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 – PNNL

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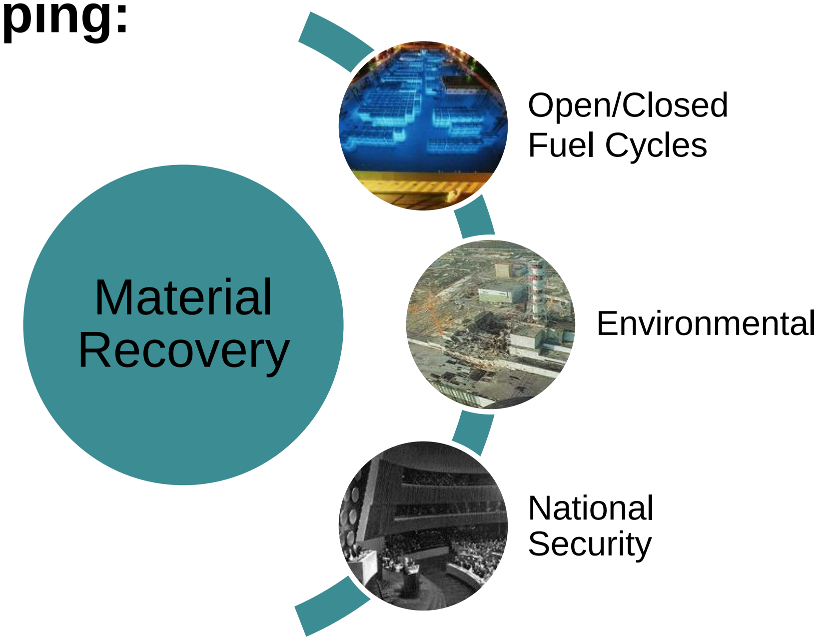
Material Recovery & Waste Form Development

Campaign Objectives

- **Develop advanced fuel cycle material recovery and waste management technologies that improve current fuel cycle performance and enable a sustainable fuel cycle, with minimal processing, waste generation, and potential for material diversion to provide options for future fuel cycle policy decisions**
- **Campaign strategy is based on developing:**
  - **Technologies** for economical deployment
    - Concept through engineering-scale demonstration
  - **Capabilities** for long-term science-based, engineering driven R&D, technology development and demonstration
  - **People** to provide the next generation of researchers, instructors, regulators and operators



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MRWFD Campaign Structure
Aimed to Improve Once-Through and Enable Recycle

Campaign Mgt & Integration
- Provide technical leadership in separations and waste forms, leading to effective options for future fuel cycles
- Manage Campaign research and development to include: prioritization, planning, reporting, and technical reviews
- Collaborate with university researchers, other campaigns, program offices, and international organizations

Reference Tech & Alternatives
- Provide a framework and data to evaluate technology improvements, performance targets, and identify gaps
- Develop and demonstrate material recovery technologies that enable processing a broad range of fuels with stringent separation requirements (focused on aqueous processing of LWR oxide fuel)

Minor Actinide Sigma Team
- Develop and demonstrate technologies that enable TRU separations from LWR fuel
- Develop cost effective separations processes for MA recycle

Off-Gas Sigma Team
- Develop and demonstrate technologies that enable fuel treatment under current regulatory environment
- Develop cost effective solutions to off-gas management from fuel treatment and other nuclear applications

Advanced WF & Processes
- Develop next generation, high performance, waste forms consistent with advanced separations technologies
- Demonstrate waste processes cost effective, reliable fabrication of next generation waste forms

Waste Form Characterization
- Enhance disposal options for existing and high-performance waste forms
- Develop fundamental understanding of waste form behavior in a variety of disposal environments
- Work with international partners to develop consensus degradation rate law(s)

Fund Science & Mod/Sim
- Develop advanced methods and fundamental understanding of separation chemistry and processes
- Develop predictive models based on fundamental data

Domestic Echem Process
- Develop and demonstrate deployable and sustainable technology to enable recycle of U/TRU for metal fast reactor fuel

Fuel Resources
- Develop and demonstrate extractants and engineered systems to further improve performance and lower cost supply of uranium from seawater

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**

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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

Approach: On-line Spectroscopic Measurements

Raman measurements of

- Actinide oxide ions (U(VI) and Pu(VI))
- Organics: solvent components and complexants
- Inorganic oxo-anions (NO_3^-, CO_3^{2-}, OH^-, SO_4^{2-}, etc)
- Water, acid (H^+), base (OH^-), pH in weak acid/weak base

UV-vis-NIR measurements of

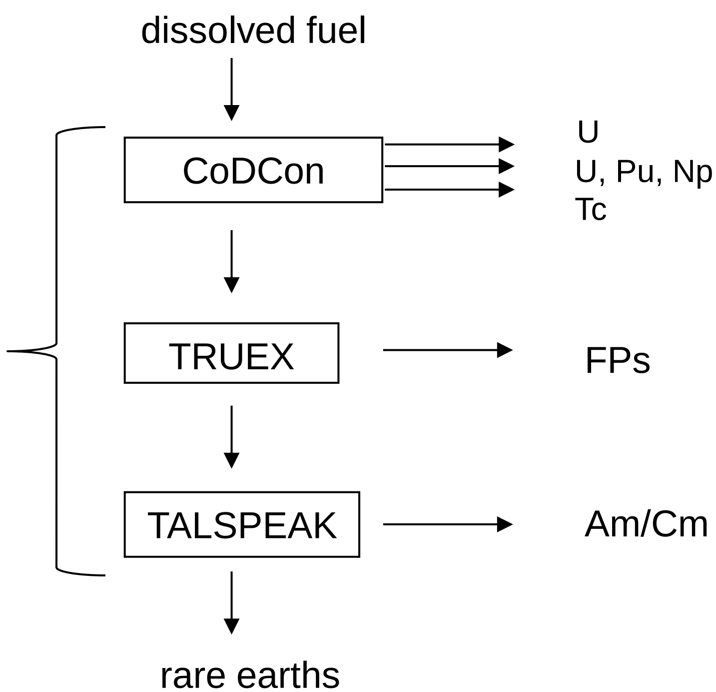
- trivalent and tetravalent actinide and lanthanide ions

Potential Uses

- Process control (operator)
- Process monitoring for safeguards verification (IAEA)

Process Monitoring Can Be Achieved Throughout the Flowsheet

Monitoring of strong acid or pH desired



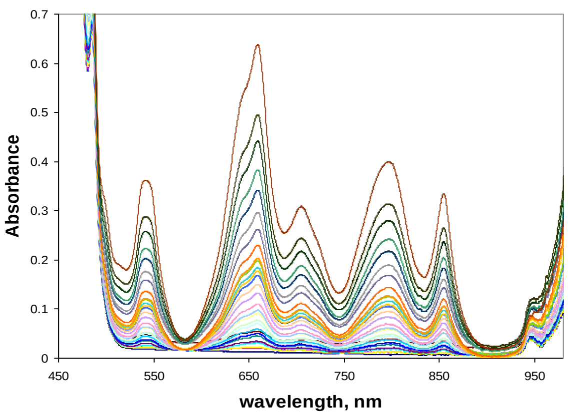
Global vision:
Process monitoring/control at various points in flowsheet

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

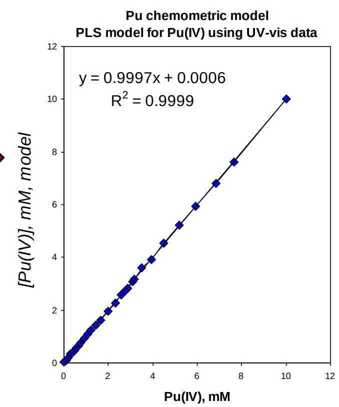
Monitoring Is Not Flowsheet Specific

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

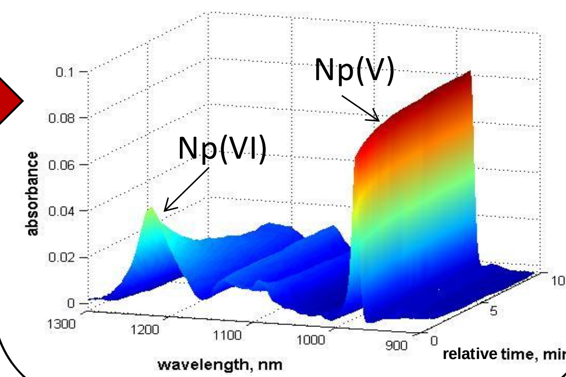
Static measurements: Model training database



Chemometric model development

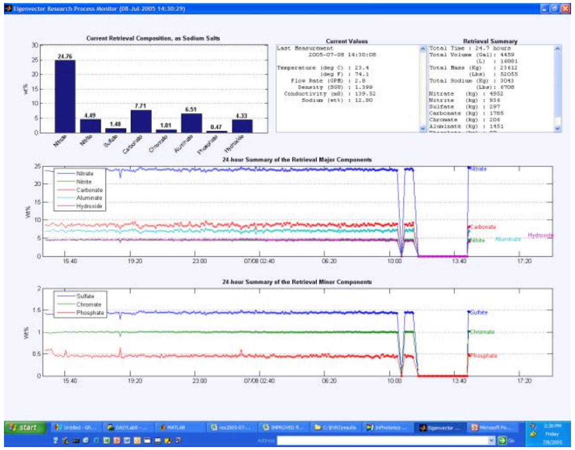


On-line model verification and translation



Integrated software for data collection, processing, storage and archiving

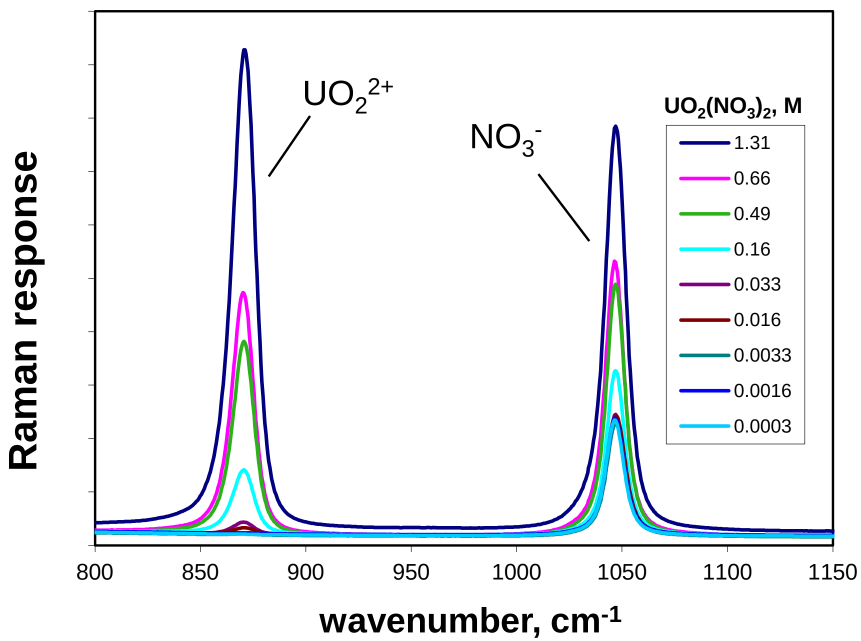
Real-time on-line concentration data display



Optical spectroscopy for monitoring UO_2^{2+}, Pu, and Np species in fuel solutions

Raman spectroscopy

Variable $UO_2(NO_3)_2$ in 0.8M HNO_3

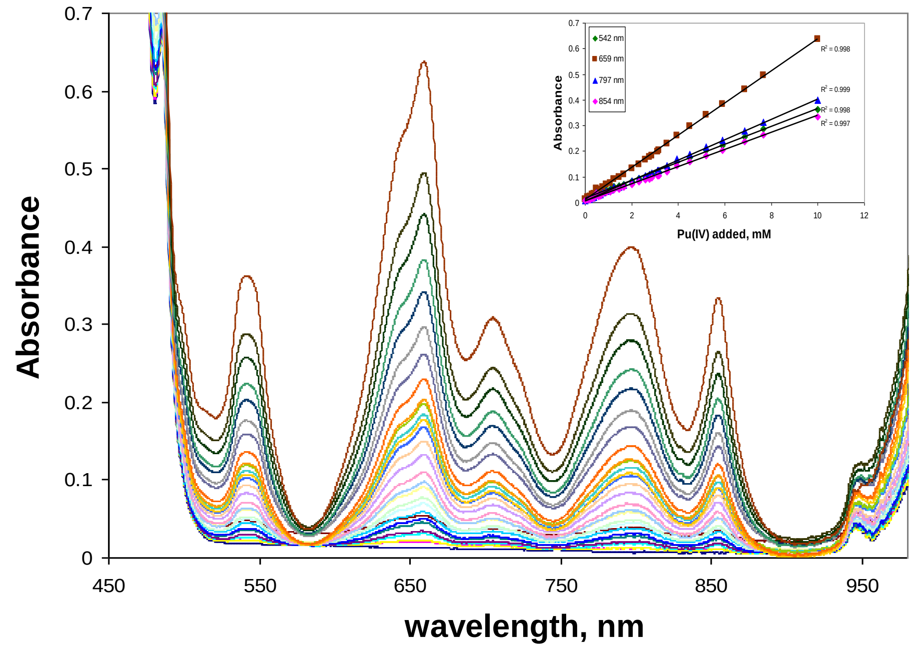


Detection limits:

- 3.1 mM for UO_2
- 0.08 mM for Pu(IV)

Vis-NIR spectroscopy

Variable Pu(IV) in fuel feed simulant



Pu(IV) concentration variable 0.1 to 10 mM

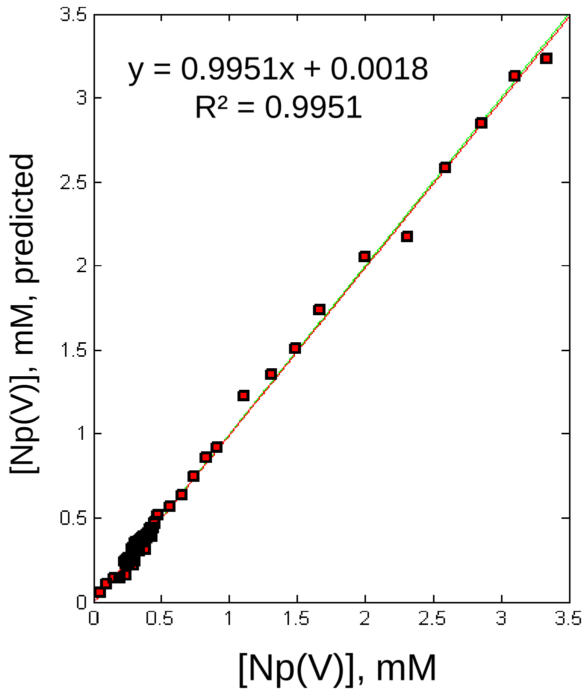
Feed composition: 1.3 M $UO_2(NO_3)_2$ in 0.8 M HNO_3

$UO_2(NO_3)_2$ does not interfere with Pu measurements

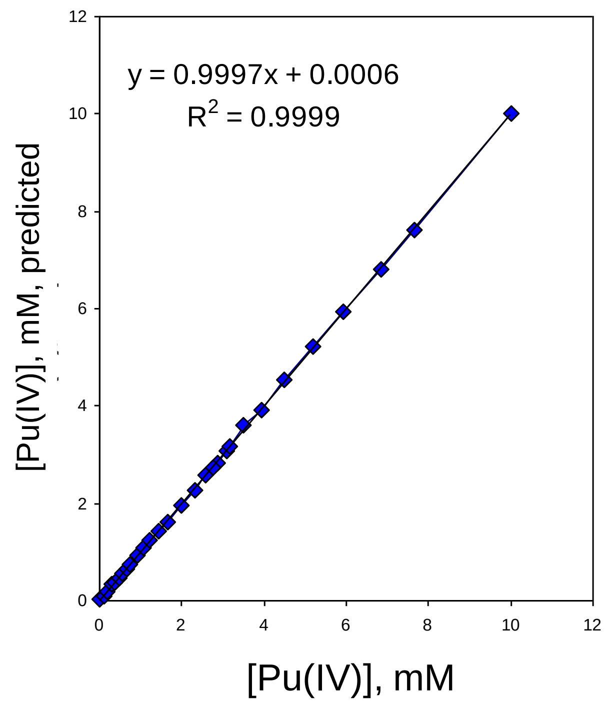
Chemometric PLS models for quantitative analysis

Pu(IV), Np(V) and UO_2^{2+} (Raman and vis-NIR)

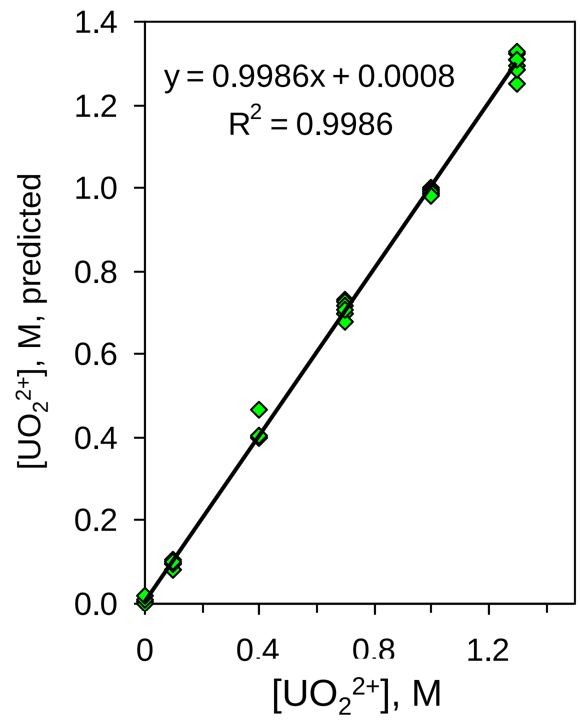
Np(V) model



Pu(IV) model



U(VI) model



Use Static spectral database for process monitor model development

Linear fit with slope = 1 indicates agreement between actual and predicted values, and successful model performance

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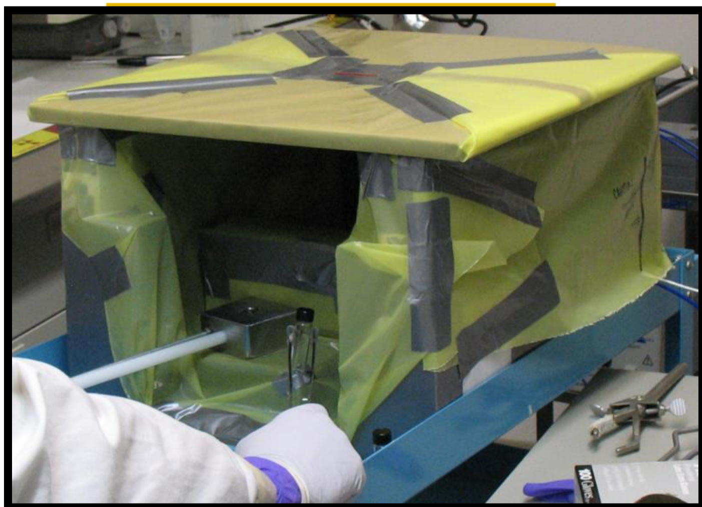
Task objectives FY16/17

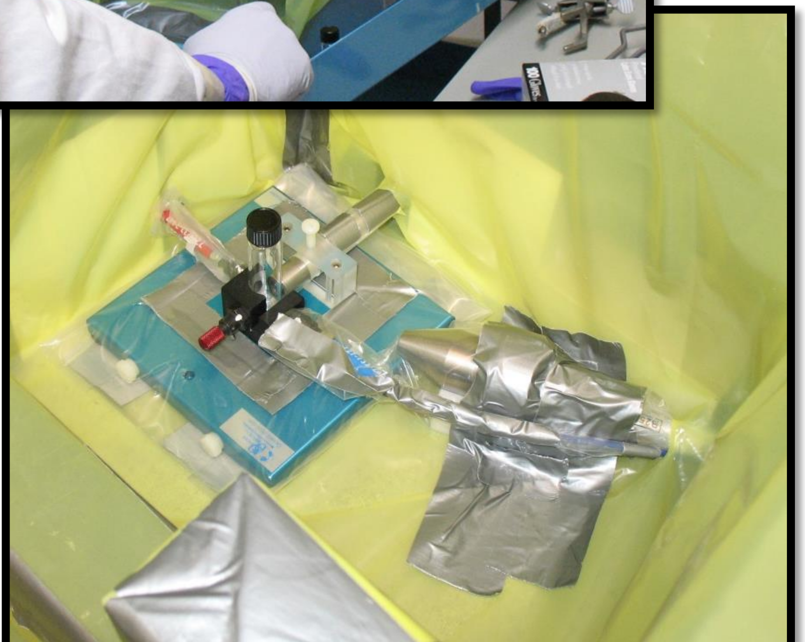
Support the roadmap for on-line monitoring and help define the activities required for a technology transfer to an operating reprocessing plant

- **CEA-DOE collaboration**
  - Demonstrate micro-Raman probe for use on U and HNO_3 measurements
  - Interface micro-Raman probe for measurement at the microfluidic scale
- **CoDCon deployment**
  - Demonstration of advanced on-line spectroscopic tools within a ~1 kg Uranium test
- **SBIR Grant: Spectra Solutions, Inc. / PNNL**
  - Phase-1 FY15: Development of combined Raman/UV-vis probe for use in reprocessing environment :
  - Phase-1, FY16: Microfluidic Spectroscopic Sensor for Nuclear Fuel Reprocessing Solutions:

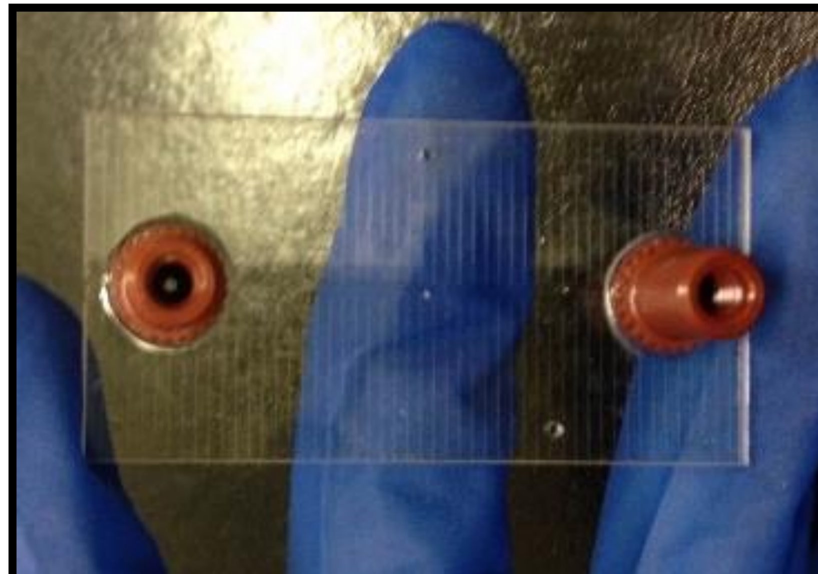
From Macroscale to Microscale

- **Reduce sampling volume**
  - Dose to personnel
  - Dose to equipment
  - Waste volume





Significant experience in macroscale process monitoring



Apply this experience to monitoring solutions on the microscale level

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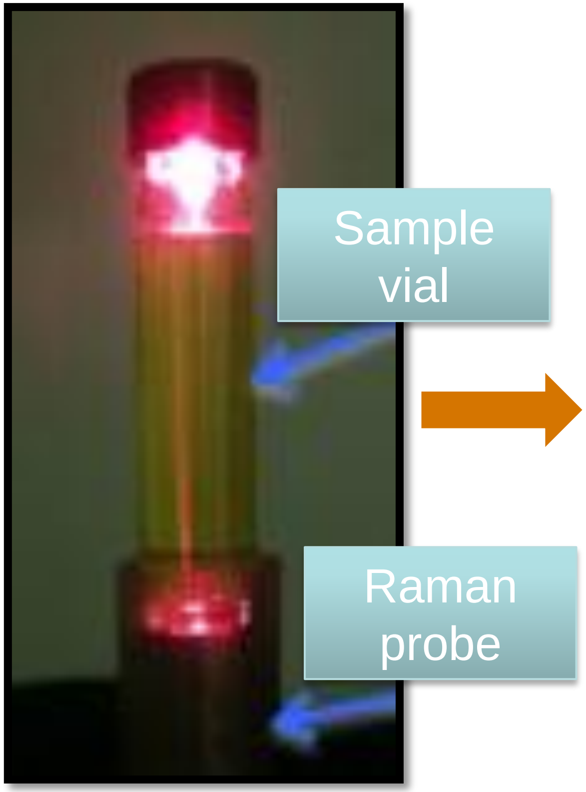
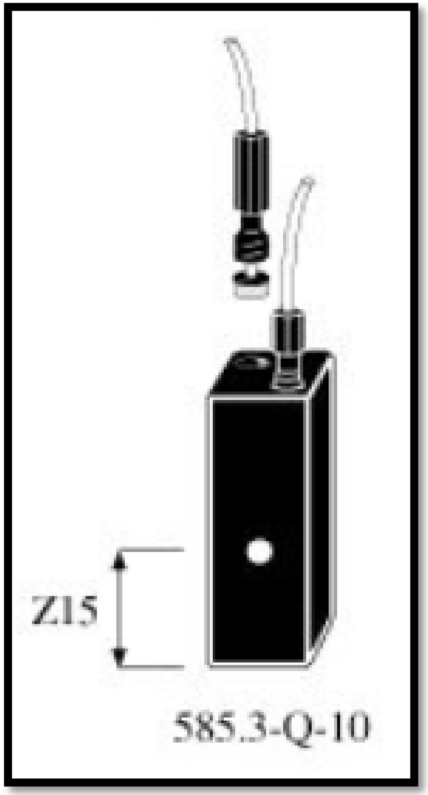
Microfluidics: Reduced Sampling Volume

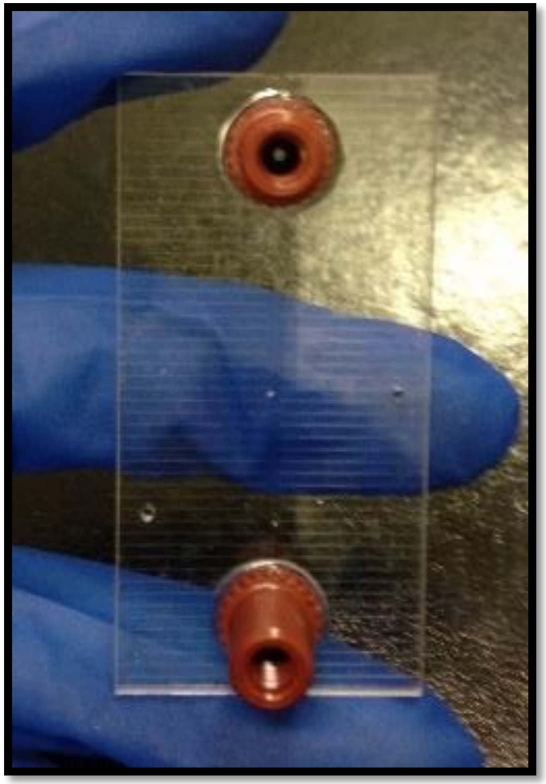
Vial:
4 cm path length



Micro flow cell:
1 cm path length

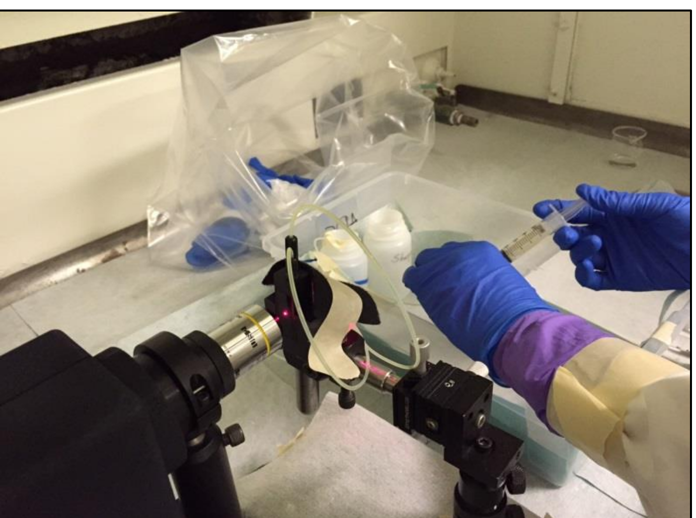


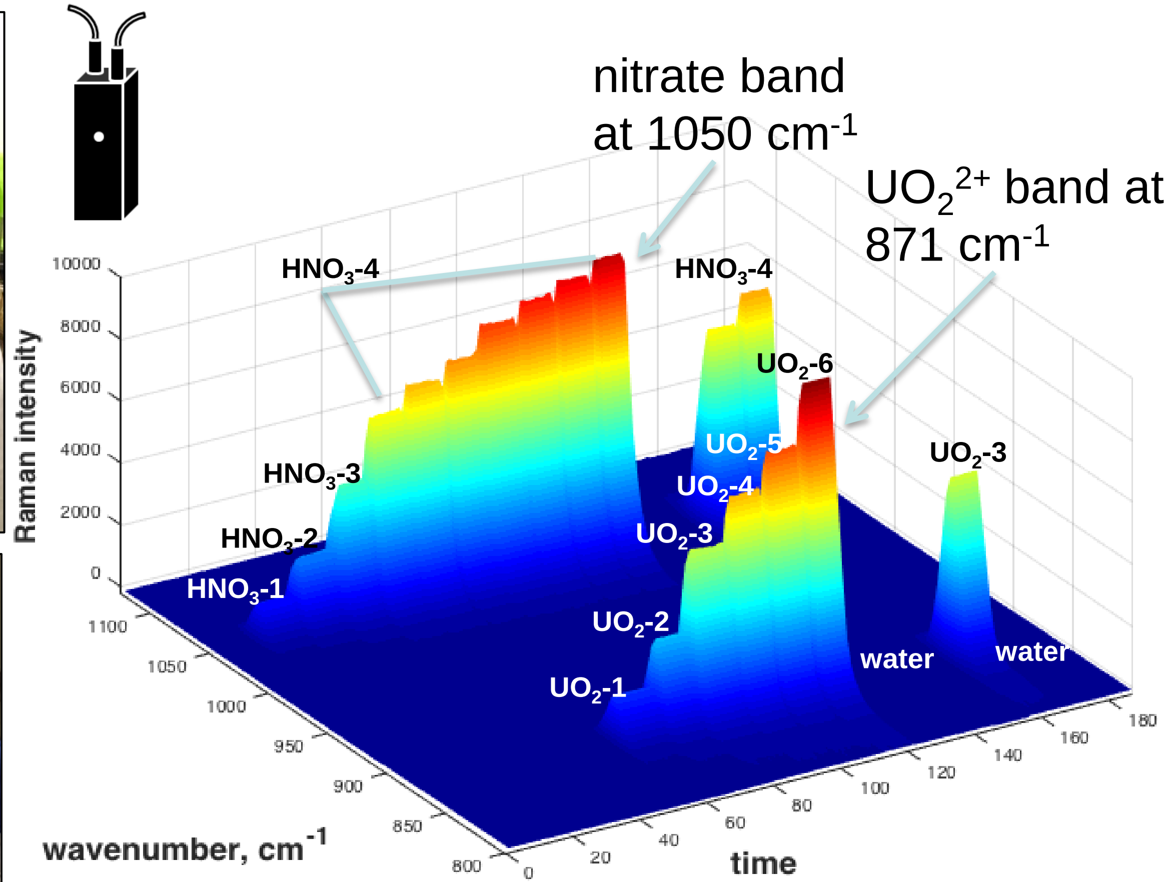
Microfluidic device:
100 µm path length



Test system response under ideal conditions (long path length, static conditions) and compare to response at lower path lengths and flow conditions

MicroRaman spectra as a function of time for varying $UO_2(NO_3)_2$ and nitric acid Solutions in 8 µL cell





Nitric acid range: 0 – 3M
$UO_2(NO_3)_2$ range: 0 – 2M
total nitrate range: 0 – 7M

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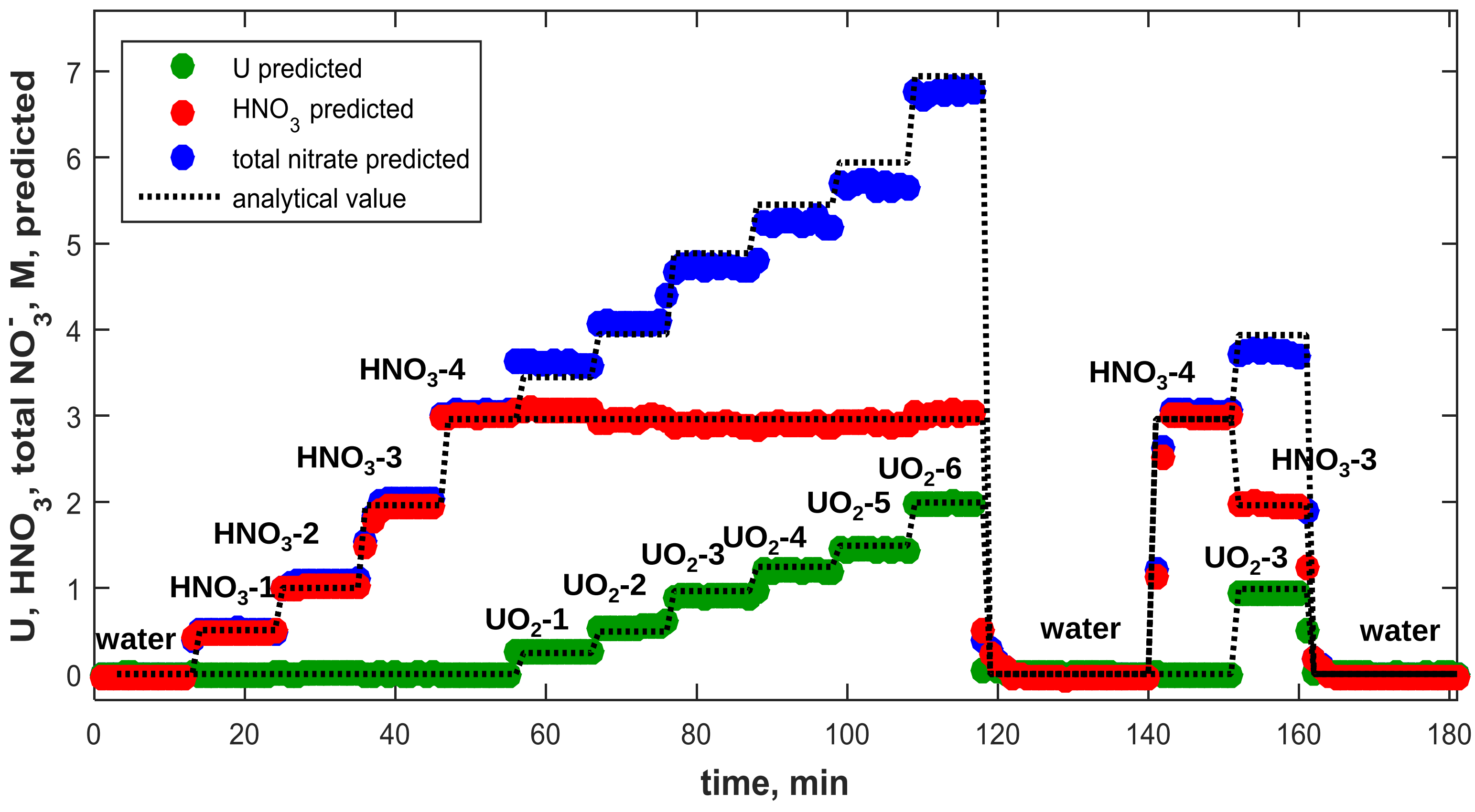
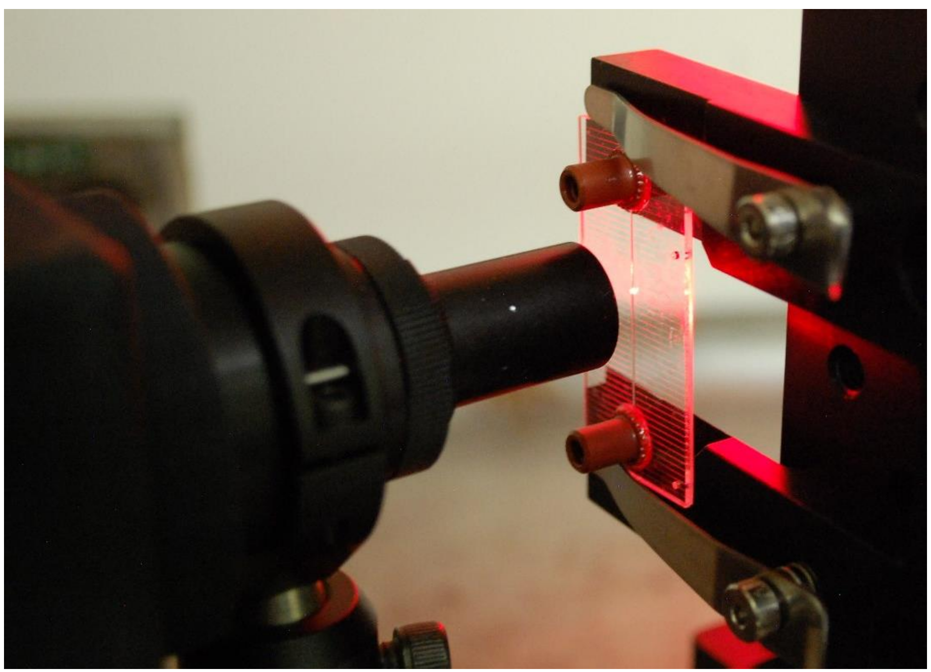
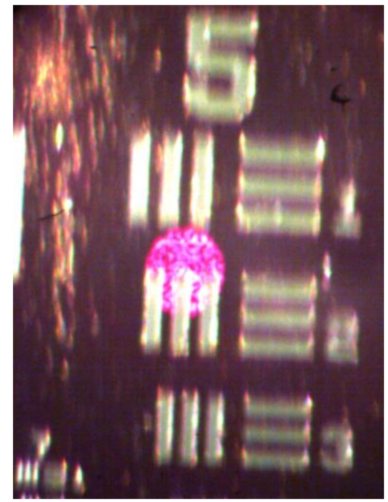
Model predictions of varying $UO_2(NO_3)_2$ and nitric acid solutions in 8 µL cell



MicroRaman probe

- Fiber optically coupled Raman microscope with integrated video imaging
- High sensitivity Raman system with a focal point capable of measurements inside a microfluidic chip





1st generation objective focal point diameter ~70 μm

2nd generation objective focal point diameter ~35 μm

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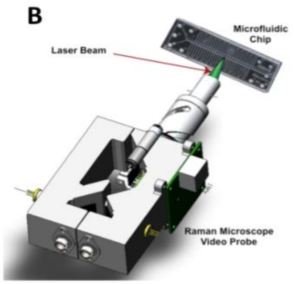
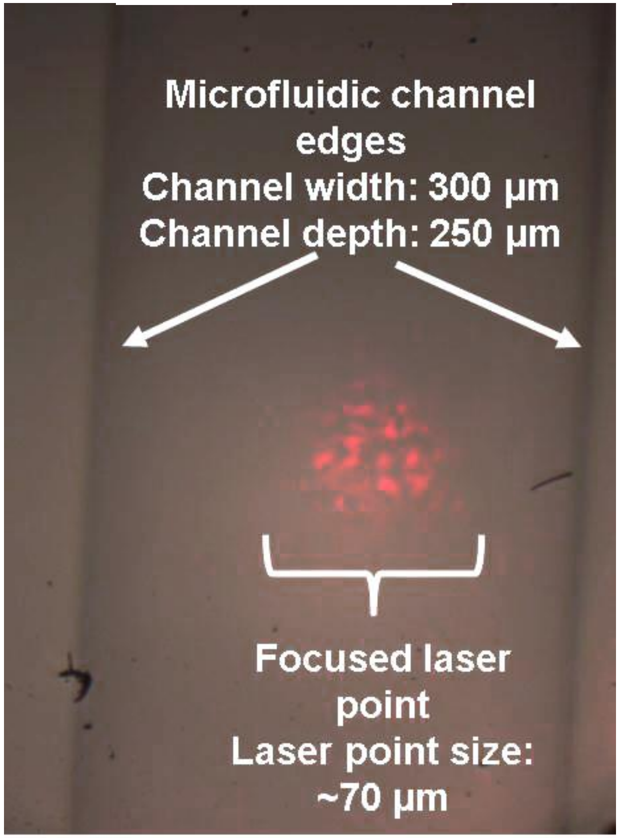
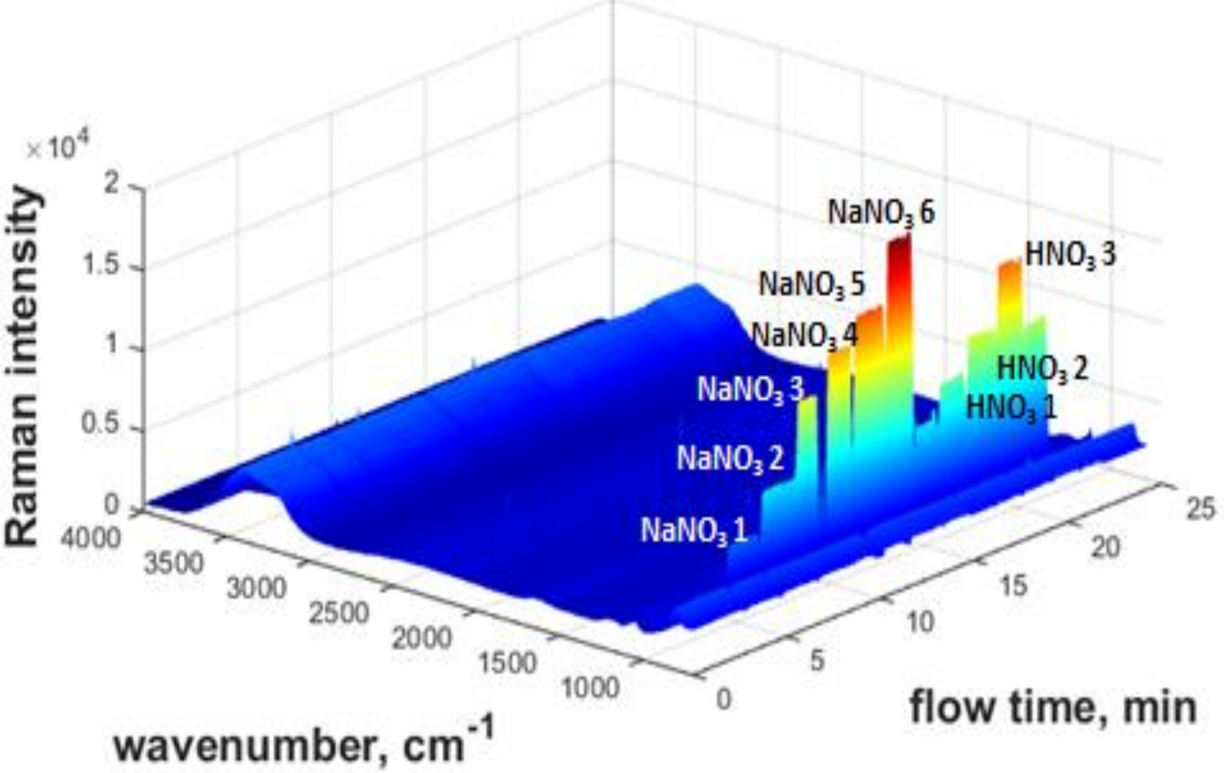
Raman measurements using micro-fluidic device with flow solutions





$NaNO_3$ / HNO_3 Solution Series



$NaNO_3$ range: 0 – 4M
Nitric acid range: 0 – 2M

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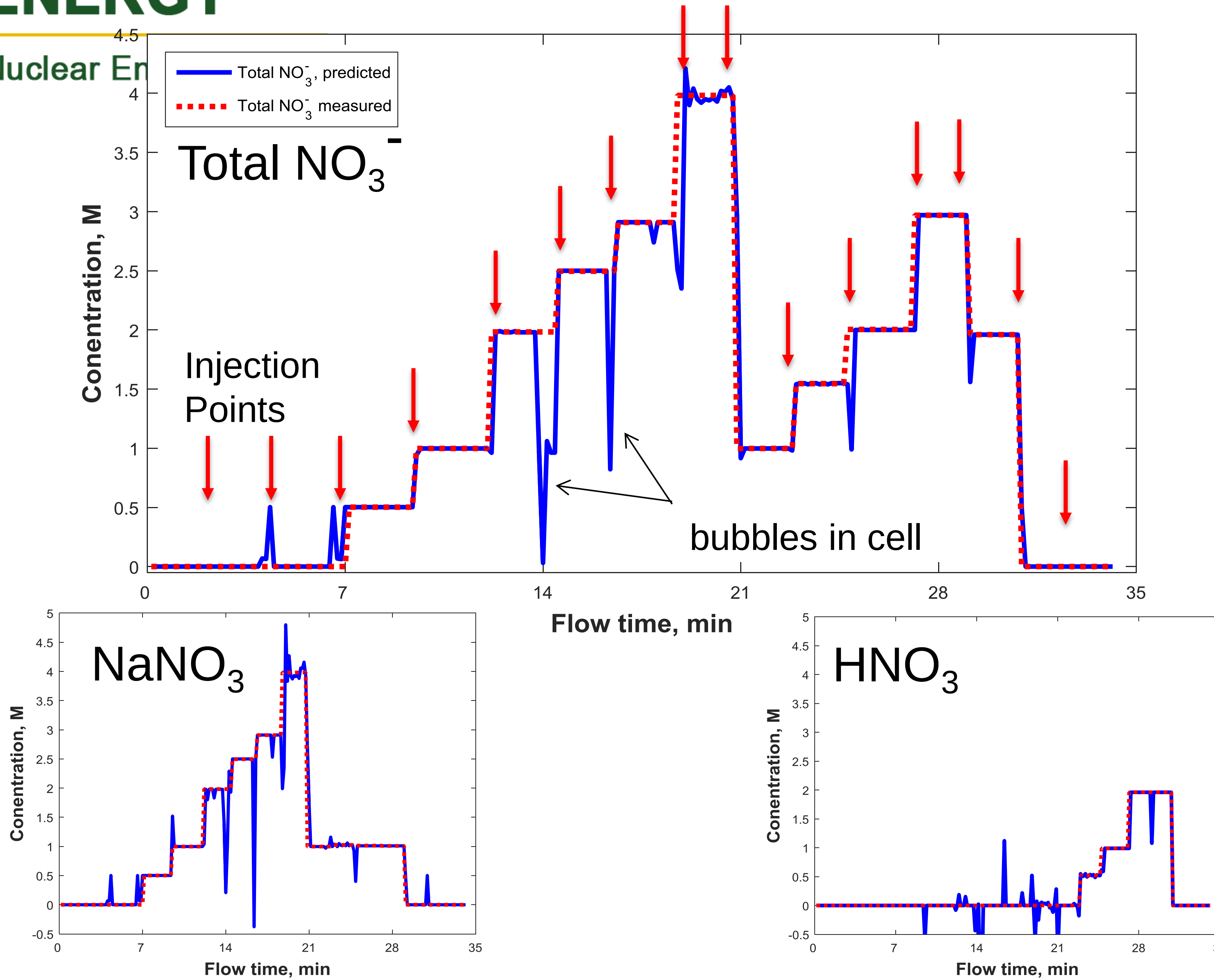
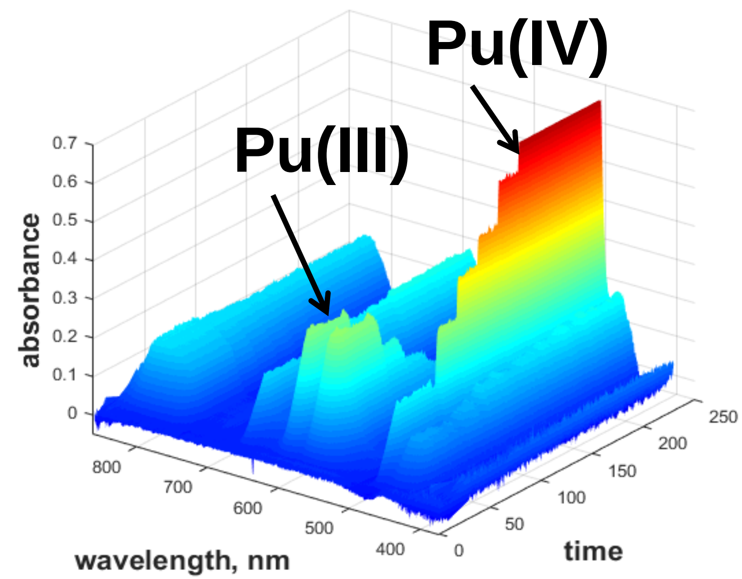
Microfluidic device: Model Predictions



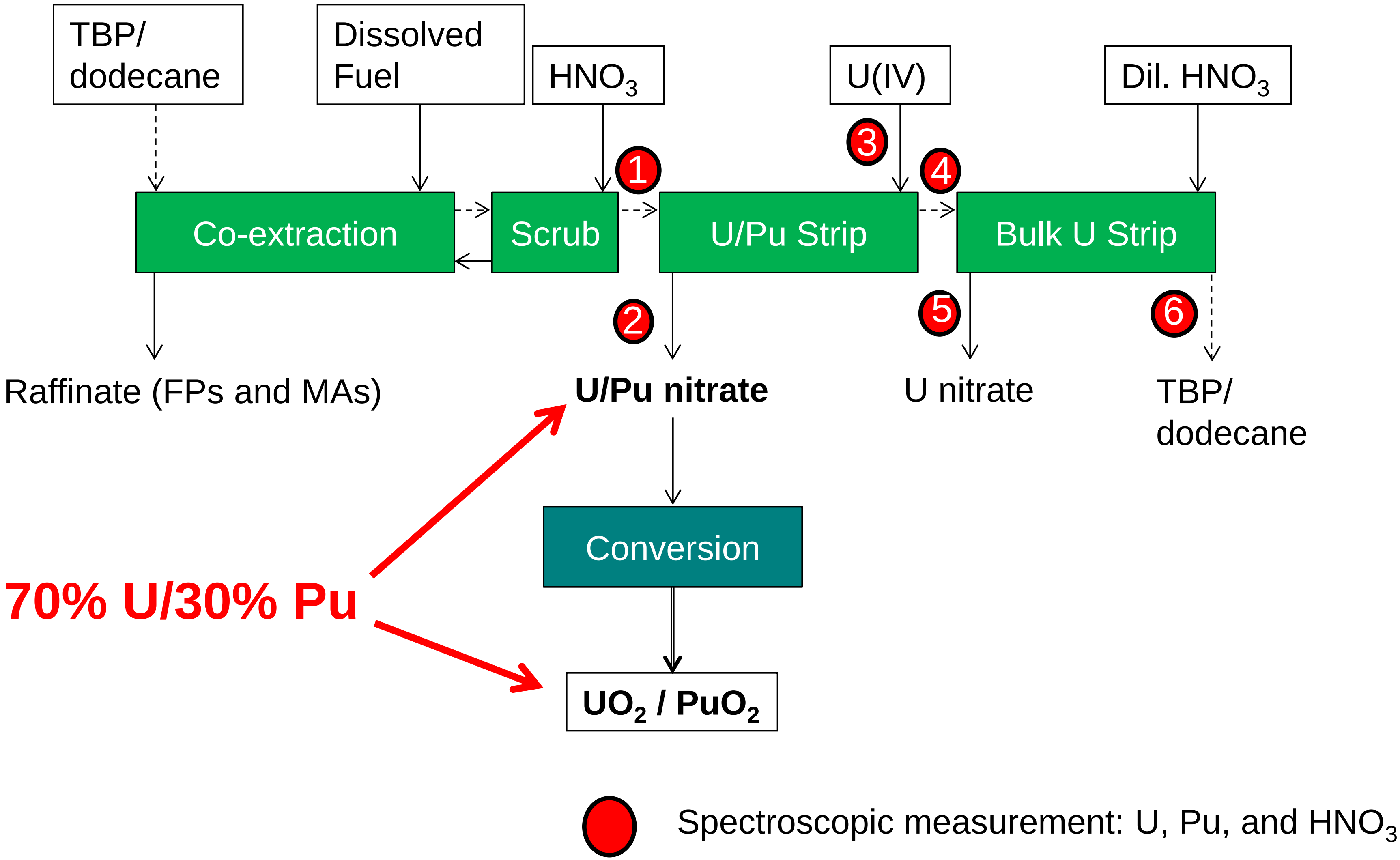
Overview of CoDCon testing effort

- **Key tasks to be performed**
  - Development of co-conversion method
  - Development of electrochemical method to produce U(IV)
  - Preparation of simulant containing U and Pu
  - Solvent extraction to produce a combined U/Pu nitrate solution
  - Conversion of the U/Pu nitrate solution to a solid U/Pu oxide product

- **Advanced on-line spectroscopic tools will be used to monitor and control the testing parameters**
  - Raman spectroscopy
    - U(VI) and HNO_3 concentrations
  - UV/Vis/NIR Spectrophotometry
    - Pu and Np variable oxidation states and U(IV)

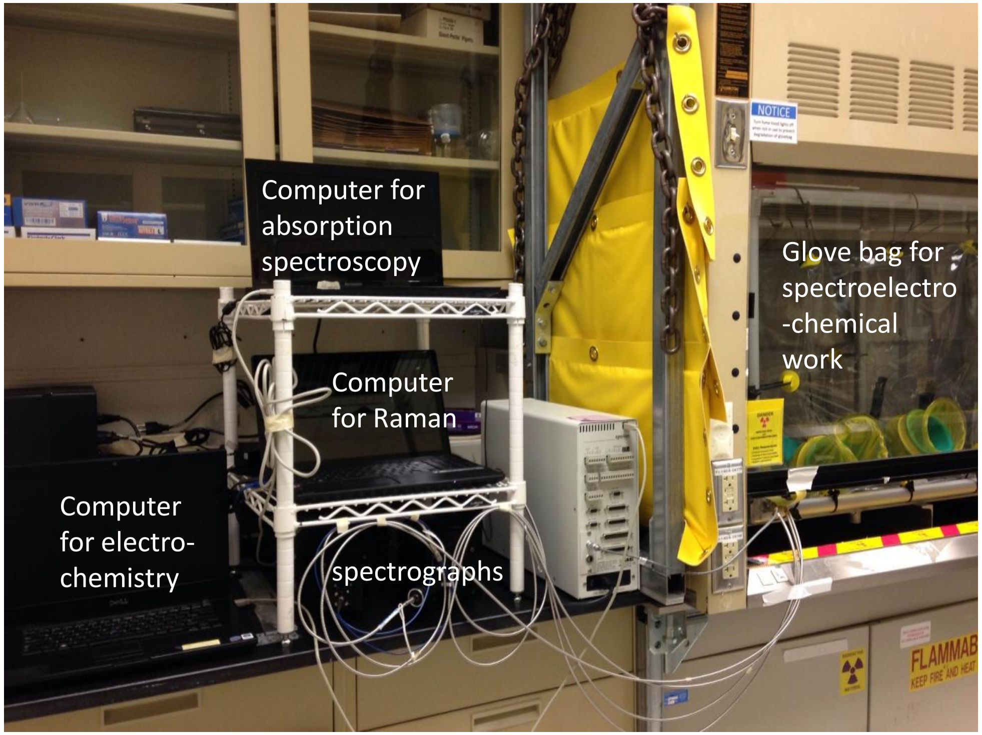


CoDCon demonstration concept: instrumentation locations



Develop chemometric model for quantification of species: Approach

- **Collect spectroscopic data of all analytes of interest over wide range of concentrations/solution conditions**
- **Model must capture matrix effects, interferents, etc.**
- **Example: Pu(IV) spectral dependence on HNO_3 concentration**
- **Use spectroelectrochemistry to collect training set data**
  - Electrochemically hold wide range of Pu and/or U concentrations and oxidation states
- **Develop software to provide real time analysis/visualization of data**



Conclusions

- **Demonstrated quantitative spectroscopic measurement under fuel reprocessing conditions**
  - Fuel simulants
  - Actual commercial fuel (BWR Spent Fuel)
    - Raman for on-line monitoring of U(VI), nitrate, and HNO_3 concentrations, for both aqueous and organic phases
    - Vis/NIR for on-line monitoring of Np(V/VI), Pu(IV/VI), Nd(III)

- **Demonstrated micro-Raman probe for use on U and HNO_3 measurements**
  - Detection limits and predictive modeling of U, HNO_3 and nitrate using static solutions
  - Interfaced micro-Raman probe with commercial micro-flow cell
  - Demonstrated monitoring of variable HNO_3 and $UO_2(NO_3)_2$ with micro-volume flow cells

- **Current plans for on-line process monitoring**
  - Collaborative demonstration on larger lab-scale (CoDCon)

Acknowledgement

- **U.S. Department of Energy (DOE) : Fuel Cycle Research and Development (FCR&D), Separations Campaign (NE)**
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- **FCRD young investigator of the year awardee (Amanda Casella)**