U.S. DEPARTMENT OF ENERGY | Nuclear Energy

Office Of Nuclear Energy Sensors and Instrumentation Annual Review Meeting

Materials Recovery and Waste Form Development (MRWFD) Overview

On-line Sampling & Monitoring and CoDCon (co-decontamination) projects

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Material Recovery & Waste Form Development

Instrumentation and Controls needs within MRWFD

- **Advanced fuel cycles, if deployed, will likely be implemented in 2-3 decades**
- **There is a need for monitoring process operation in near real time**
  - Currently, only tank volumes, temperatures, pressures, etc. are monitored, chemical analysis of the process is obtained, via sampling, which has a lag time of several hours from the time the sample is taken until the operators know the results of the analysis
- **Chemical performance data (i.e. concentrations of key chemical species at any given time) would greatly improve operations and reduce the need for taking and analyzing samples**
- **Separation process operation would benefit from the near-real-time analysis of a number of chemical species**

On-line Monitoring Demonstration within MRWFD Campaign

- **The MRWFD campaign has been developing methods to monitor key chemical components of a separation process, in near real time**

- **On-line Process Monitoring project**
  - Development of monitoring equipment to be utilized in future fuel cycle

- **CoDCon (co-decontamination) project**
  - Demonstrate, a separation process producing 70% uranium / 30% plutonium mixed oxide, at a scale of ~1 kg Uranium/test
  - Demonstration of Advanced on-line spectroscopic tools

CoDCon project: Motivation

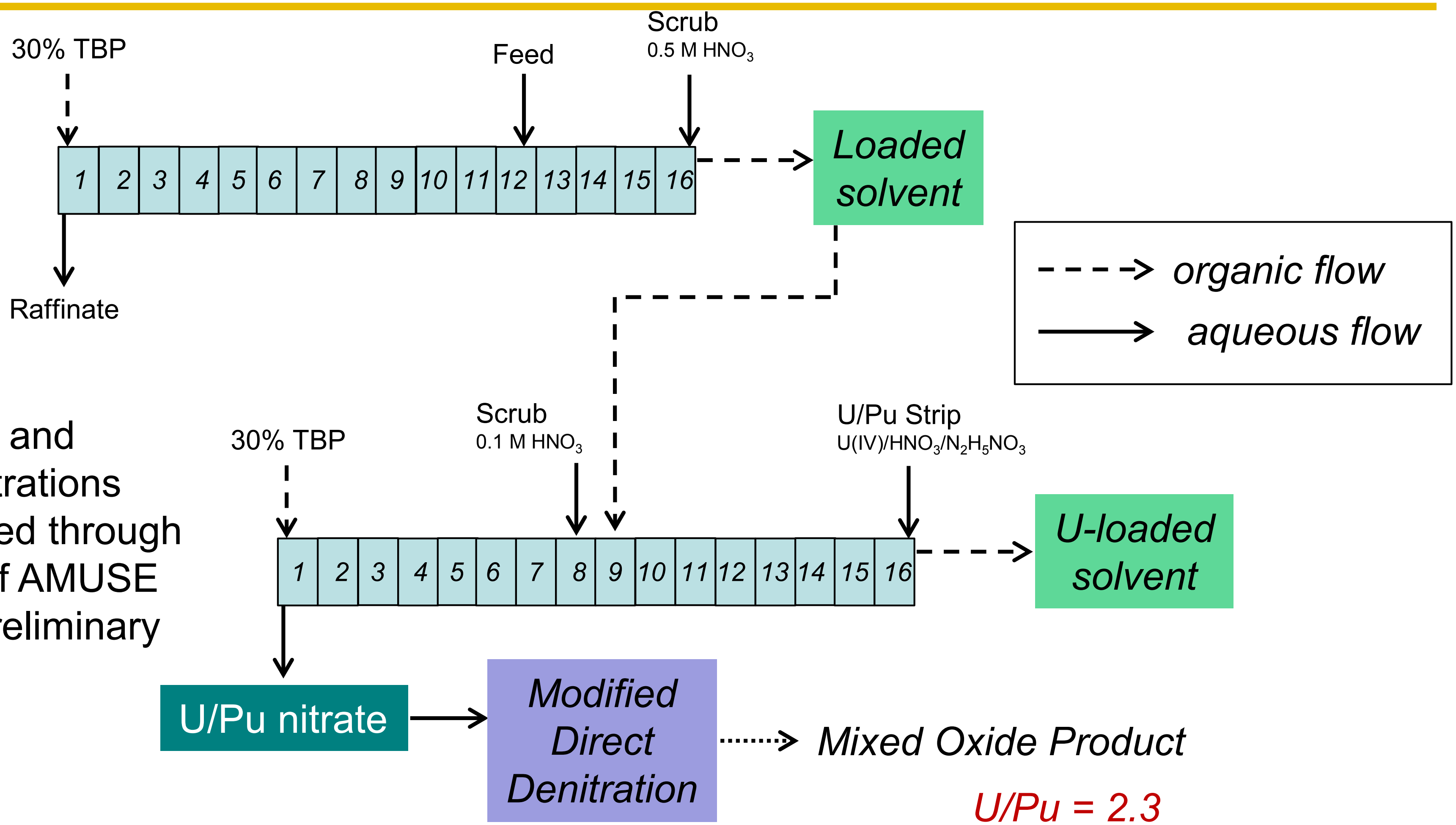
- **Separation of pure Pu presents a proliferation risk**
  - Rigorous safeguarding of PUREX-based fuel recycling facilities is required
- **Options for used nuclear fuel recycling have been proposed that do not separate pure Pu**
  - Some level of U (and perhaps Np) are maintained in the Pu-containing process streams and mixed oxide (MOX) product
- **But these questions arise:**
  - How accurately can the U/Pu ratio be controlled?
  - How can the international safeguards community verify that the U/Pu ratio is indeed what has been declared by the plant operators?
- **The CoDCon project seeks to generate technical data to help answer these questions.**

CoDCon project: Objectives

- **Quantify the accuracy and precision to which a specific uranium-to-plutonium (U/Pu) ratio can be achieved in TBP-based solvent extraction flowsheet**
  - The target is a U mass fraction = 0.70 based on the sum masses of U + Pu
  - Using laboratory-scale equipment
  - Develop dynamic model to quantify measurement uncertainties and examine process control for a wider variety of process conditions

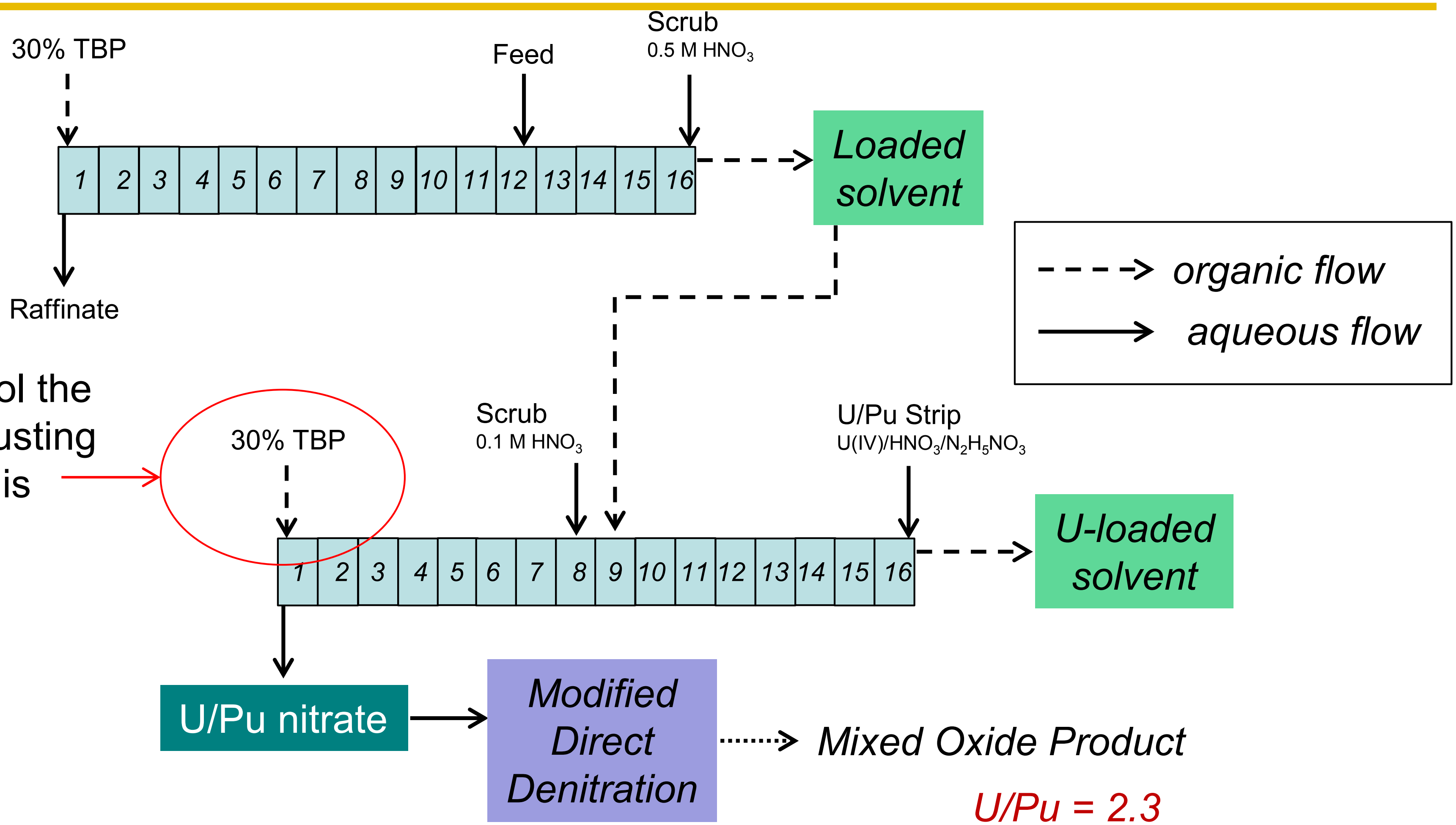
- **Demonstration of optical spectroscopic techniques for real-time monitoring of key components (e.g., Pu, U, and HNO_3 concentrations) in the process solutions**

CoDCon flowsheet



Note
Exact flow rates and reagent concentrations will be determined through a combination of AMUSE modeling and preliminary flow tests.

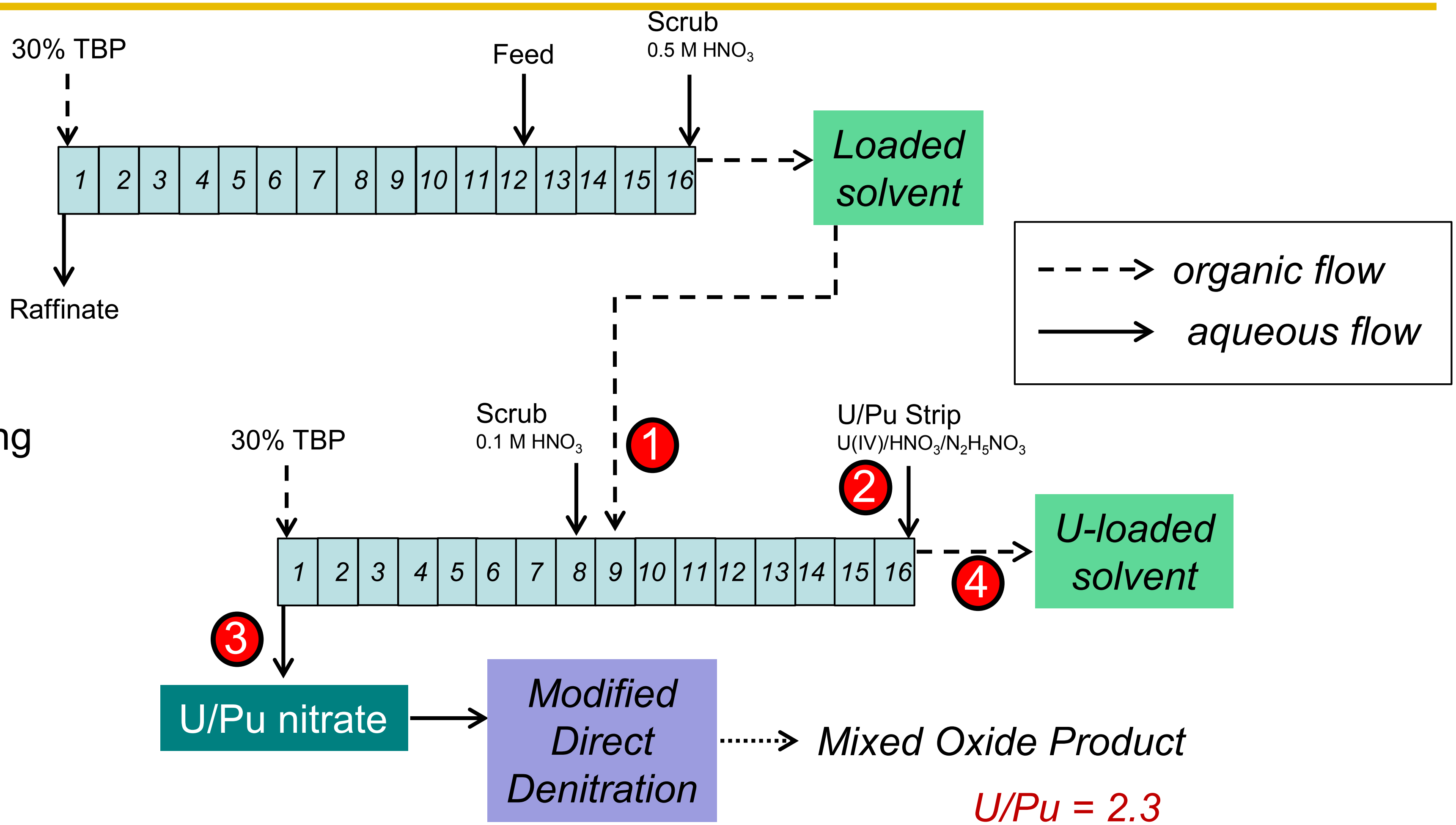
CoDCon flowsheet



Planning to control the U/Pu ratio by adjusting the flow rate of this solvent stream.

CoDCon flowsheet

Locations for process monitoring



Spectroscopic measurement: U, Pu, and HNO_3

Goals of On-Line Monitoring

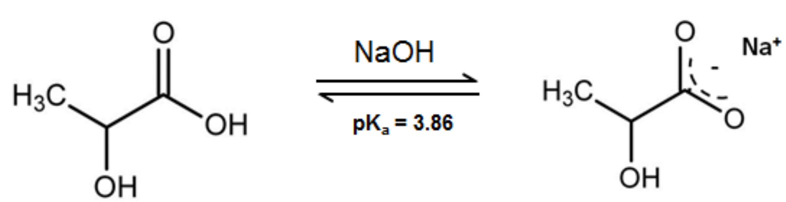
Advancement of on-line monitoring systems that provide real-time quantification of solution species and physical property measurements during process operations in nuclear fuel reprocessing applications

- **Process control**
  - Maintain optimal operating conditions
  - Efficient development of new flowsheets
- **Safeguard verification (IAEA)**

Approach: On-line Spectroscopic Measurements

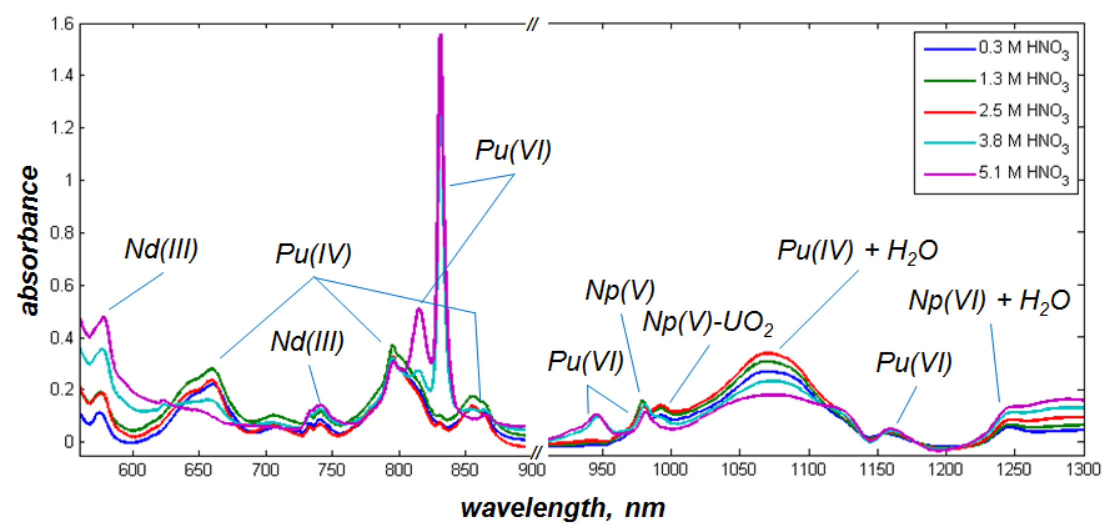
Raman spectroscopy

- **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**



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

Process Monitoring Can Be Achieved Through Multiple Flowsheets

Monitoring Is Not Flowsheet Specific

CoDCon

TRUEX

TALSPEAK

PUREX

Molten Salt

Global vision:
Process monitoring/control at various points in flowsheet

Every flowsheet contains Raman and/or UV-vis-NIR active species

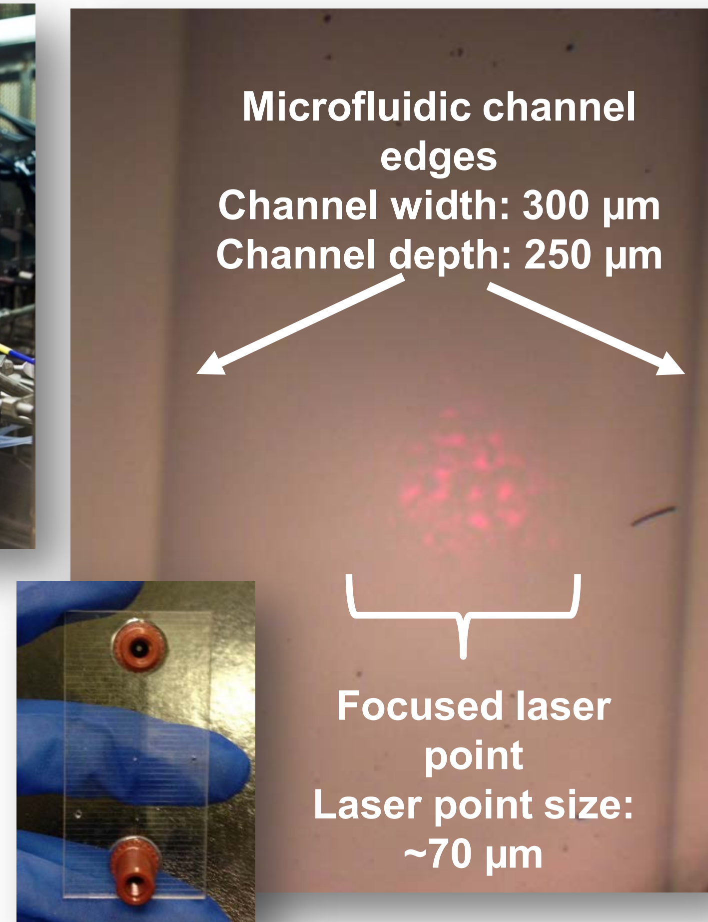
Spectroscopic and physical property measurements can be coupled

Application of technique across wide range of process scales

Commercial scale:
Hanford waste tank
100 L/min

Lab scale:
Centrifugal contactors
10 mL/min

Microscale:
Microfluidic devices
0.1 mL/min



Methodology for on-line process monitor development: from proof-of-concept to final output

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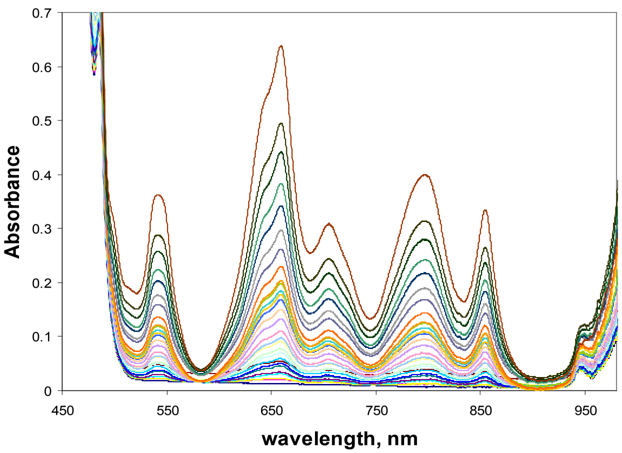
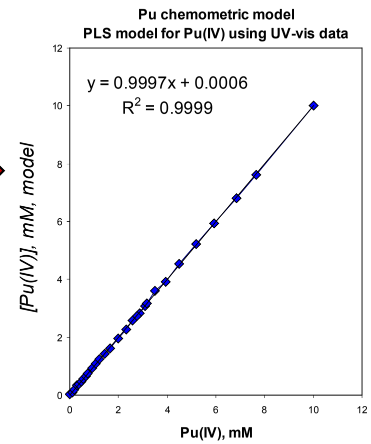
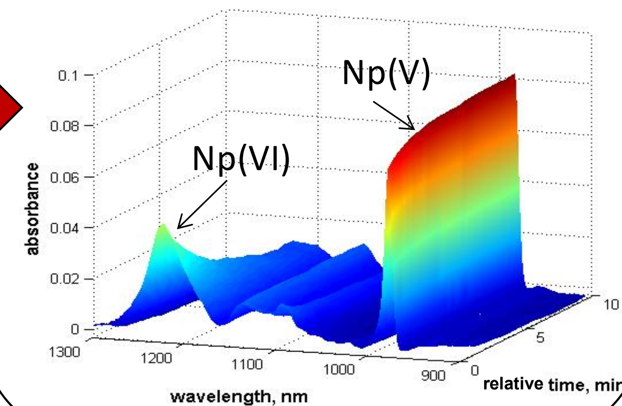
Model training database



Chemometric model development



On-line model verification and translation

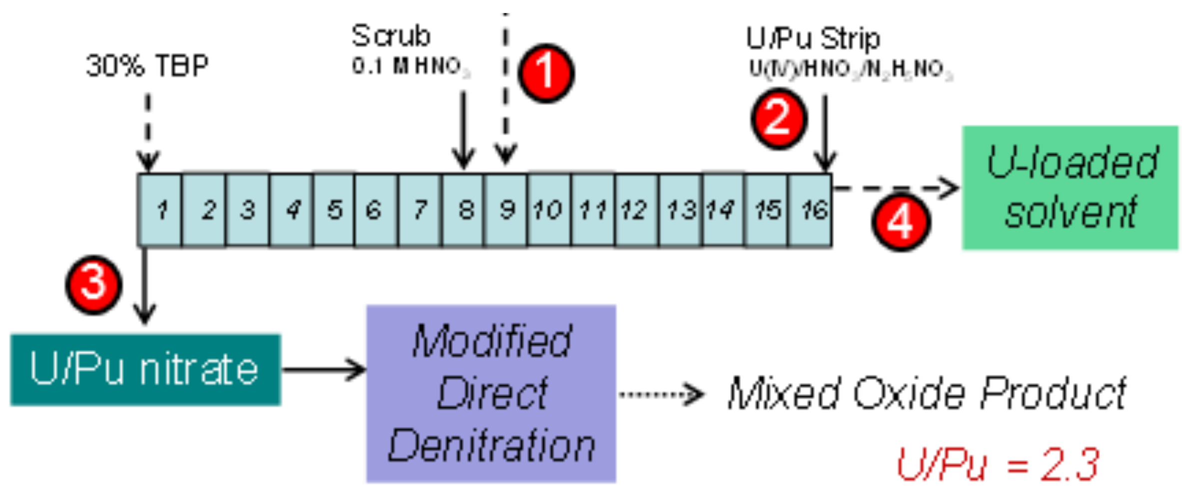


Integrated software for data collection, processing, storage and archiving

Real-time on-line concentration data display

Application to CoDCon

- **Several points throughout the process were identified as key locations where Pu/U concentrations need to be monitored**
- **Ultimate Goal: develop and deploy an on-line monitoring system capable of providing real time analysis of species in solution**
- **On-line monitoring objectives include:**
  - System design
  - Training set collection
  - Chemometric model development



CoDCon: Training set Collection and Completion

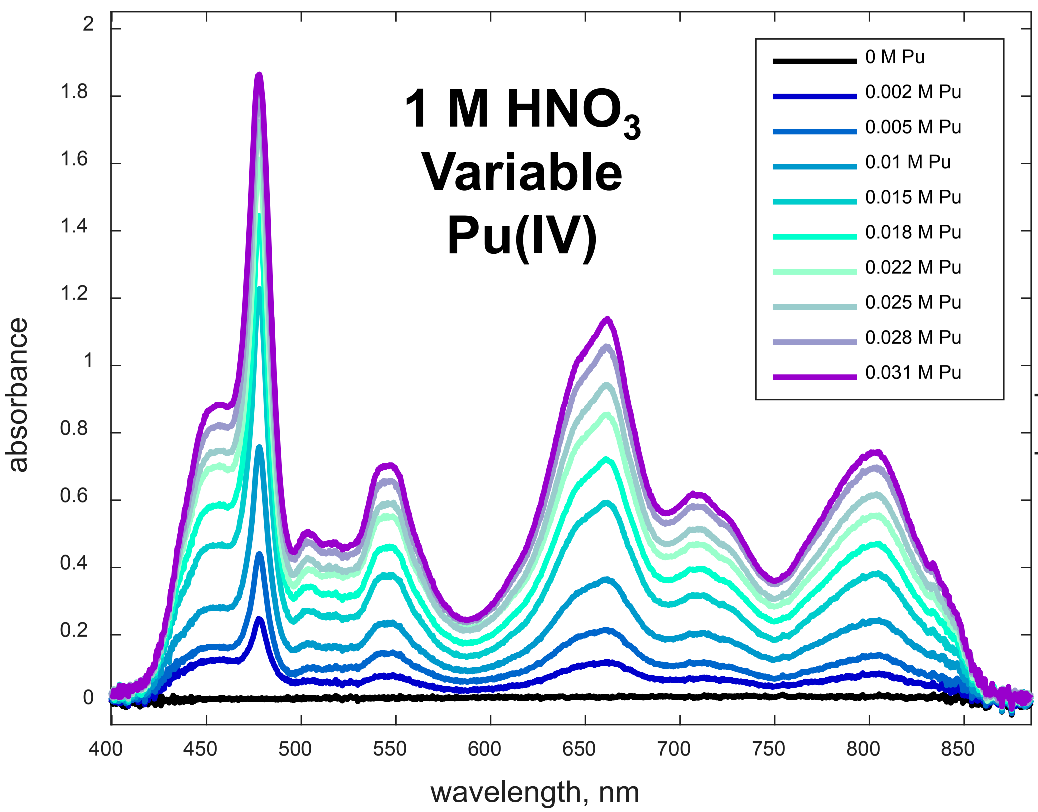
- **CoDCon and PuOx flowsheets contain a complex mixture of species**
- **Many species show spectral dependencies on system conditions**
  - Acid concentration
- **Both organic and aqueous streams will be monitored**
  - For CoDCon
- **Spectral training sets must capture all system variation to allow for robust and accurate chemometric modeling**

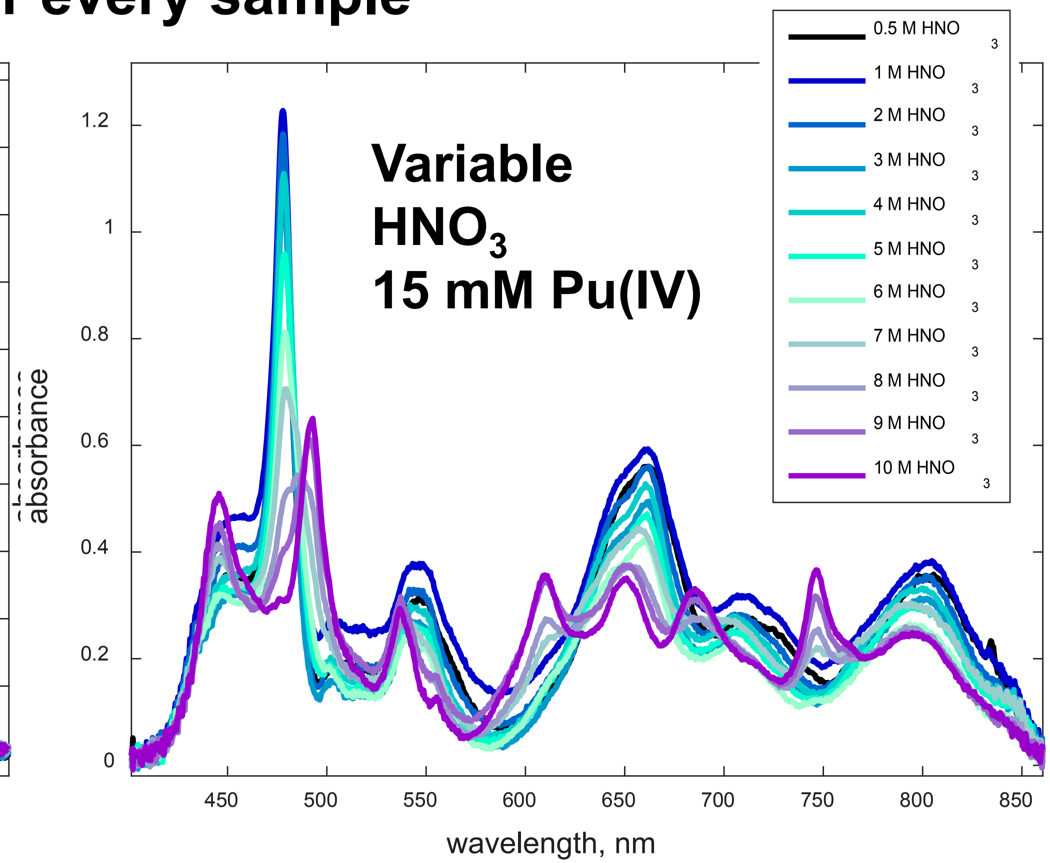
Data set	HNO_3 range covered	Primary method
Aqueous sets:		
Pure Pu(IV)	0.5-10 M	UV-vis
Mixed Pu(IV)/Pu(III)	1-5 M	UV-vis
Pure Pu(VI)	1-6 M	Both
Pure U(IV)	0-6 M	UV-vis
Pure U(VI)	0-6 M	Raman
Mixed U(IV)/U(VI)	0-6 M	Both
Mixed Pu(IV)/Pu(III)/U(IV)/U(VI)	0.5-6 M	Both
Mixed Pu(IV)/U(VI)	0.5-6 M	Both
Other (hydrazine, NO_2^-, etc.)	N/A	Raman
Organic sets:		
Pre-contact solutions	N/A	Raman
Post-contact with acids	2-4 M	Raman
Post contact with U(VI)	2-4 M	Raman
Post contact with U(IV)	1 M	UV-vis
Post contact with Pu(IV)	3 M	UV-vis

Spectral Training Sets

Pu(IV)

- **Many of the metal species of interest display some spectral variations within the anticipated acid concentration range**
- **UV-vis and Raman collected for every sample**

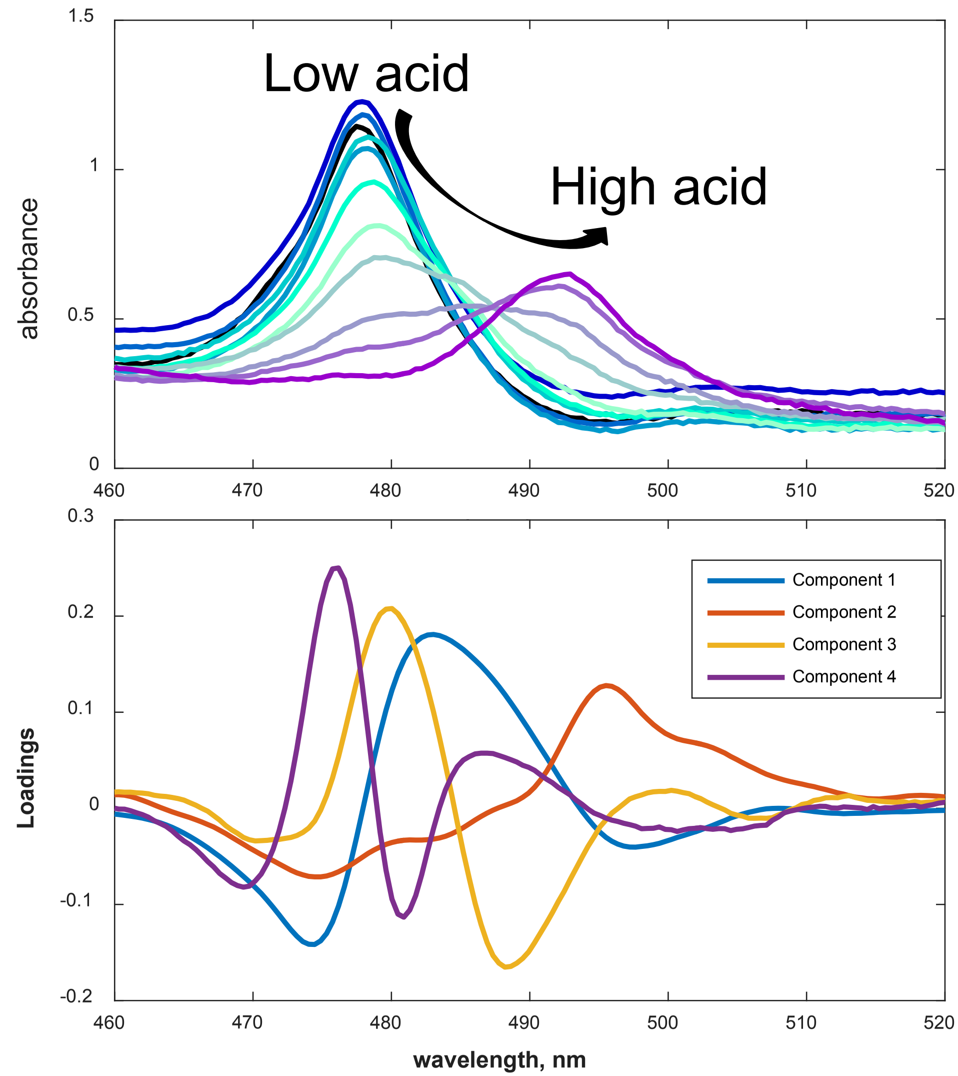




Chemometric Modeling: Identifying Key Spectral regions

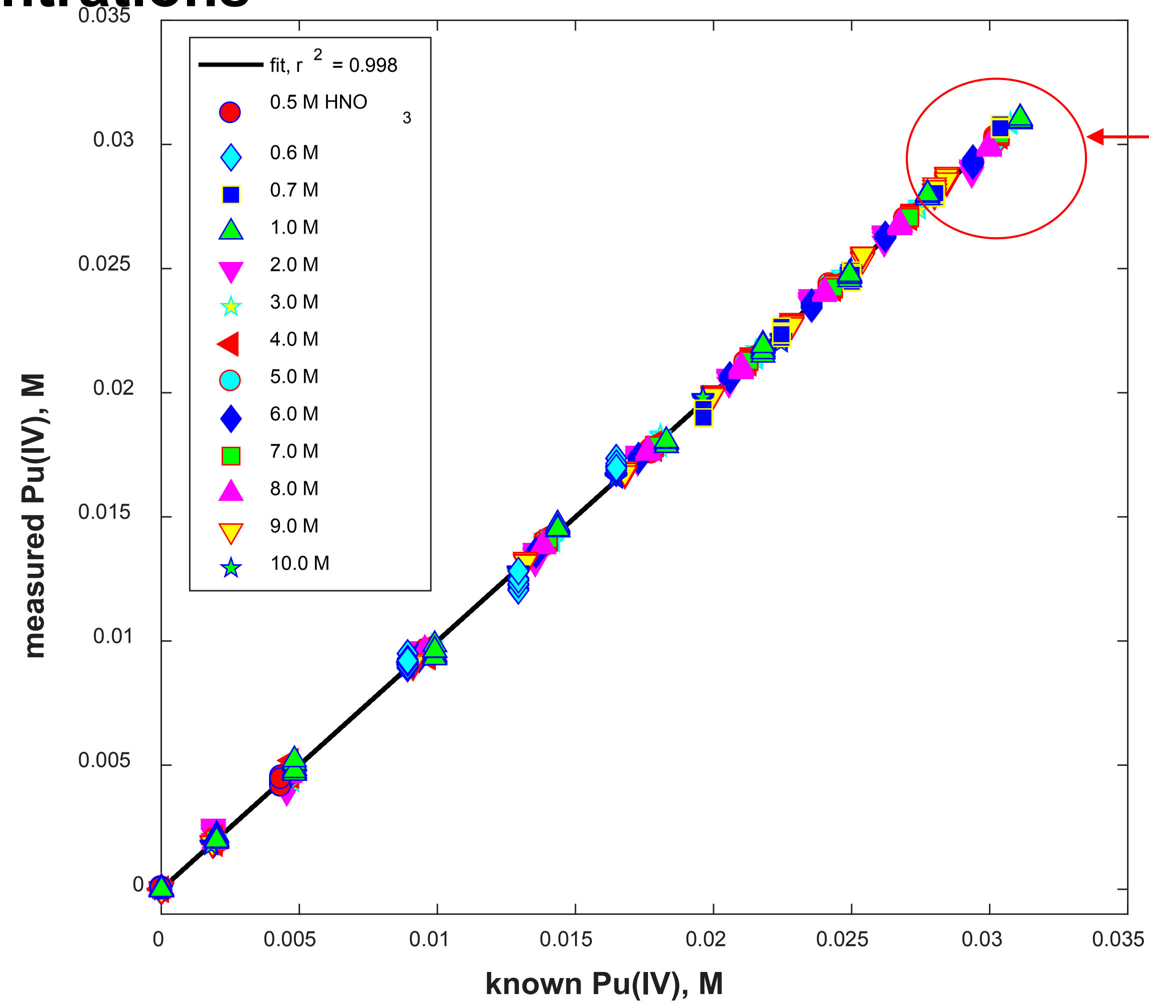
Pu(IV)

- 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



Chemometric Modeling of Pu(IV):
Determining accuracy of modeling

- **Initial modeling of Pu(IV) system across a range of HNO_3 concentrations**

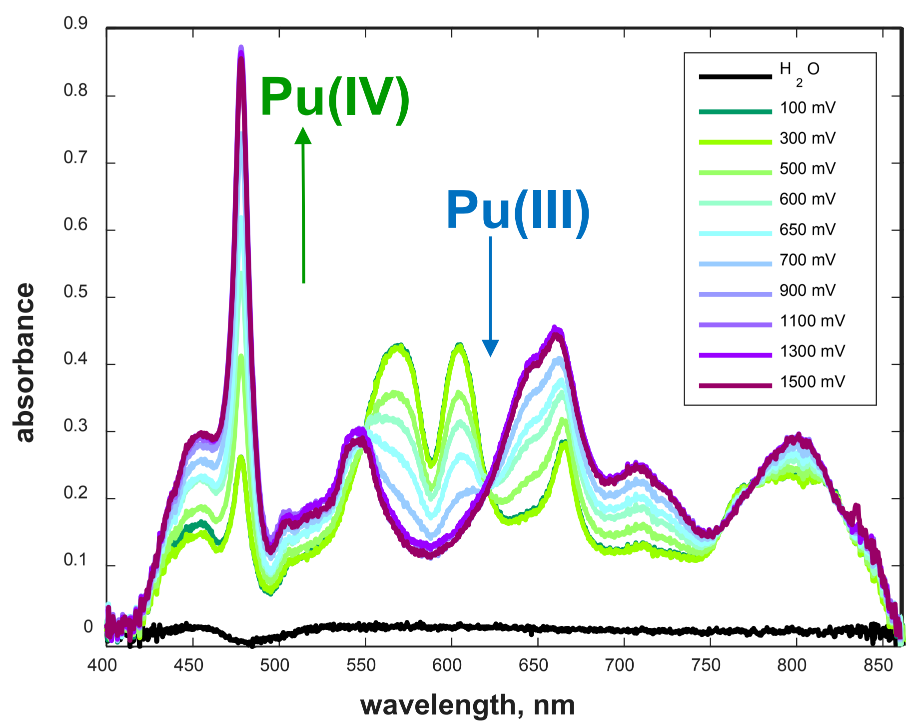


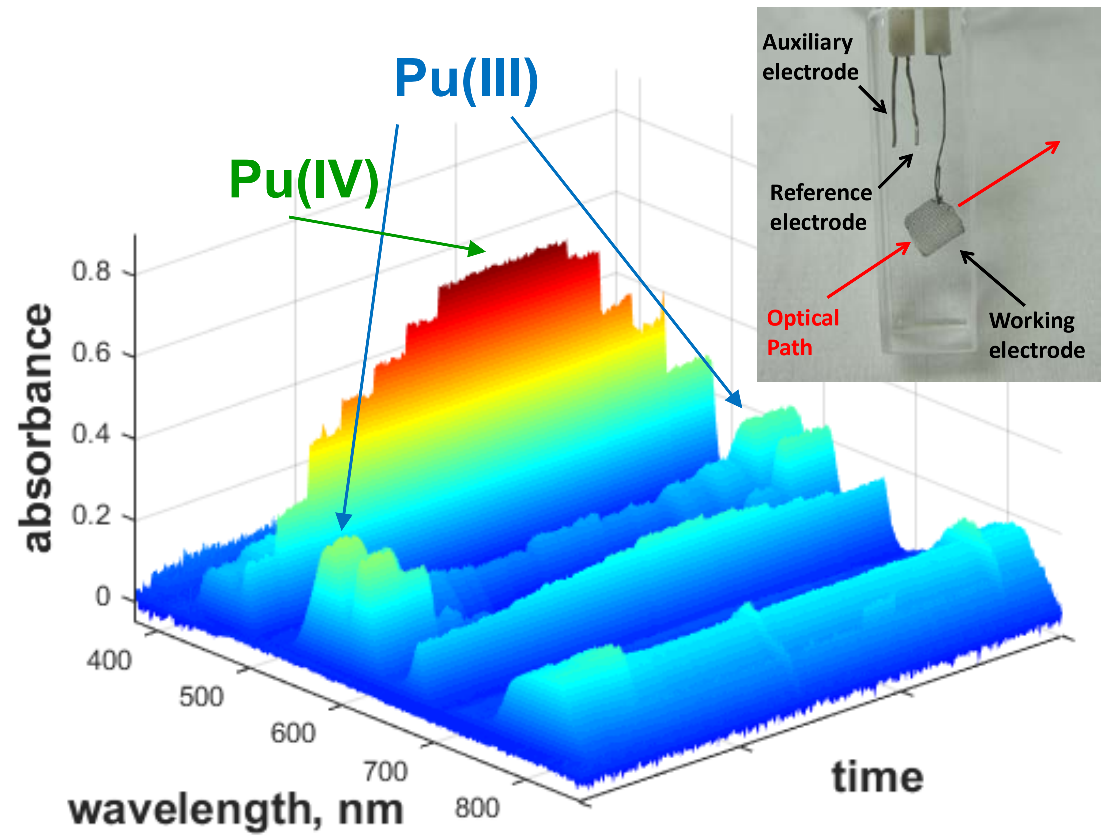
30 mM Pu(IV) at multiple HNO_3 concentrations

Spectral Training Sets

Pu(III)
Pu(IV)

- Multiple oxidation states of Pu and U are expected throughout the process
- Spectroelectrochemistry was utilized to build spectral data sets of Pu solutions to reduce the total amount of Pu required for training set development



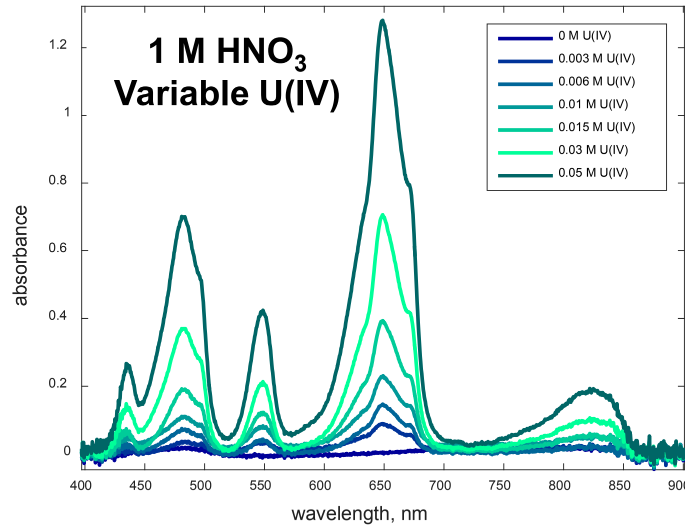


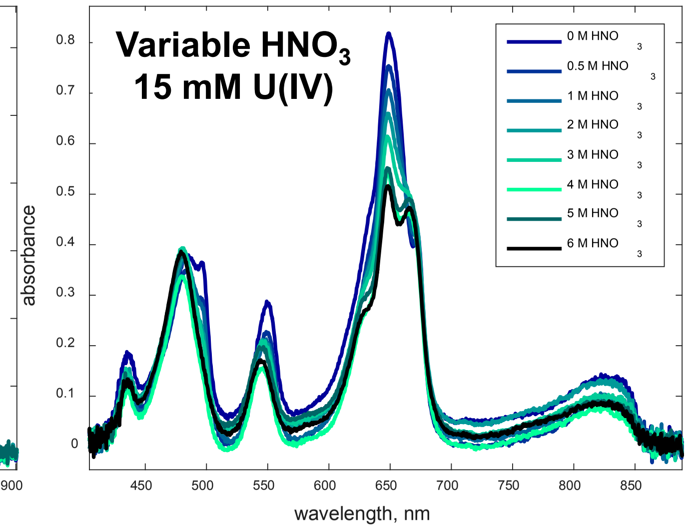
Spectral Training Sets

U(IV)
U(VI)

UV-vis

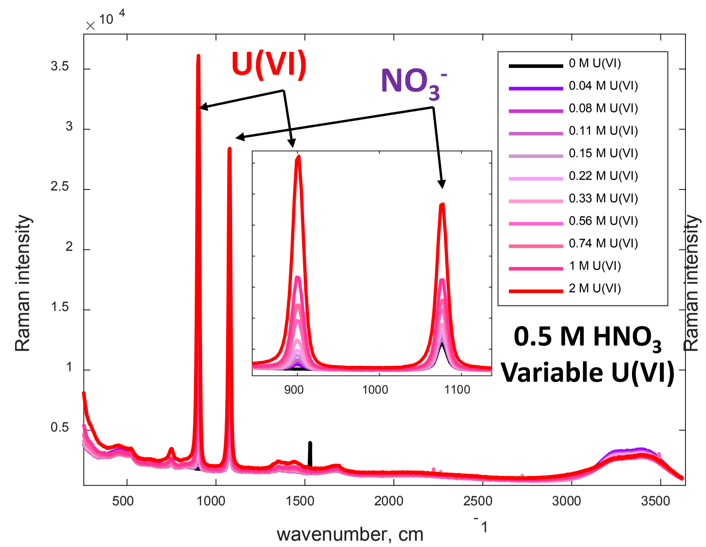
- Spectral changes with species concentration were explored over a range of HNO_3 for all species of interest, including U(IV) and U(VI)

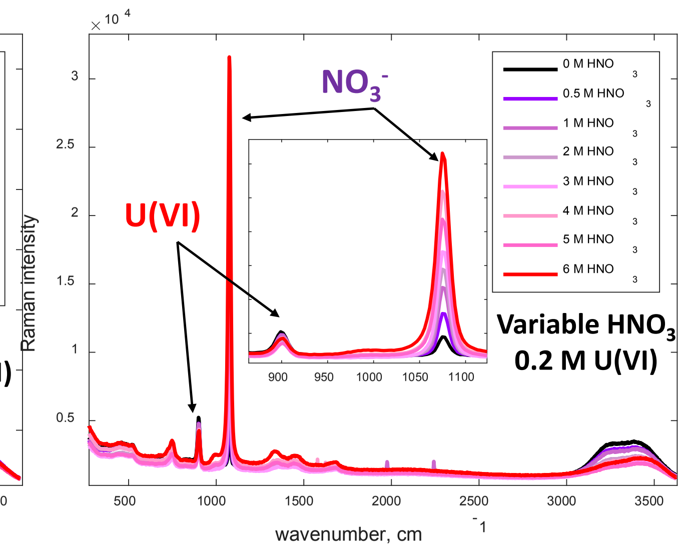




Raman

- In the case of U(VI) and HNO_3 Raman spectroscopy will be the primary tool used for identification/quantification

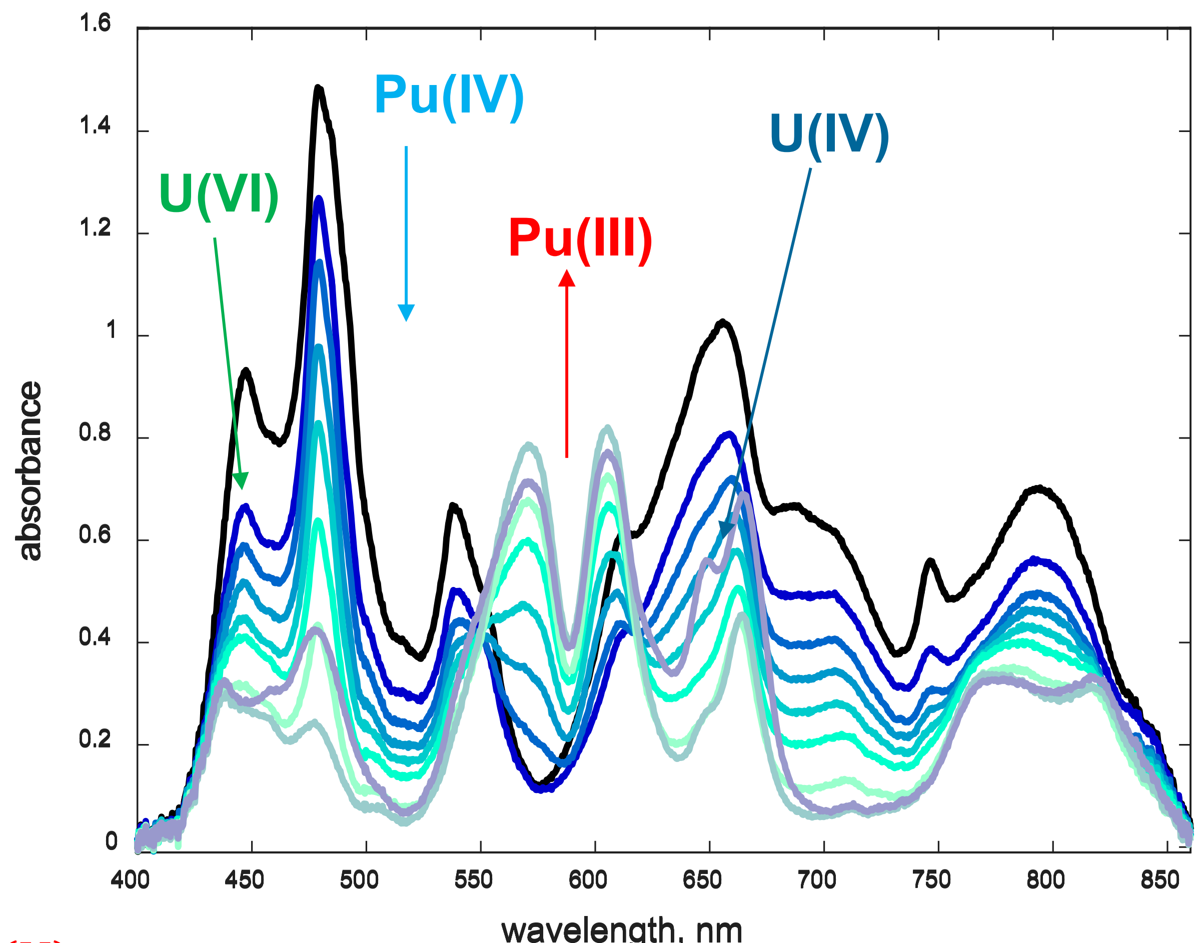




Spectral Training Sets

Pu(IV)
U(IV)

- Complexity of system captured in the training set
- Pu and U have numerous overlapping bands in the UV-vis range
- Titration of U(IV) into Pu(IV) demonstrates the complexity of the spectra
- This data collected at 6 M HNO_3, experiment was repeated at 0.5-6 M HNO_3



$$Pu(IV) + U(IV) \rightarrow Pu(III) + U(V)$$

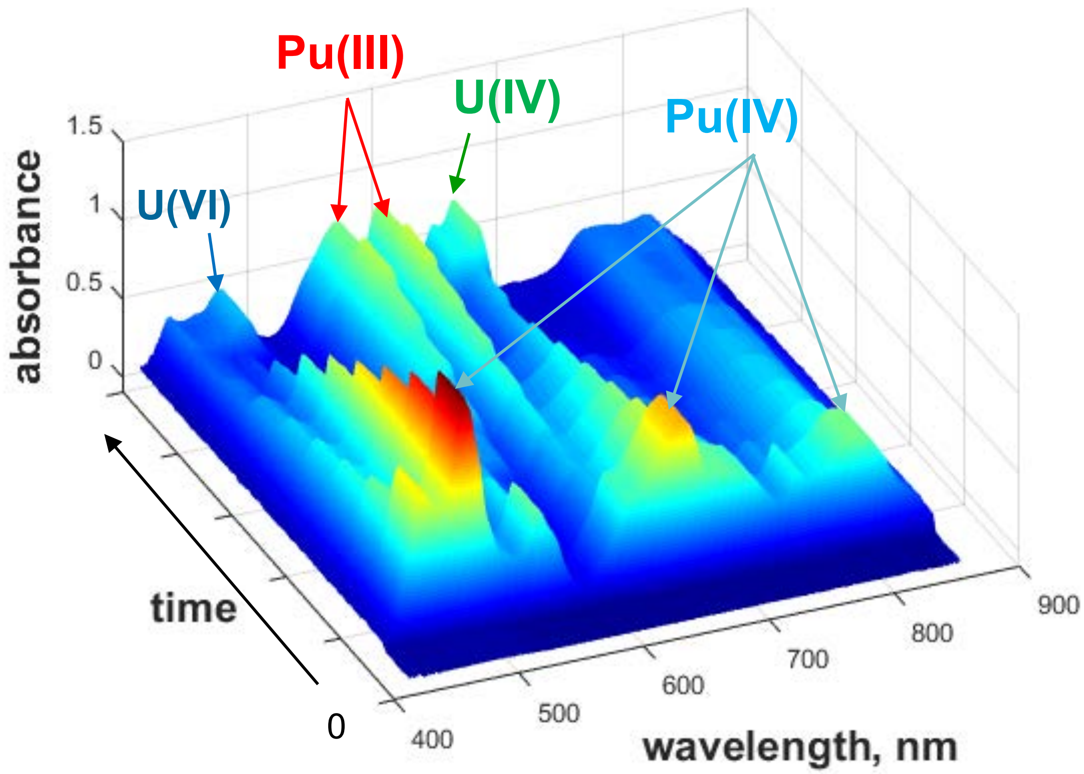
$$2U(V) \rightarrow U(IV) + U(VI)$$

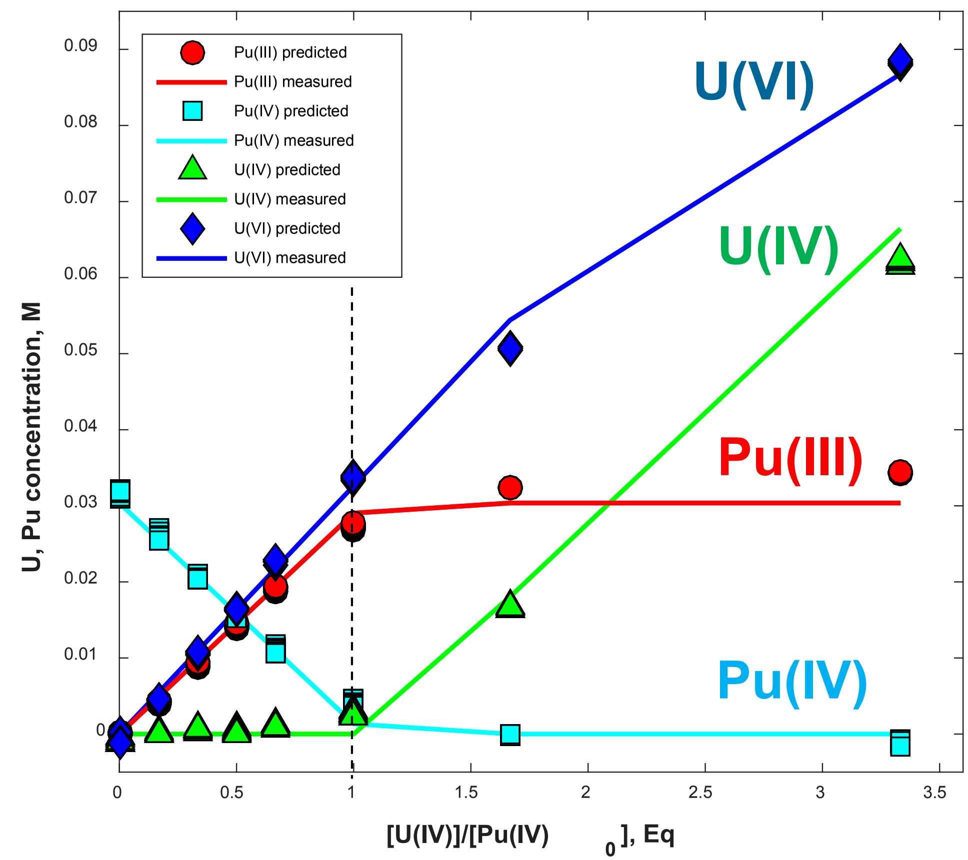
CoDCon: Chemometric Modeling Example

- Initial chemometric models accurately follow all four species

$$Pu(IV) + U(IV) \rightarrow Pu(III) + U(V)$$

$$2U(V) \rightarrow U(IV) + U(VI)$$





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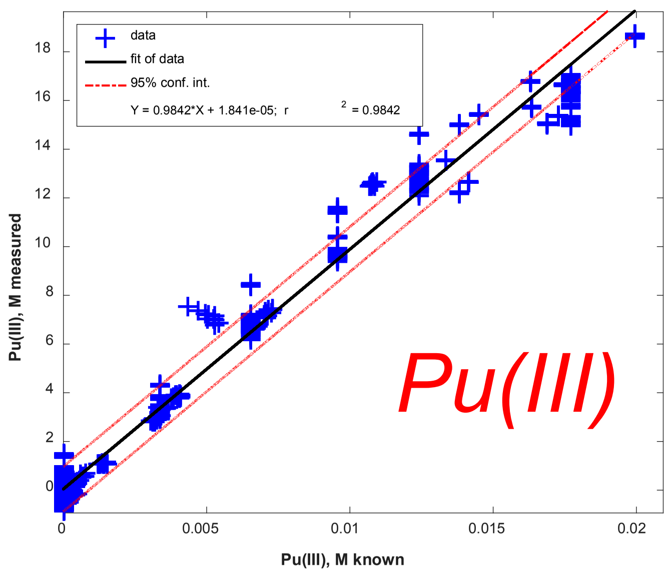
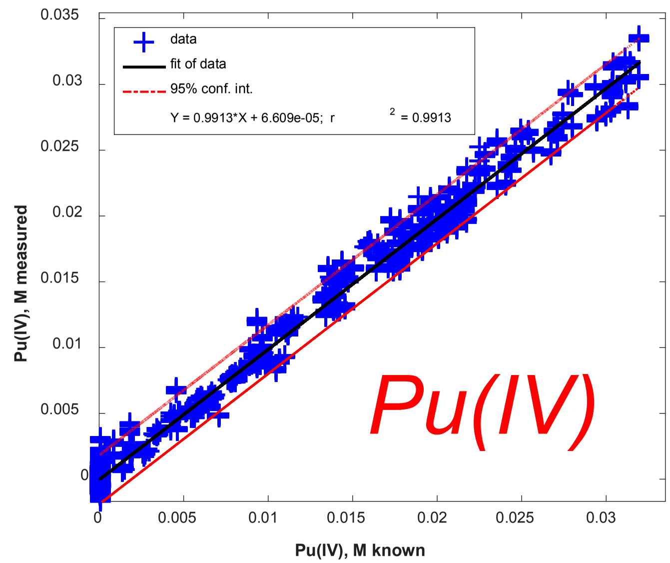
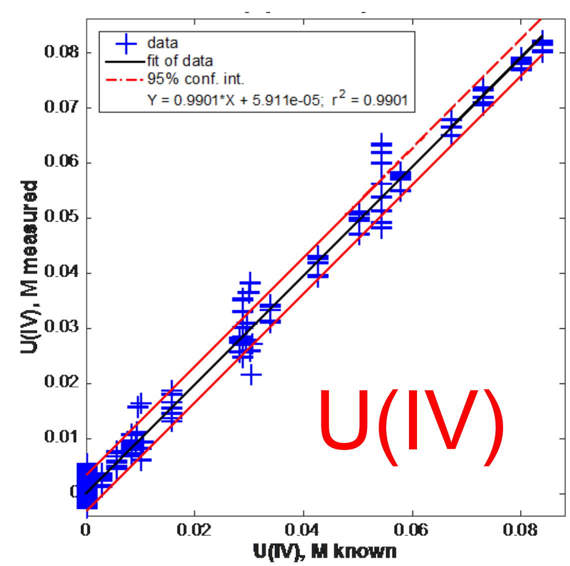
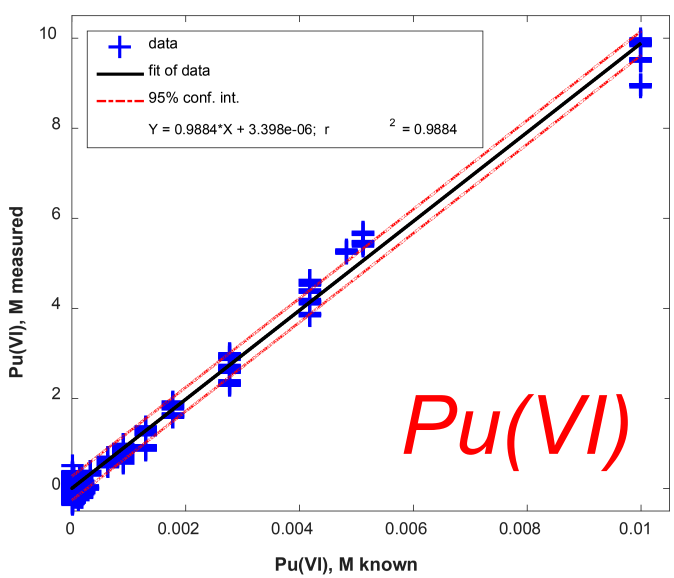
Chemometric models:

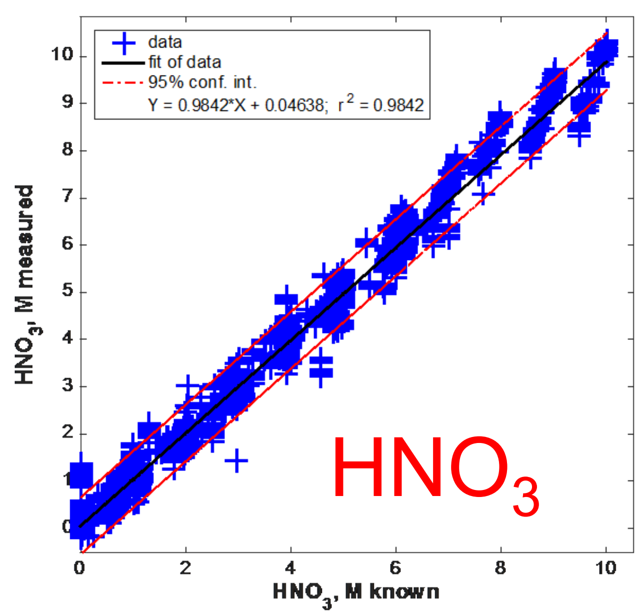
Aqueous

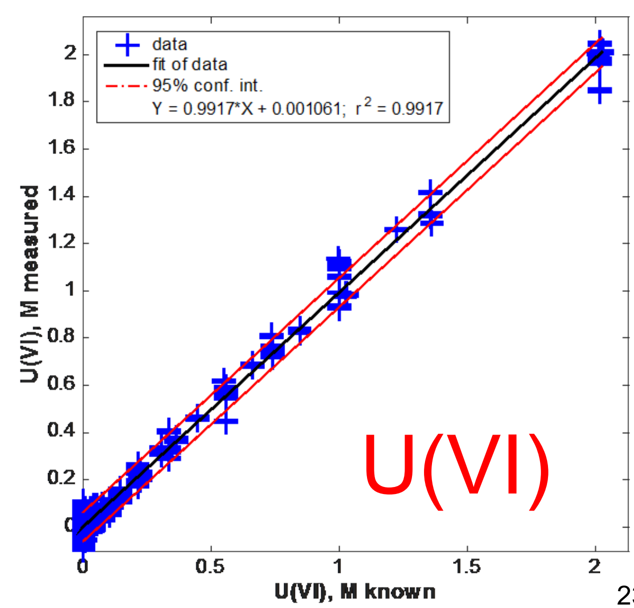












Conclusion

- **On-line monitoring with real-time analysis can provide essential information quickly**
  - 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
- **Current projects are seeing excellent progress in the development of their on-line monitoring systems**
  - CoDCon
  - PuOx