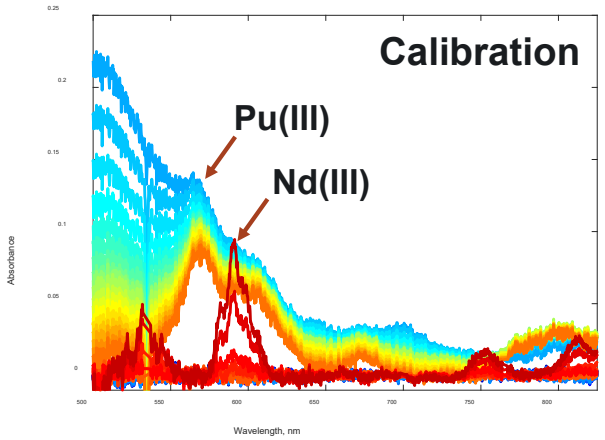
Pu(IV), 0.068 wt%
U(III), 0.071 wt %
Zr(IV), 0.089 wt%

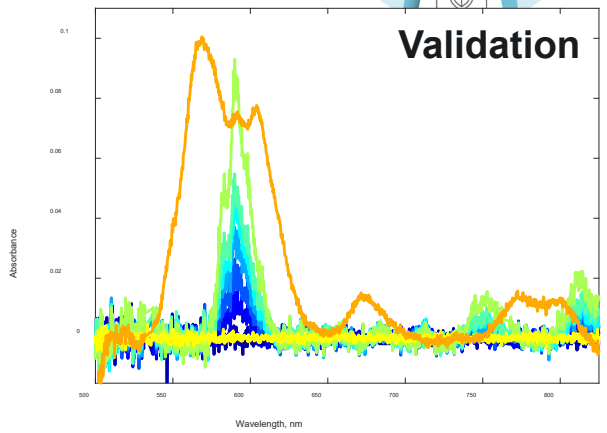
"Bad" data is not bad data

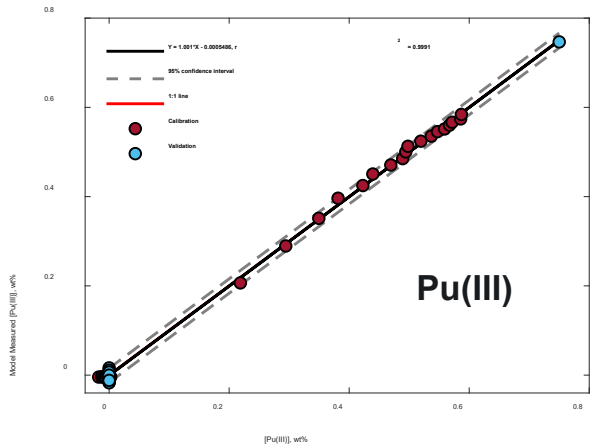
Accountancy of Pu in mixed analytes in molten chloride

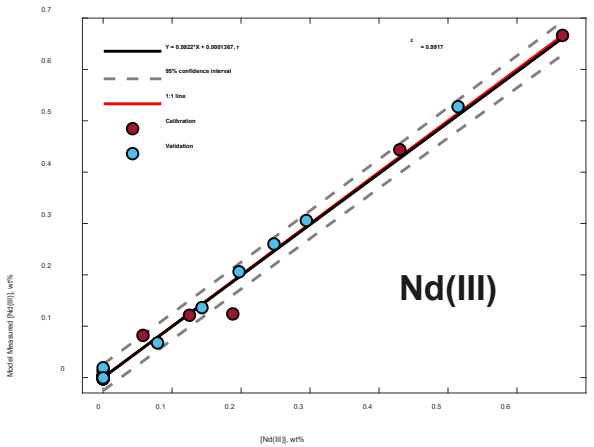
- Pu in single and multi-component salts was studied to gain an understanding of modeling uncertainties
- Individual calibration (model building) and validation (model testing) data sets were completed/collected
- Calibration data is shown here





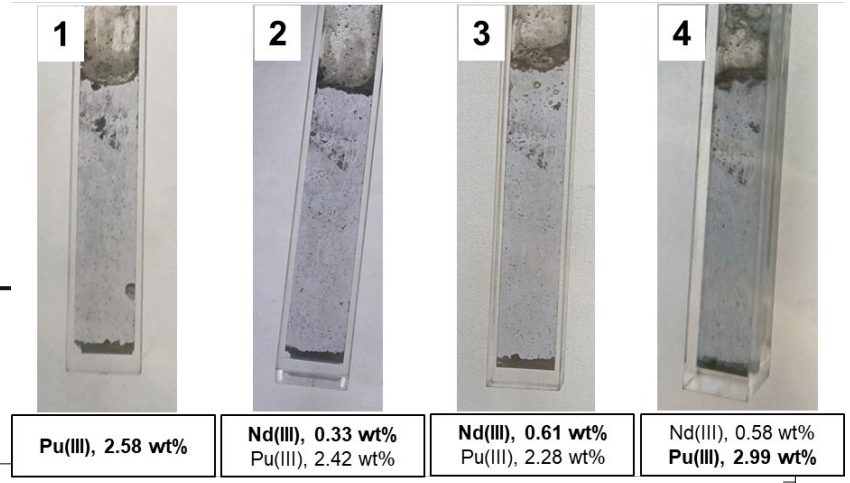


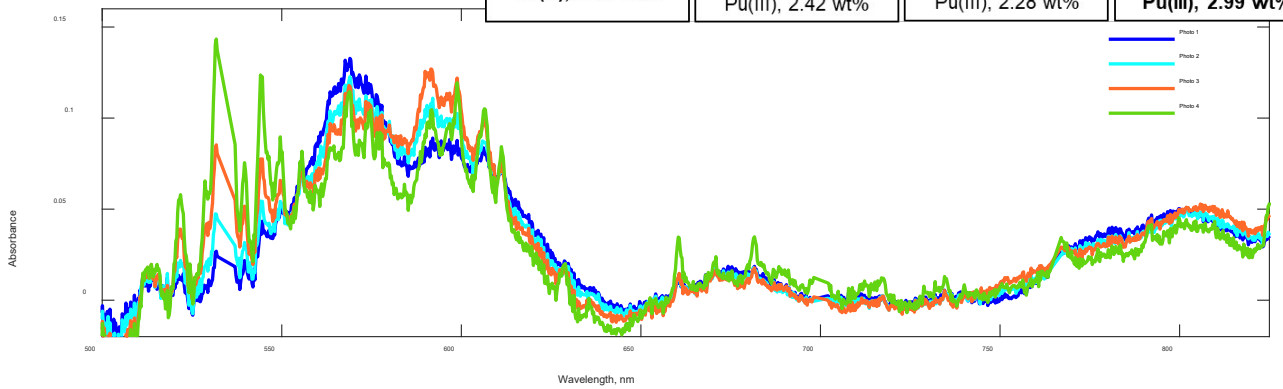




Example of better-behaved system

- Pu (λ_{max} = 568 nm) and Nd (λ_{max} = 589 nm) have broad, overlapping peaks
- Precipitation impacts use of quantification tools such as Partial Least Squares (PLS) Regression
- Multivariate Curve Resolution (MCR) loadings discern impact of interfering species (Nd) on target analyte (Pu)

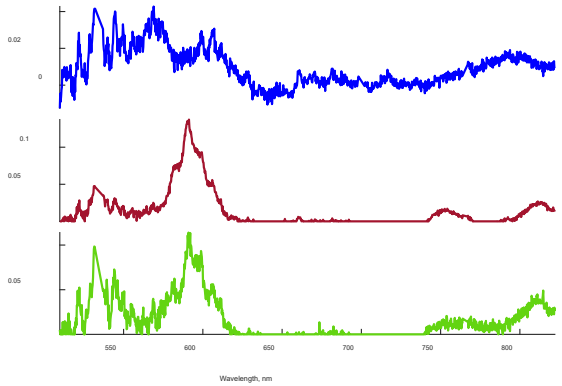


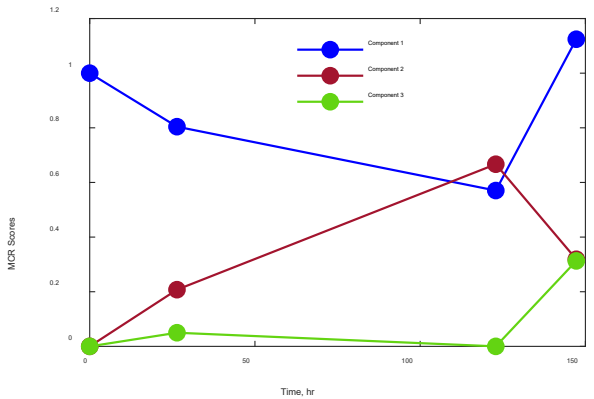


Pu(III) Component 1

Nd(III) Component 2

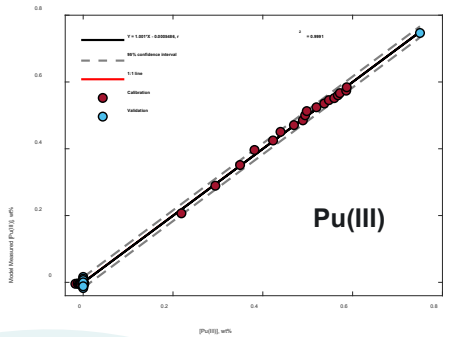
Pu(III) Component 3

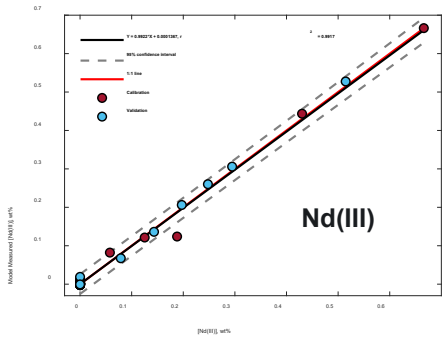




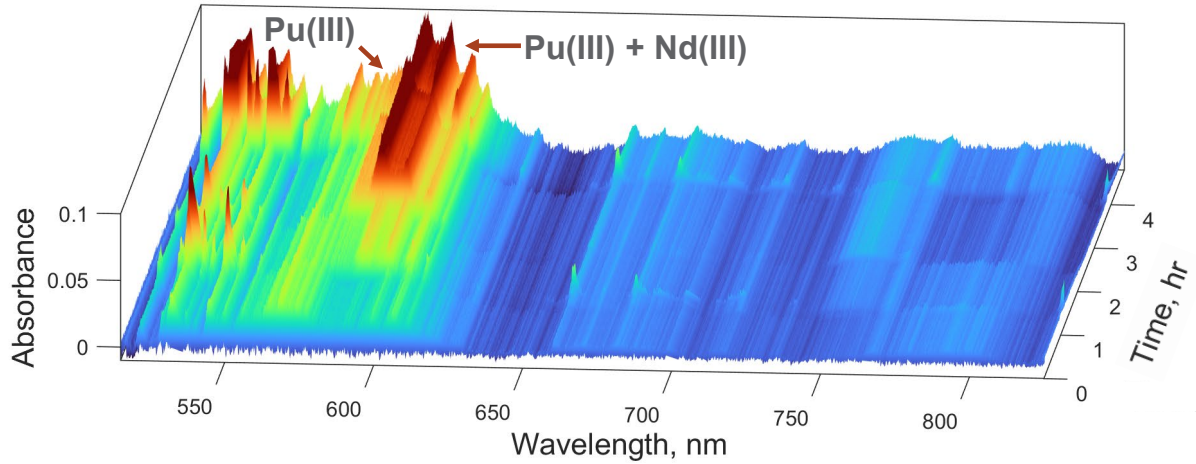
Accountancy of Pu in mixed analytes

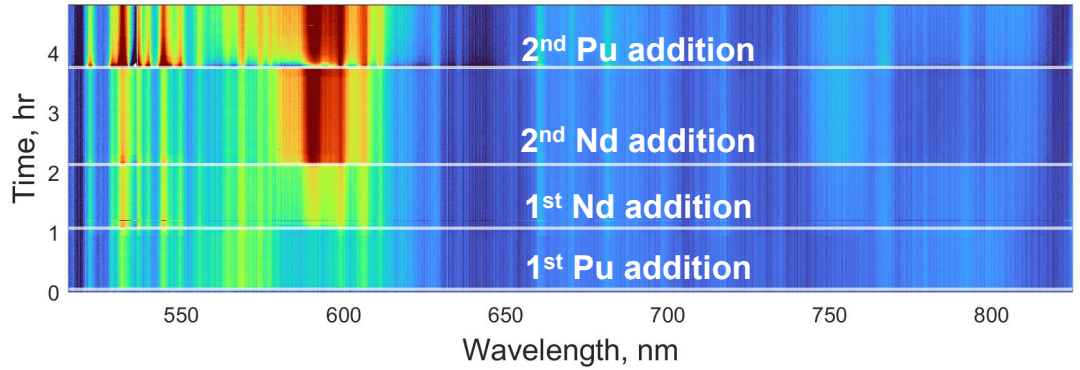
- Validation runs were completed on mixed Pu/Nd systems looking at different ratios of Pu to Nd for each experiment

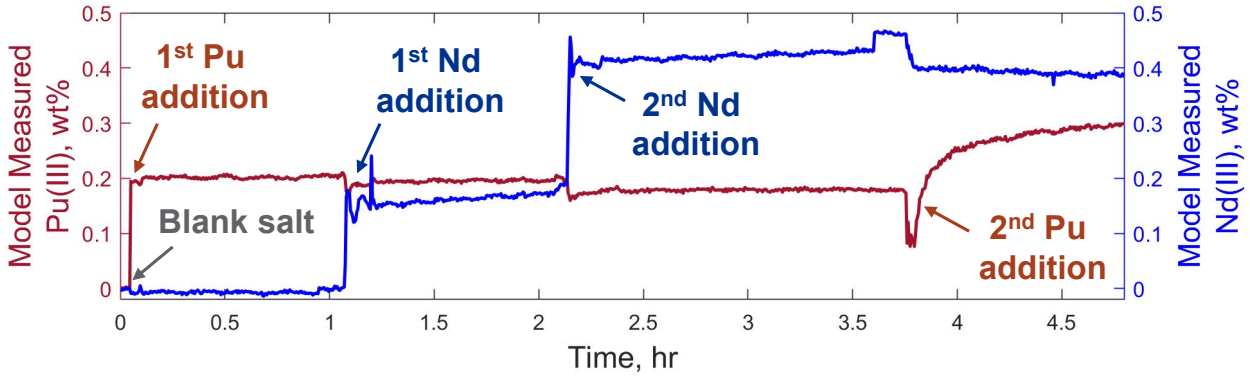




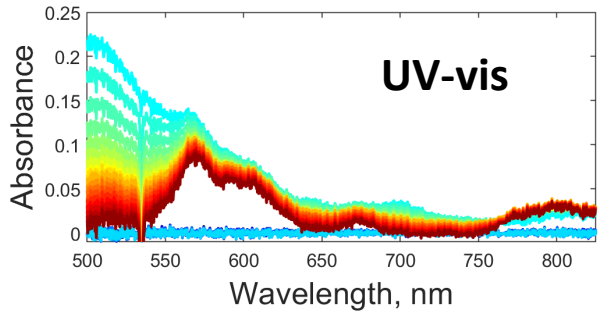
Model Statistics	Pu Uncertainty, wt%	Pu % Uncertainty	Nd Uncertainty, wt%	Nd % Uncertainty
RMSEC	0.00753	1.3	0.0123	1.8
RMSECV	0.00835	1.4	0.0148	2.2
RMSEP	0.0100	1.7	0.0109	1.6

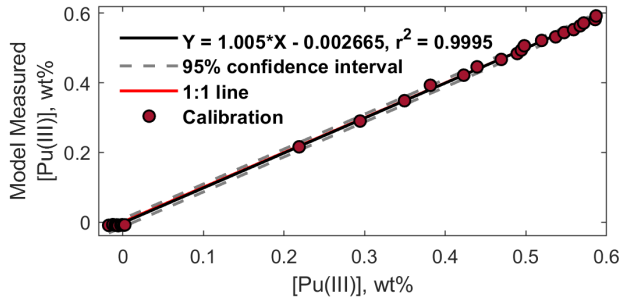


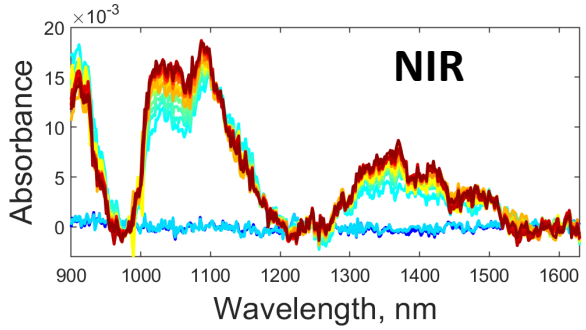


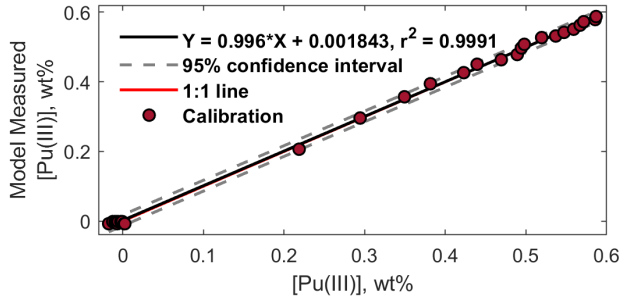


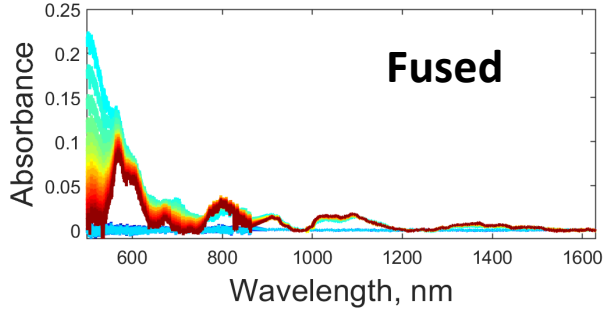
Data fusion: Robust monitoring

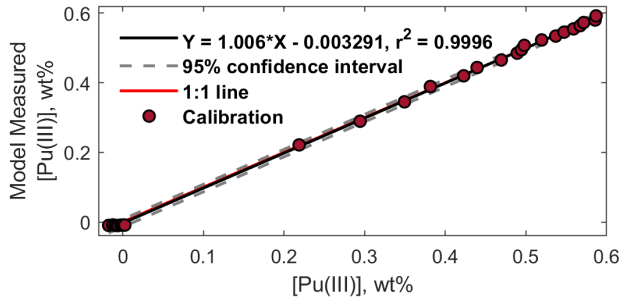












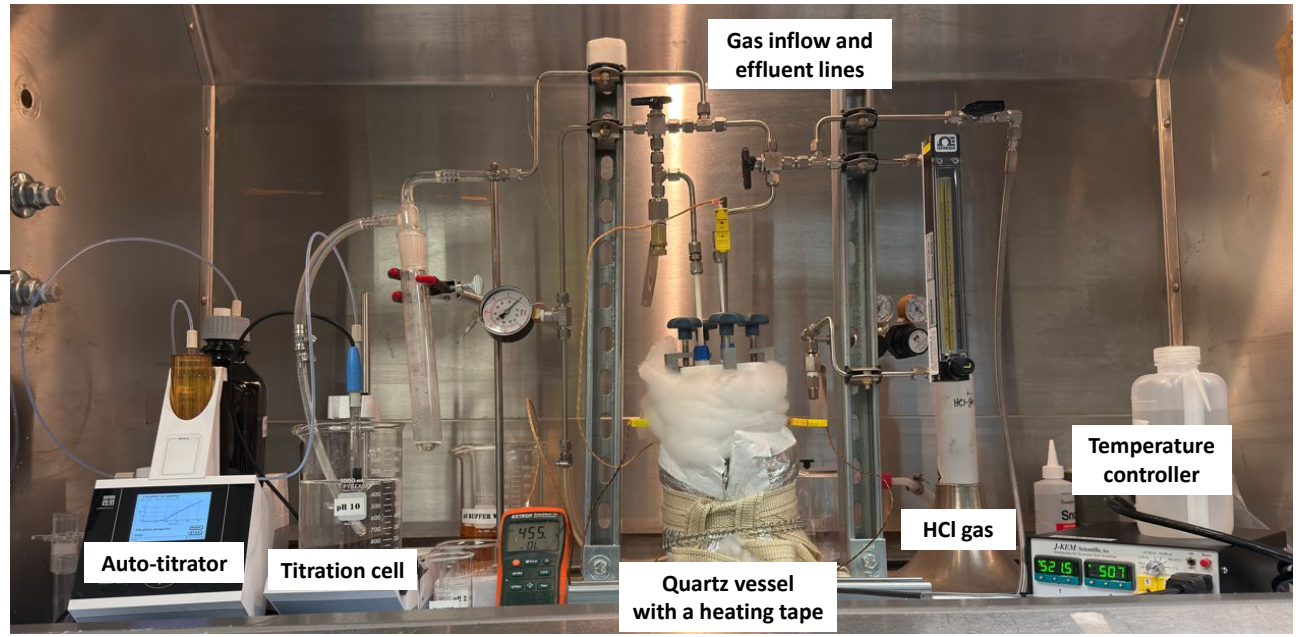
System	RMSEC, wt%	RMSECV, wt%	% Uncertainty
UV-vis	0.005577	0.006985	1.2
NIR	0.007369	0.008596	1.5
Fused	0.005481	0.006600	1.1

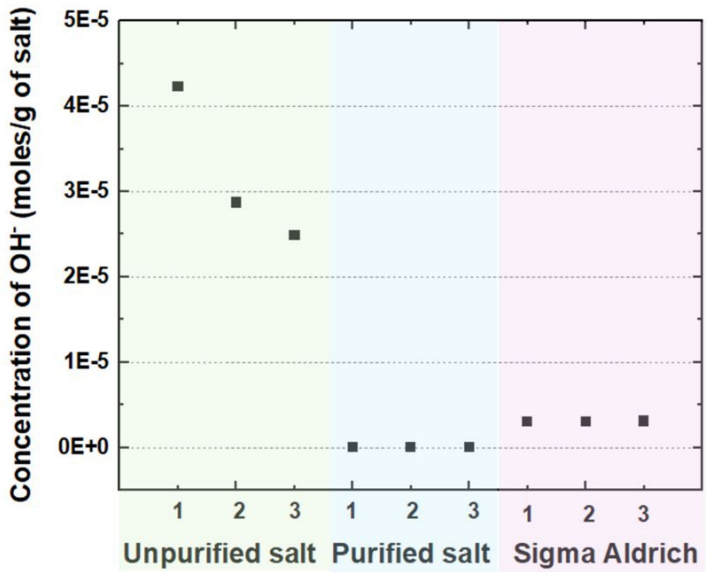
- Optical spectroscopy can leverage the entire spectrum for robust monitoring
- The model performance for one analytical technique can be used to validate another technique
- These model techniques are not limited to optical spectroscopy

Some Notes Regarding Precipitation

- Given the goal to assess accuracy/uncertainty of models, data of precipitated systems cannot be used in modeling
  - Model performance is assessed based on “known” values, precipitation adds significant uncertainty to the “known” concentration of dissolved metal species
  - U/Pu systems are a key target of study

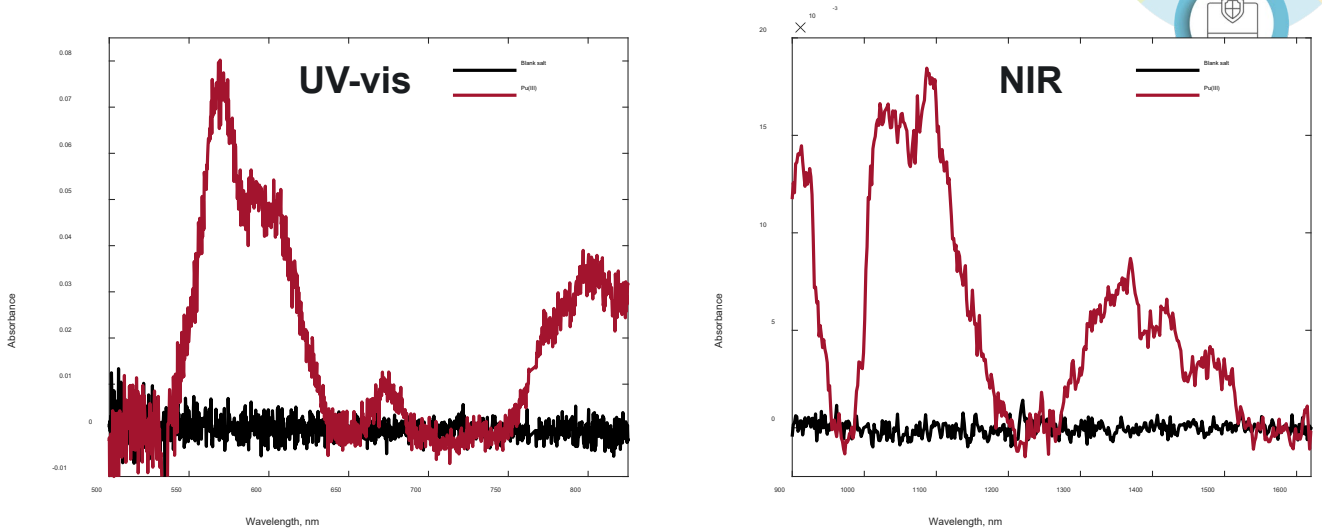
- Salt purification systems underway
  - Non-rad purification system demonstrated in FY25
  - Continuing with rad purification system in FY26 to allow for a Pu/U study in the purified salt

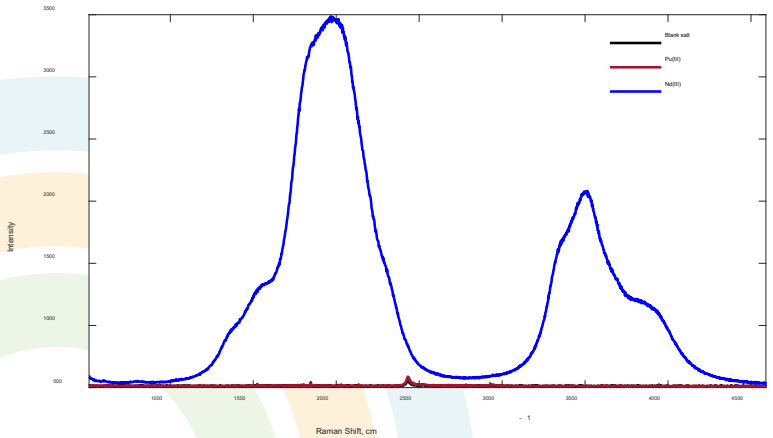




Expanding Sensors to Provide More System Flexibility

- Expansion of absorbance testing
  - Adding NIR to chemometric library
  - Potential “quiet” spots in high U systems





- Analytes of interest (e.g. U and Pu) have optical fingerprints in the NIR where some interferent species (e.g. Nd, Cr) have overlapping fingerprints

Paths forward/Acknowledgements

- Chemometric data fusion demonstrating with optical and gamma spectroscopy
- Technical evaluation on the complexity of molten salt chemistry for online monitoring
- Testing with robust monitoring tools

- PNNL OLM team
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  - Adan Schafer Medina
  - Suhee Choi
  - Jason Rakos
  - Forrest Heller
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  - Grey Batie
  - Erin Good

Questions?

Thank you!