Office Of Nuclear Energy
Sensors and Instrumentation
Annual Review Meeting
Nuclear Technology
Research and Development (NE-4) overview

ON-LINE MONITORING FOR CHEMICAL CHARACTERIZATION

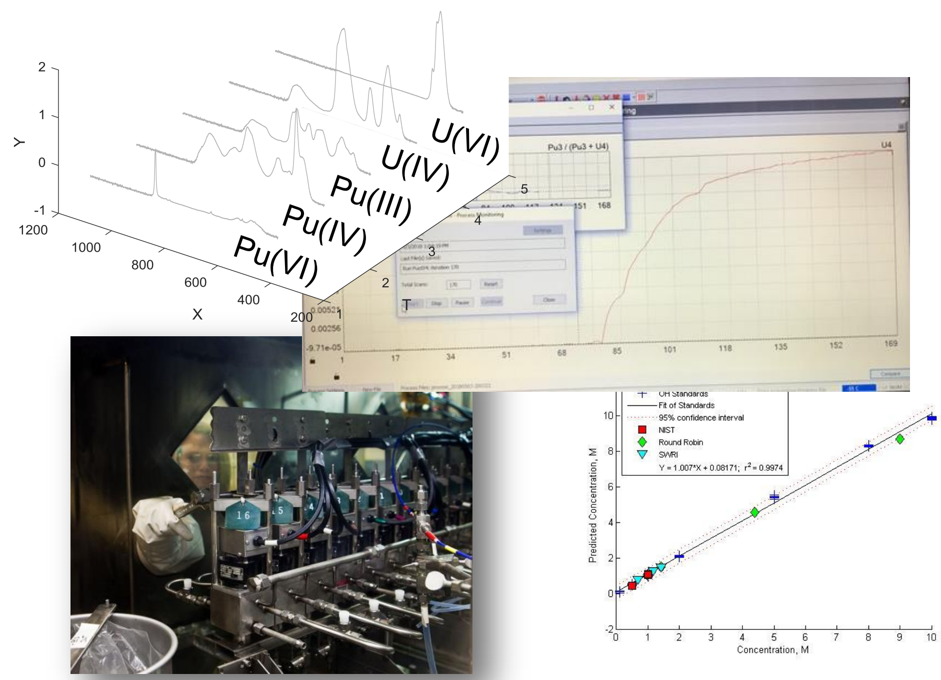
Amanda M. Lines,

Gregg J. Lumetta, Samuel A. Bryan

Goals of On-Line Monitoring

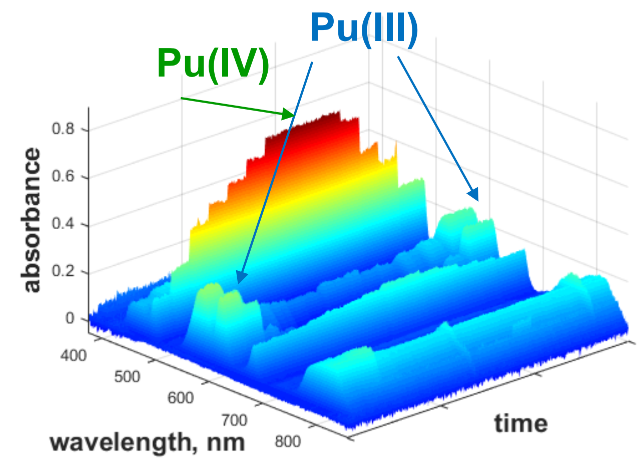
Advancement of on-line monitoring systems that provide real-time quantification of solution species and physical property measurements during process operations in nuclear fuel reprocessing applications

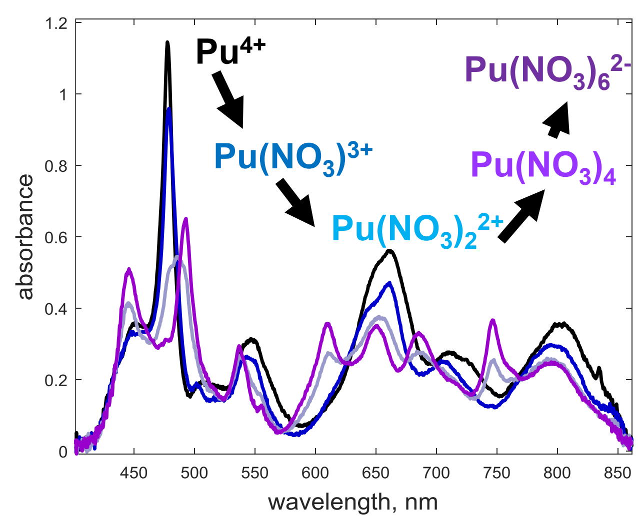
- Process control
- Process optimization
- Safeguard verification



Optical spectroscopy:
Unique benefits

- Provides chemical information
  - Oxidation State
    - Essential information for control of systems: separations, molten salt reactors, etc.
  - Speciation
    - Essential information to understand/control separation efficiency or general system behavior
- Fast
- Robust
- Versatile





Approach:

Raman spectroscopy

- **Actinide oxide ions** (UO_2^{2+})
- **Organics**:
  - solvent components and complexants
- **Inorganic oxo-anions**
  - NO_3^-, CO_3^{2-}, OH^-, SO_4^{2-}
- **Water, acid (H^+), base (OH^-)**
- **pH** of weak acid buffer systems

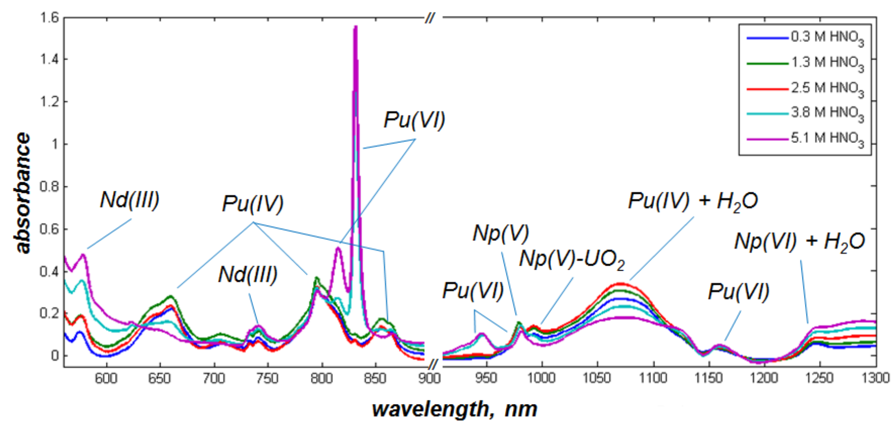
Numerous, versatile tools available to capture fingerprints of huge range of fission products/species of interest to the fuel cycle

UV-vis-NIR absorption

- **Actinides and lanthanides in multiple oxidation states**
  - Pu (III/IV/VI)
  - Np (III/IV/V/VI)
- **Various metal-ligand complexes**

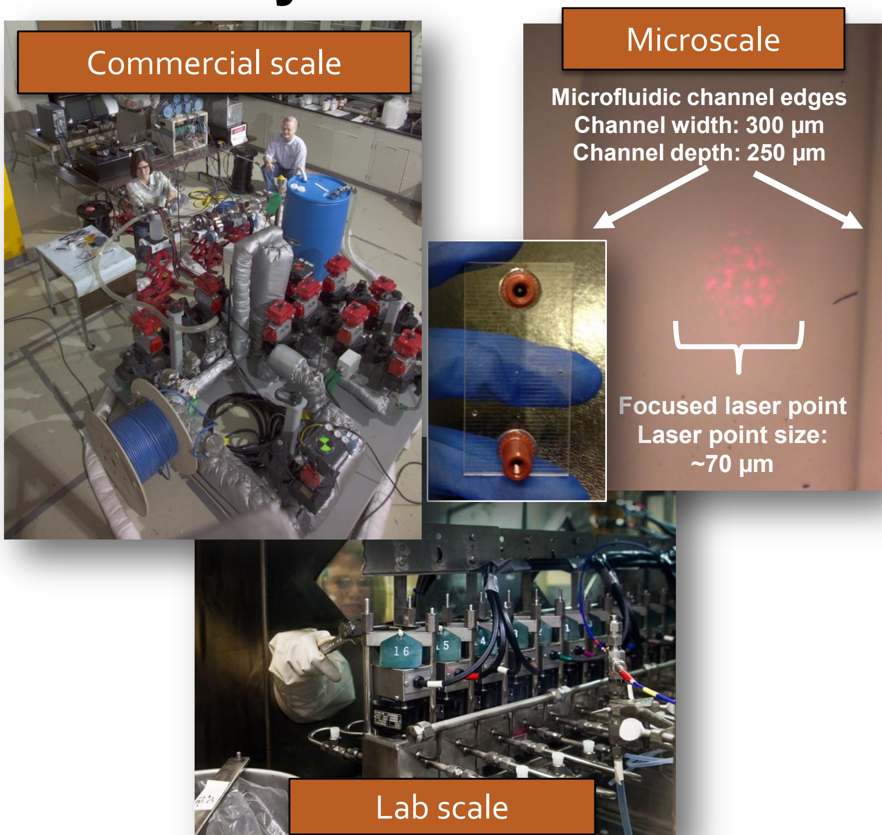
Several other options

- **FTIR**
  - Organic complexants
- **Light scatter**
  - turbidity
- **Optical density**
  - Formation of complexes



Optical spectroscopy:
Versatility

System scale



System matrix

Solid

Liquid

Gas

Molten salt

Applications

- DOE NE
  - CoDCon (Co-decontamination project)
  - On-line process monitoring

> - used nuclear fuel simulant (complex signals)
> - aqueous and non-aqueous streams
> - Micro and lab scale applications
> - Process control

- EM
  - On-line monitoring for liquids processing
  - On-line monitoring of off-gas condensate
  - In-situ characterization of tank solids

> - Complex Hanford tank waste chemical systems
> - Process control and validation
> - Lab and commercial scale applications
> - Design for highly regulated processes

- Internal
  - On-line monitoring of actinides in molten salts
  - On-line monitoring of gaseous fluorination products

> - High temperature, high corrosion
> - Laying foundation for future advancements

Applications

- DOE NE
  - CoDCon (Co-decontamination project)
  - On-line process monitoring

- used nuclear fuel simulant (complex signals)
- aqueous and non-aqueous streams
- Micro and lab scale applications
- Process control

- EM
  - On-line monitoring for liquids processing
  - On-line monitoring of off-gas condensate
  - In-situ characterization of tank solids

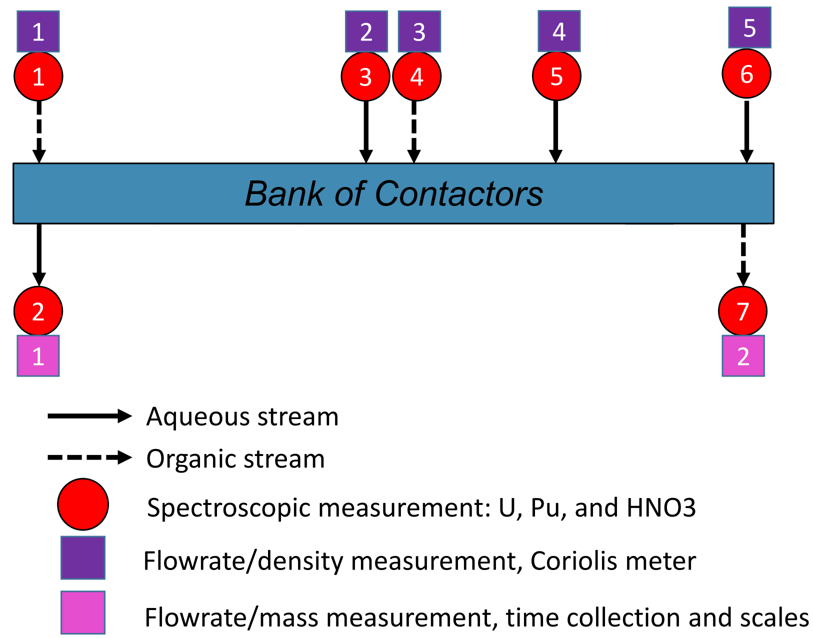
- Complex Hanford tank waste chemical systems
- Process control and validation
- Lab and commercial scale applications
- Design for highly regulated processes

- Internal
  - On-line monitoring of actinides in molten salts
  - On-line monitoring of gaseous fluorination products

- High temperature, high corrosion
- Laying foundation for future advancements

CoDCon:
On-line monitoring

- On-line monitoring flow cells installed at all inlets and outlets of the bank of contactors
- Flow cells allow for measurement of UV-vis and Raman signals
- Data is analyzed in real-time using chemometric models to quantify target analytes
- Real-time analysis informs operators and allows for process adjustments to maintain target product output
- Mass flow measurements are also collected and, in future designs, can be correlated to spectroscopic concentration measurements to provide mass balance

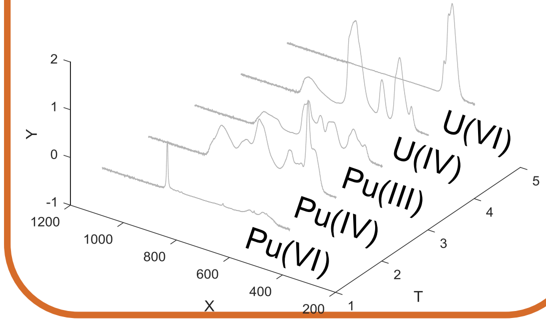


Methodology of on-line monitor development:
From proof-of-concept to final output

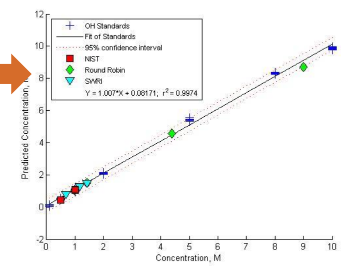
U.S. DEPARTMENT OF ENERGY | Office of Nuclear Energy

NTRD Nuclear Technology Research & Development

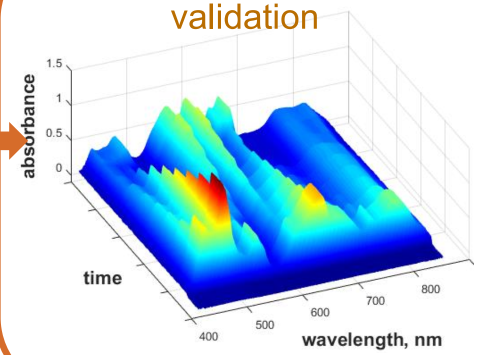
Identify target analytes and collect representative training set



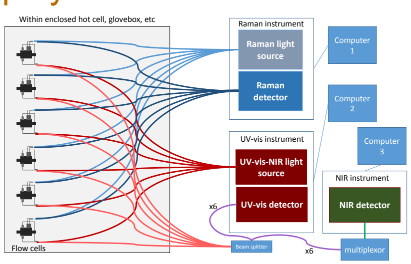
Build chemometric models



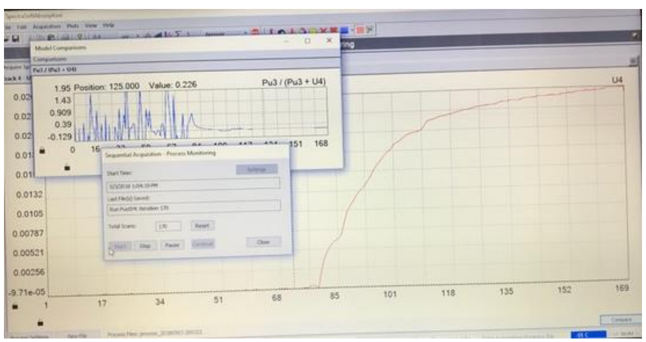
On-line monitoring validation



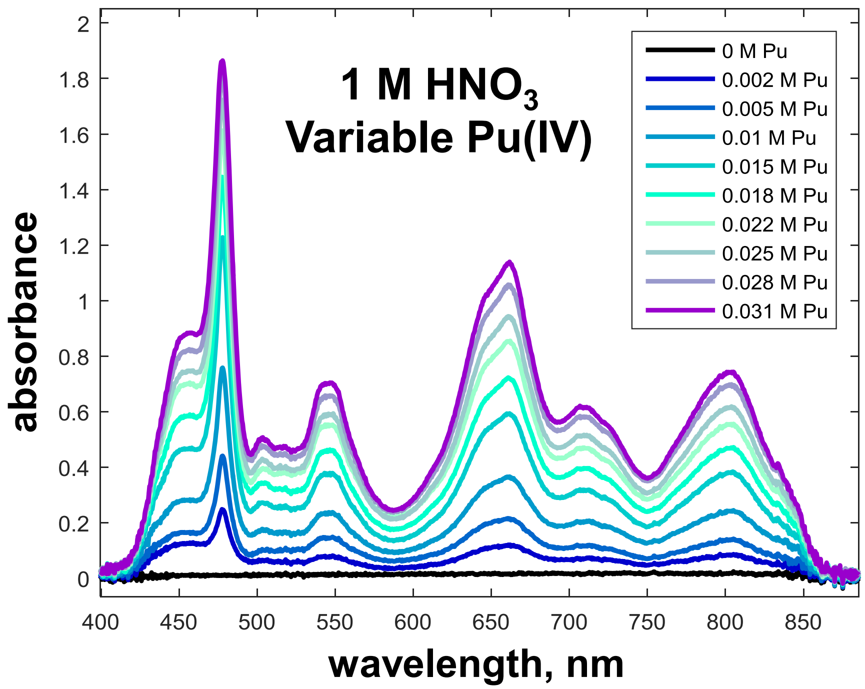
Deployment of instrumentation



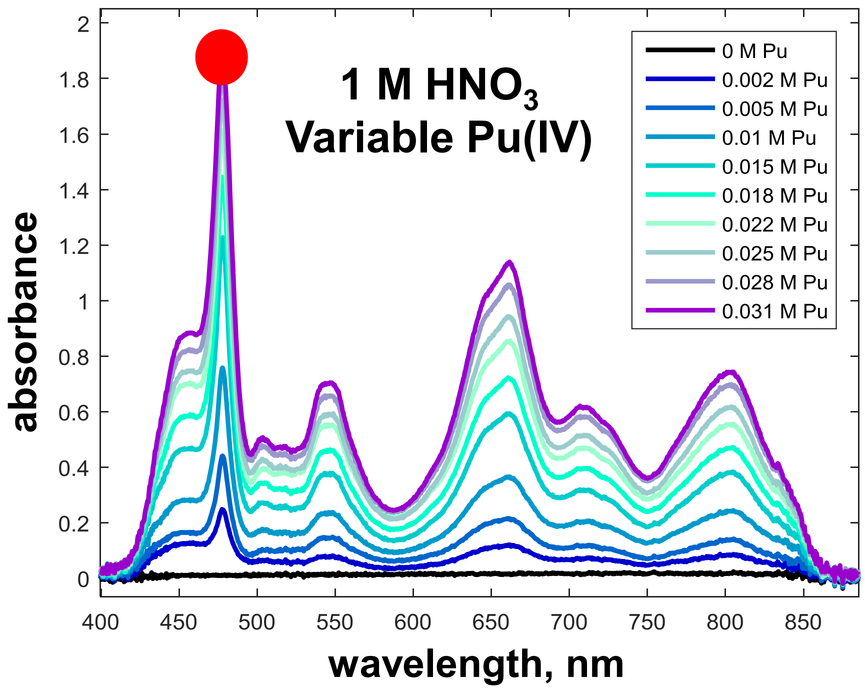
Real-time analysis: turning data into info

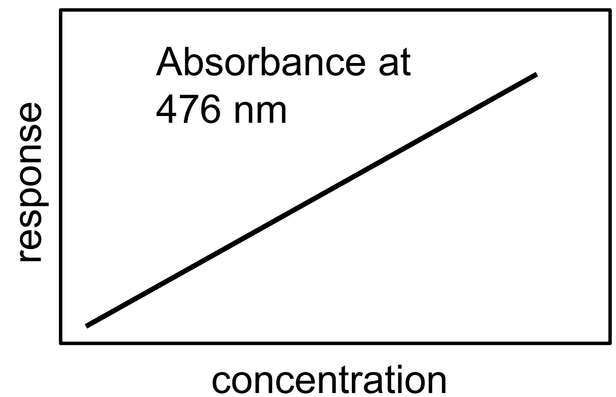


Chemometric modeling:
Comparison to univariate approach



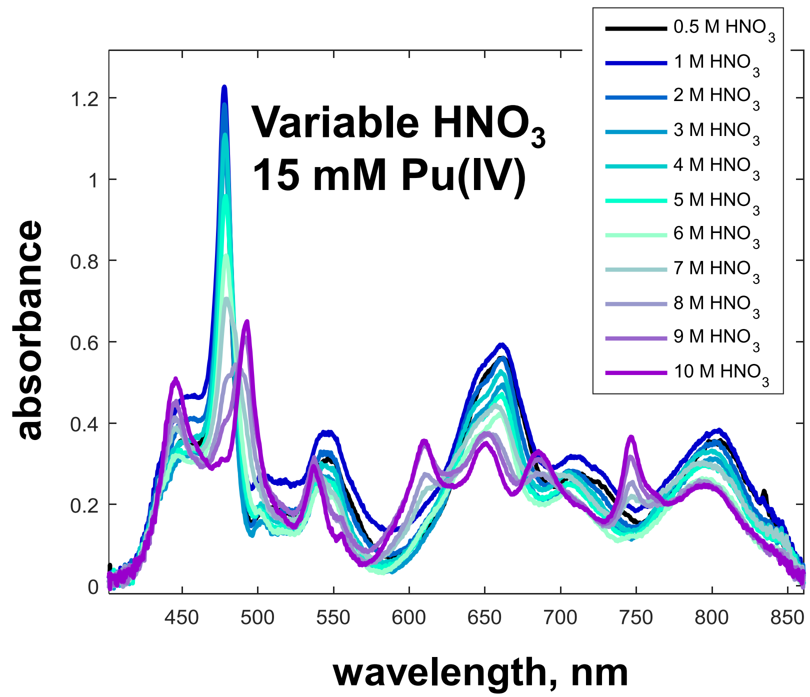
Chemometric modeling:
Comparison to univariate approach





Chemometric Modeling:
Identifying Key Spectral regions

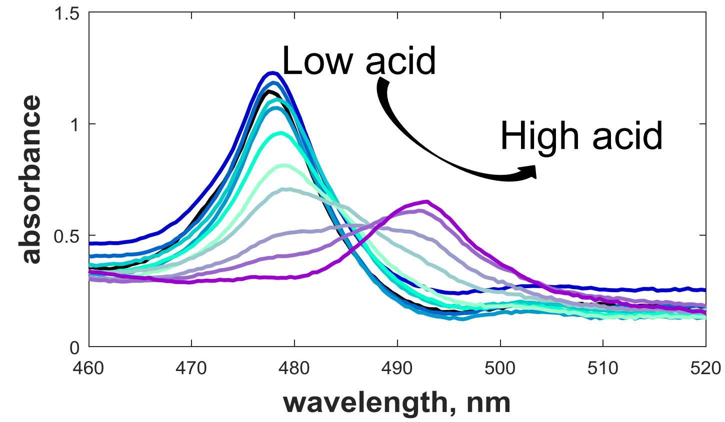
- Spectral data is simplified by representing variables (e.g. spectral data) as vectors within a 3D space
- New vectors (PC's or loadings) that capture primary spectral variance are captured
- Pu(IV) system shows heavy weighting of variables around the bands in the 460-500 nm region
- This has chemical significance in that it can be related back to the Pu-nitrate speciation

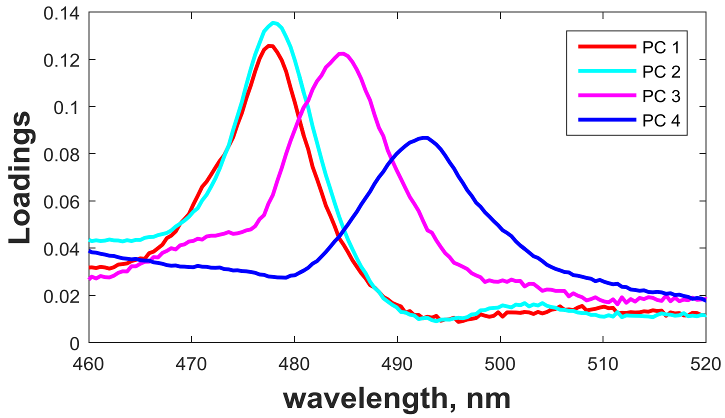


Lines, Adami, Sinkov, Lumetta, Bryan. Multivariate Analysis for Quantification of Plutonium(IV) in Nitric Acid Based on Absorption Spectra. *Anal Chem.* 2017

Chemometric Modeling:
Identifying Key Spectral regions

- Spectral data is simplified by representing variables (e.g. spectral data) as vectors within a 3D space
- New vectors (PC's or loadings) that capture primary spectral variance are captured
- Pu(IV) system shows heavy weighting of variables around the bands in the 460-500 nm region
- This has chemical significance in that it can be related back to the Pu-nitrate speciation

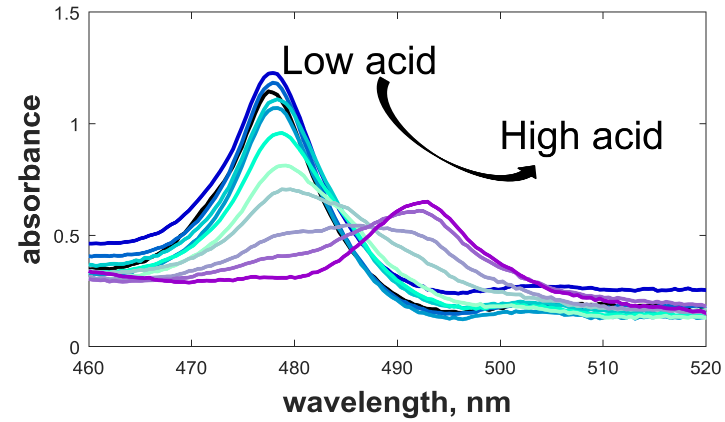


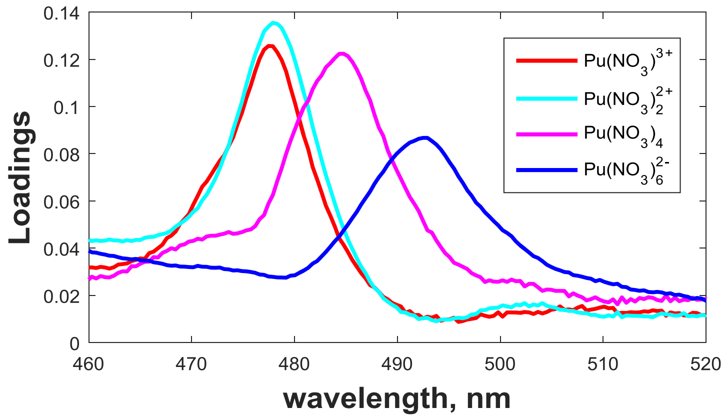


Lines, Adami, Sinkov, Lumetta, Bryan. Multivariate Analysis for Quantification of Plutonium(IV) in Nitric Acid Based on Absorption Spectra. *Anal Chem.* 2017

Chemometric Modeling:
Identifying Key Spectral regions

- Spectral data is simplified by representing variables (e.g. spectral data) as vectors within a 3D space
- New vectors (PC's or loadings) that capture primary spectral variance are captured
- Pu(IV) system shows heavy weighting of variables around the bands in the 460-500 nm region
- This has chemical significance in that it can be related back to the Pu-nitrate speciation

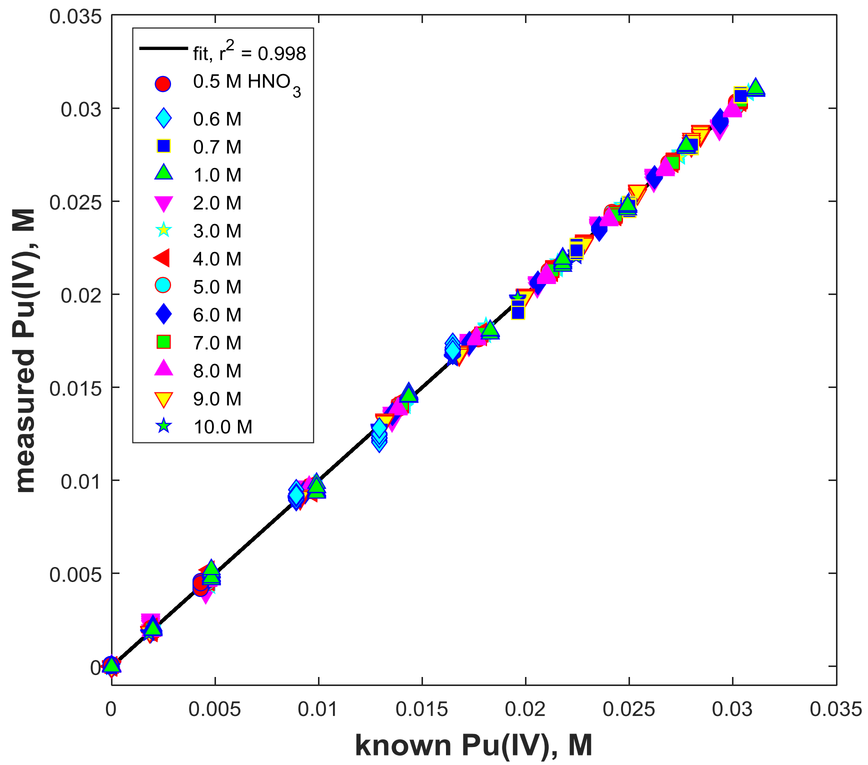




Lines, Adami, Sinkov, Lumetta, Bryan. Multivariate Analysis for Quantification of Plutonium(IV) in Nitric Acid Based on Absorption Spectra. *Anal Chem.* 2017

Chemometric Modeling of Pu(IV):

Determining accuracy of modeling

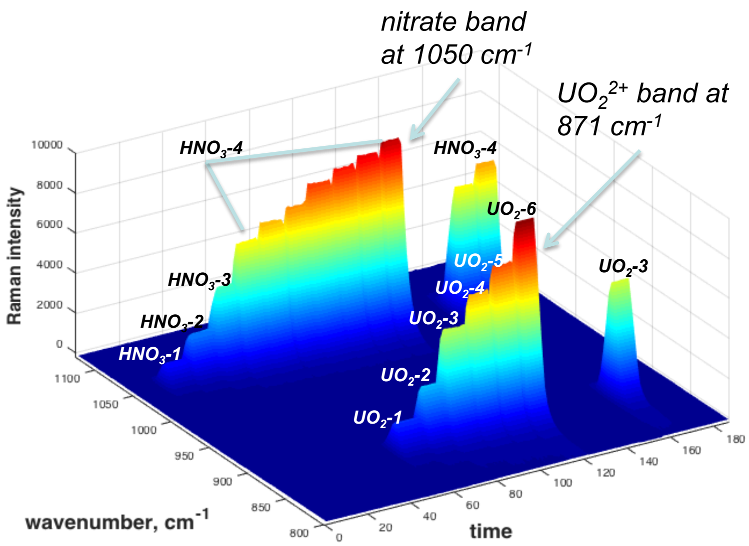


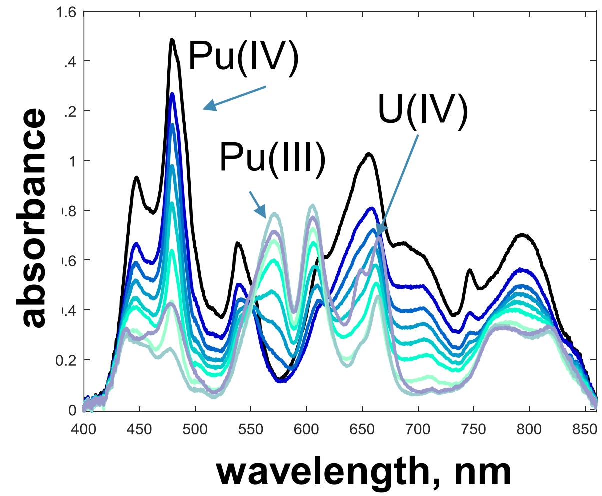
U.S. DEPARTMENT OF ENERGY | Office of Nuclear Energy

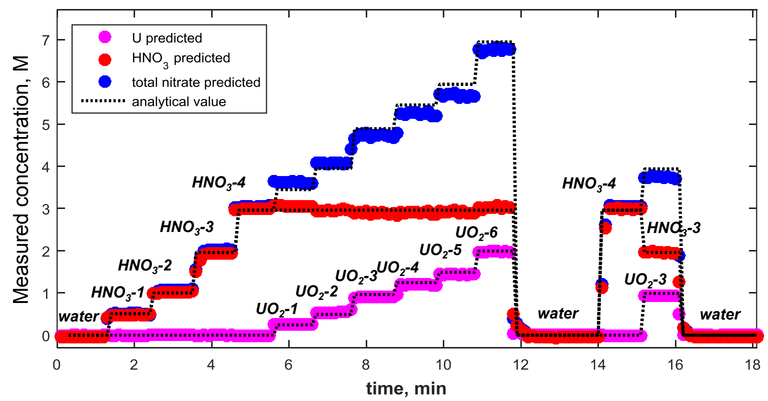
NTRD Nuclear Technology Research & Development

Chemometric modeling:
spectral complexities

- Matrix effects
- Overlapping bands
- Confounded bands
- Baseline effects





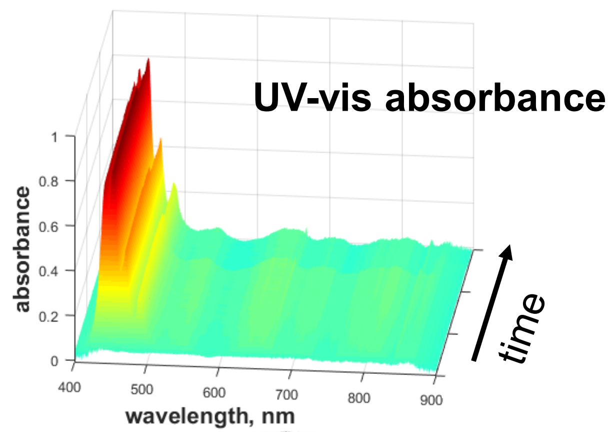


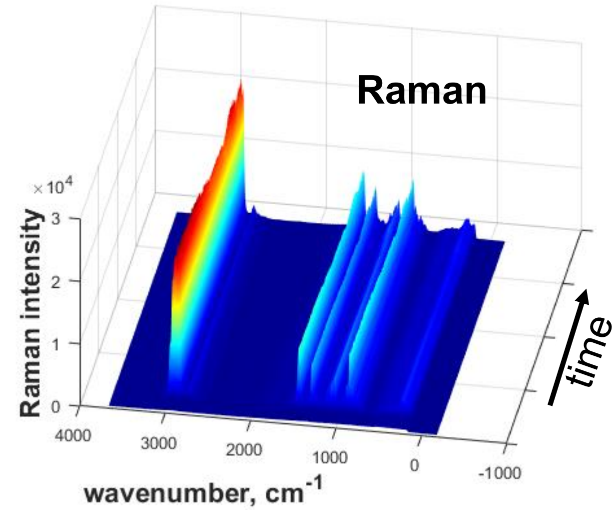
Lines, Bello, Clark, Bryan. Multivariate analysis to quantify species in the presence of direct interferents: micro-Raman analysis of HNO3 in microfluidic environments. *Anal Chem.* 2018

CoDCon:

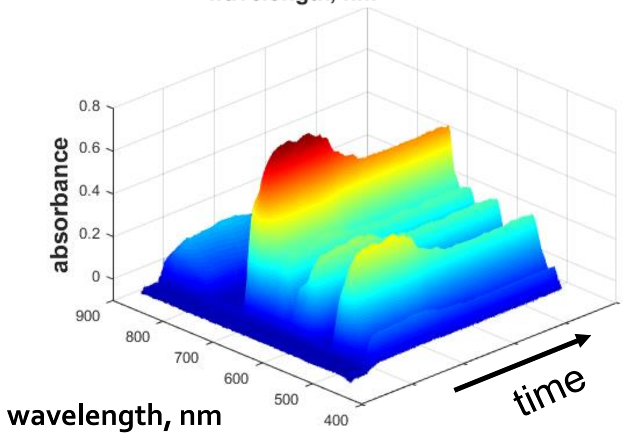
Following Pu in all inlets and outlets

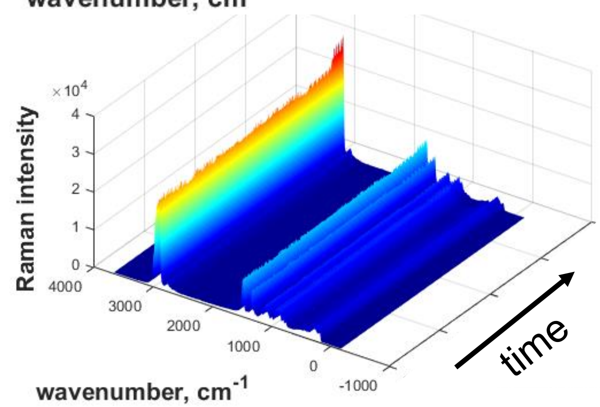
Inlet:
Loaded solvent





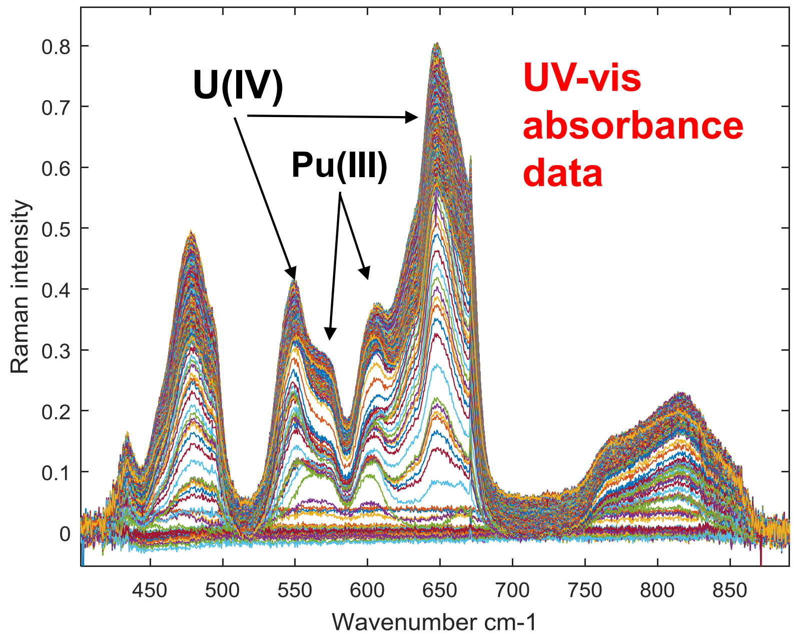
Outlet:
Aqueous product

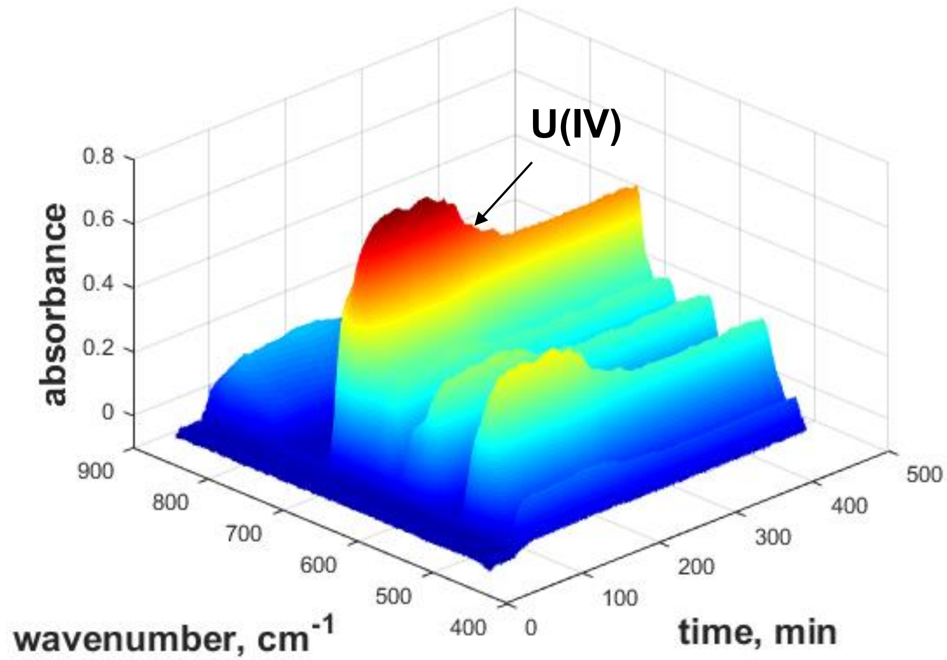




On-line tests:
Application of models to CoDCon separation campaign

- Product stream of key interest
- Real-time feedback used to modify run conditions





U.S. DEPARTMENT OF ENERGY | Office of Nuclear Energy

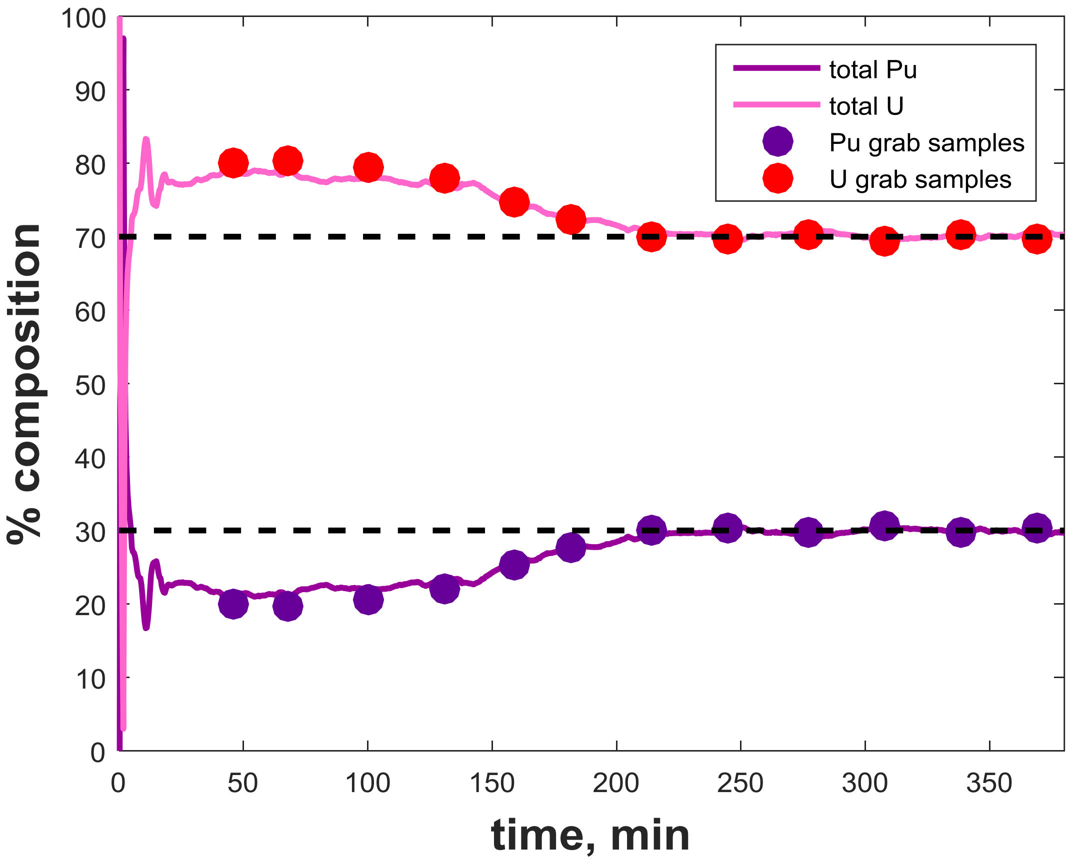
NTRD Nuclear Technology Research & Development

On-line tests:

Application of models to CoDCon separation campaign

- Models are accurately measuring concentrations
- Spectroscopy can identify off-normal behavior in addition to quantifying target analytes

On-line Real-time monitoring enabled real-time process control to produce desired U/Pu product



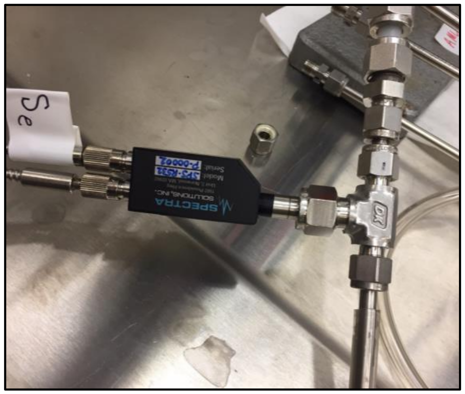
U.S. DEPARTMENT OF ENERGY | Office of Nuclear Energy

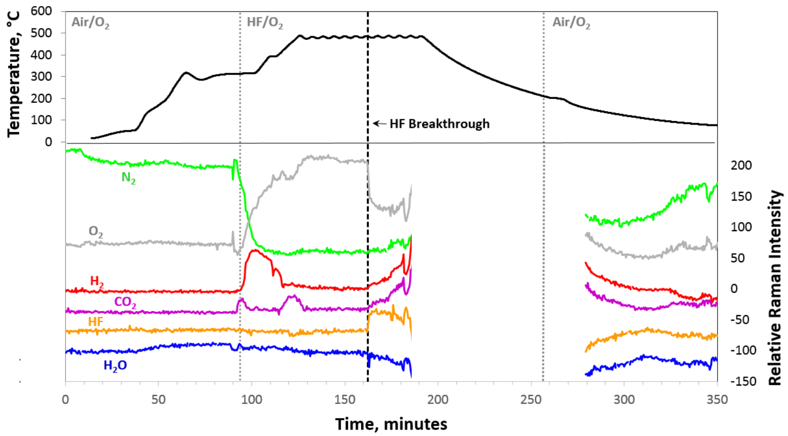
Expanding on-line monitoring to other harsh environments

NTRD Nuclear Technology Research & Development

Fluorination off-gas

- Gas phase probe to monitor highly corrosive streams
  - HF, NF_3, O_2, H_2, CO_2, etc.
- Initial focus on Raman but pursuing routes to utilize sensor fusion to expand potential analytes



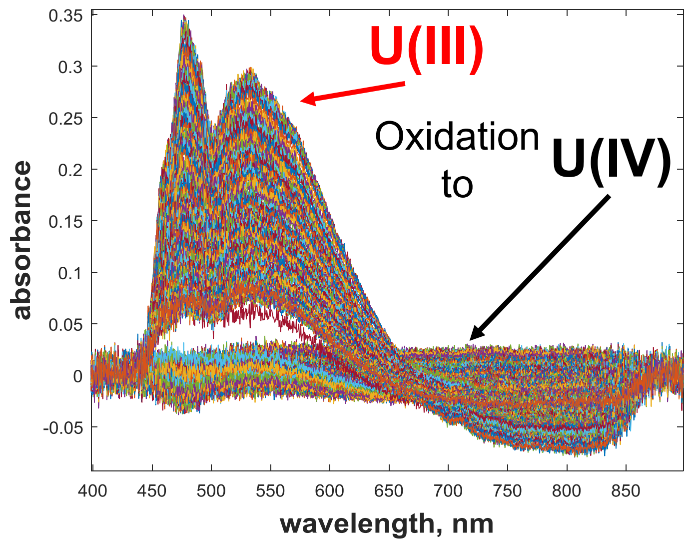


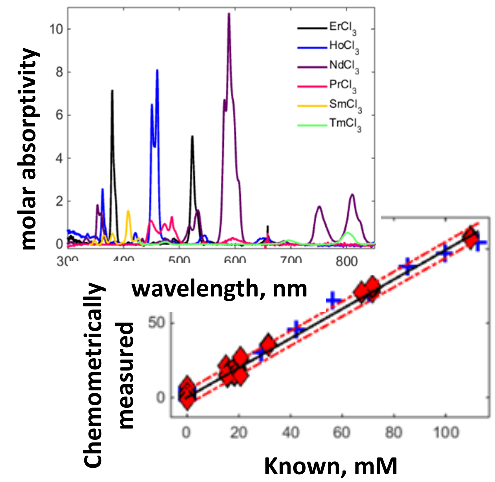
Casella, AJ et al. In stream monitoring of off-gasses from plutonium fluorination, 2018

Expanding on-line monitoring to other harsh environments

- Internal investments building on past DOE-NE advancements for characterizing components within molten salt environments

Molten salt





1. Schroll, CA; Lines, AM, Heineman, WR; Bryan, SA; Absorption spectroscopy for the quantitative prediction of lanthanide concentrations in the 3LiCl-2CsCl eutectic at 723 K; *Anal Meth*; 2016, 8, 7731
2. Schroll, CA…Bryan, SA; Spectroelectrochemistry of EuCl3 in Four Molten Salt Eutectics; 3LiCl-NaCl, 3LiCl-2KCl, LiCl-RbCl, and 3LiCl-2CsCl; at873 K; *Electroanalysis*; 2016, 28, 2158
3. Schroll, CA…Bryan, SA; Electrochemistry and Spectroelectrochemistry of Europium(III) Chloride in 3LiCl–2KCl from 643 to 1123 K; *Anal Chem*; 2013, 85, 9924

Collaboration to develop mass balance systems

- Combining chemical characterization with physical property measurements
- Several institutions are developing the technologies necessary to preform physical property measurements on different advanced reactor systems
  - ORNL, INL, Universities, etc
- With combined on-line approaches real-time mass balance is achievable

U.S. DEPARTMENT OF ENERGY | Office of Nuclear Energy

NTRD Nuclear Technology Research & Development

Conclusions

- On-line monitoring with real-time analysis can provide essential information for immediate process control
  - Quantification of multiple analytes [Pu(III), Pu(IV), Pu(VI), U(IV), U(VI), $HNO_{3,}$ etc.]
  - Flexibility with solution phase (Organic vs. Aqueous) and process scale
  - Facilitates process control and safeguards
- Application of chemometric analysis allows for accurate quantification in complex systems
  - Matrix effects
  - Confounding bands
  - Baseline shifts

U.S. DEPARTMENT OF ENERGY | Office of Nuclear Energy

NTRD Nuclear Technology Research & Development

Acknowledgements

- The CoDCon work was funded by the U.S. Department of Energy, Office of Nuclear Energy, through the Nuclear Technologies R&D Program.
- Small Business Innovative Research (SBIR) Grant, Office of Science (SC); collaboration with Spectra Solutions Inc.
- Visiting Faculty Program and Next Generation Safeguards Internship program

Team:

Amanda J. Casella
Gabe Hall
Jarrod Allred
Gregg J. Lumetta
Samuel A. Bryan
Shirmir Branch
Job Bello
Forrest Heller
Susan Adami

Students/visiting faculty:

Gilbert Nelson
Hope Lackey
Jen Wilson