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Office Of Nuclear Energy Sensors and Instrumentation Annual Review Meeting

Materials Recovery and Waste Forms Overview

On-line Sampling & Monitoring – PNNL

Samuel A. Bryan

Pacific Northwest National Laboratory

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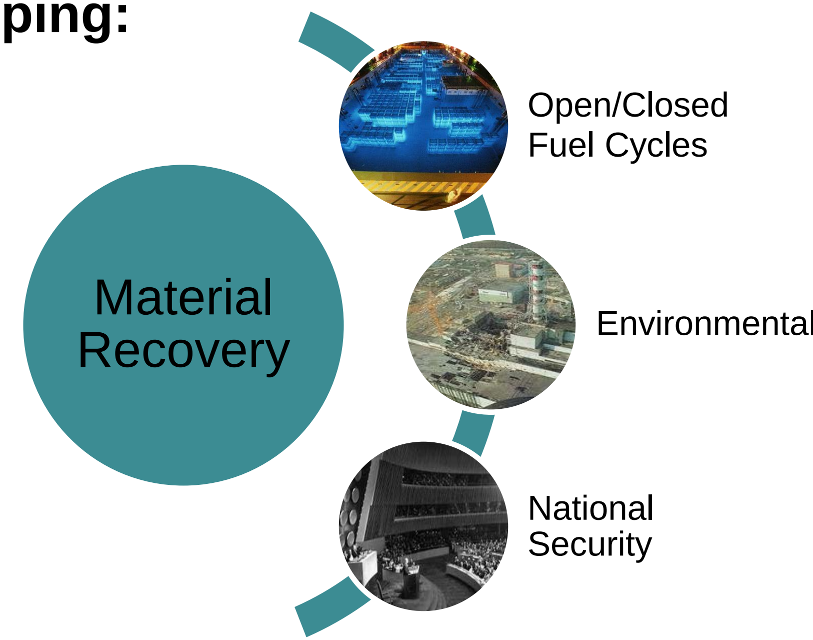
Campaign Objectives

- **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

- **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

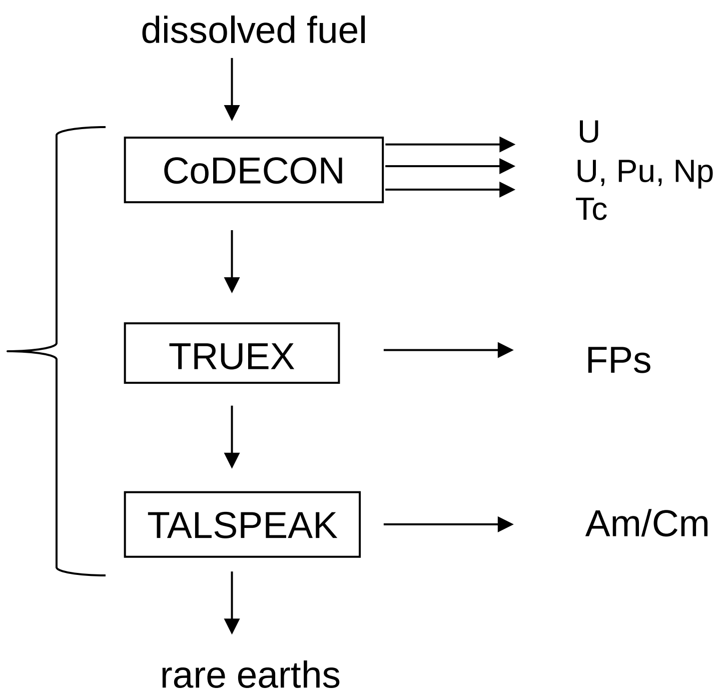
- **The MRWFD campaign has been developing methods to monitor key chemical components of a separation process, in near real time**
- **Aqueous processing**
  - Sam Bryan, PNNL
- **Electrochemical pyroprocessing**
  - Mark Williamson, ANL

Approach: On-line Spectroscopic Measurements

- **Raman measurements of**
  - Actinide oxide ions
  - 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 monitoring for safeguards verification (IAEA)
  - Process control (operator)
- **Previous Experience: Hanford Site including deployments**
  - Real-time, online monitoring of high-level nuclear waste in tanks and to the waste pretreatment process

Process Monitoring Can Be Achieved Throughout the Flowsheet

Monitoring of strong acid or pH desired



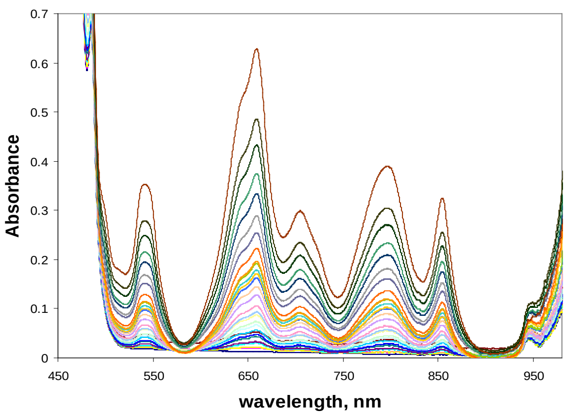
Global vision:
Process monitoring/control at various points in flowsheet

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

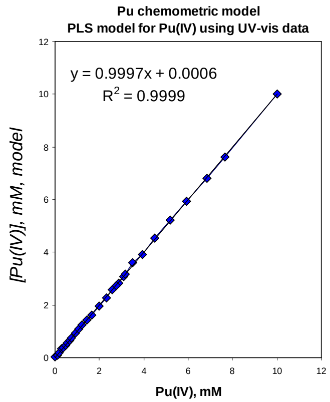
Monitoring Is Not Flowsheet Specific

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

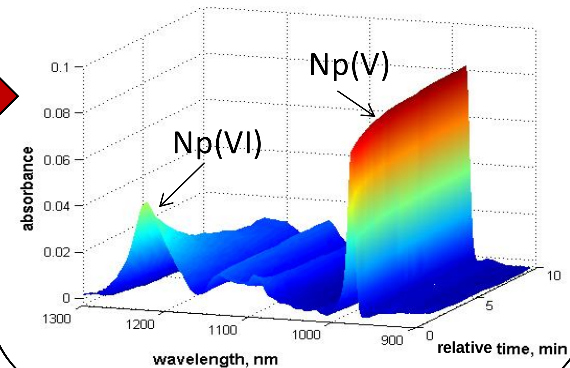
Static measurements: Model training database



Chemometric model development

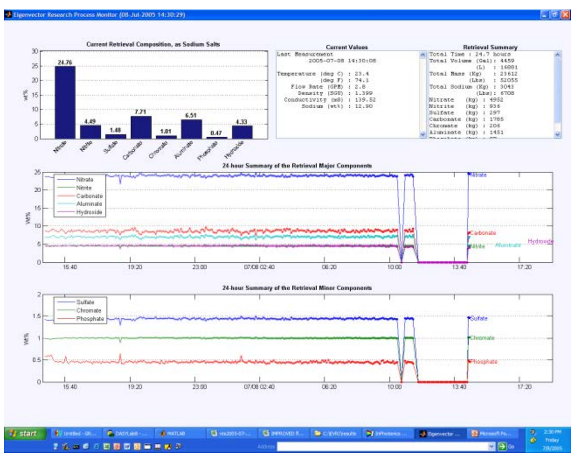


On-line model verification and translation



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

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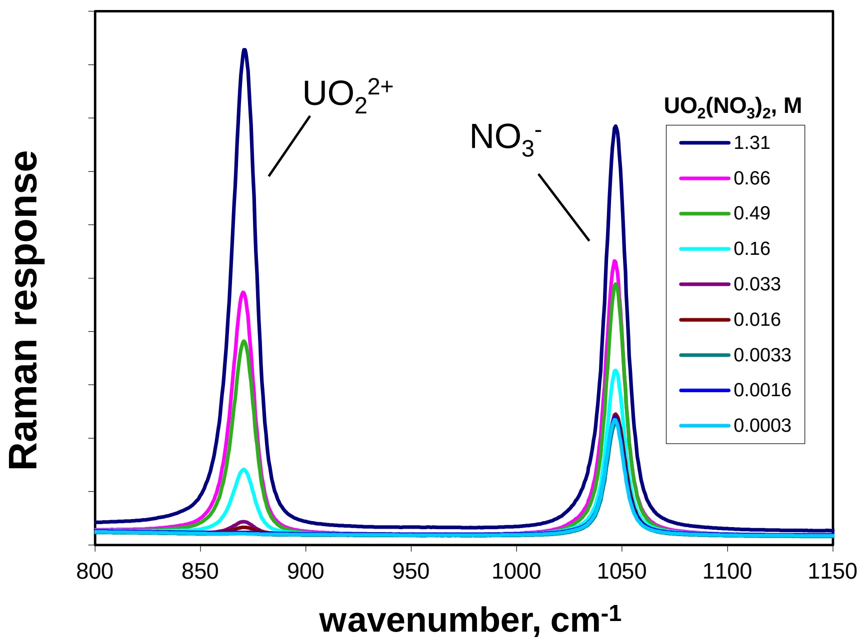
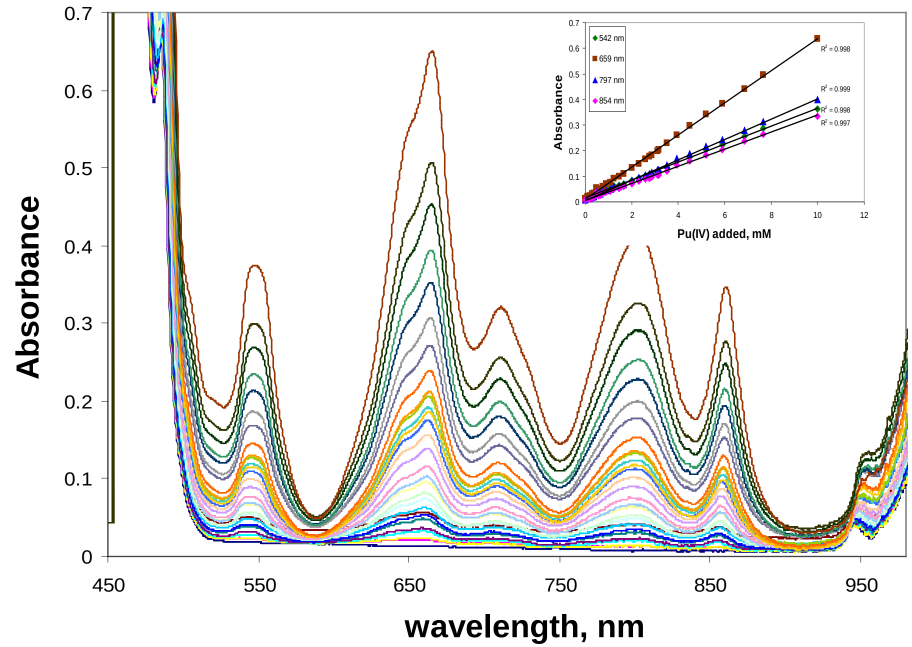
Raman spectroscopy

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



Vis-NIR spectroscopy

Variable Pu(IV) in fuel feed simulant



Detection limits:

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

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

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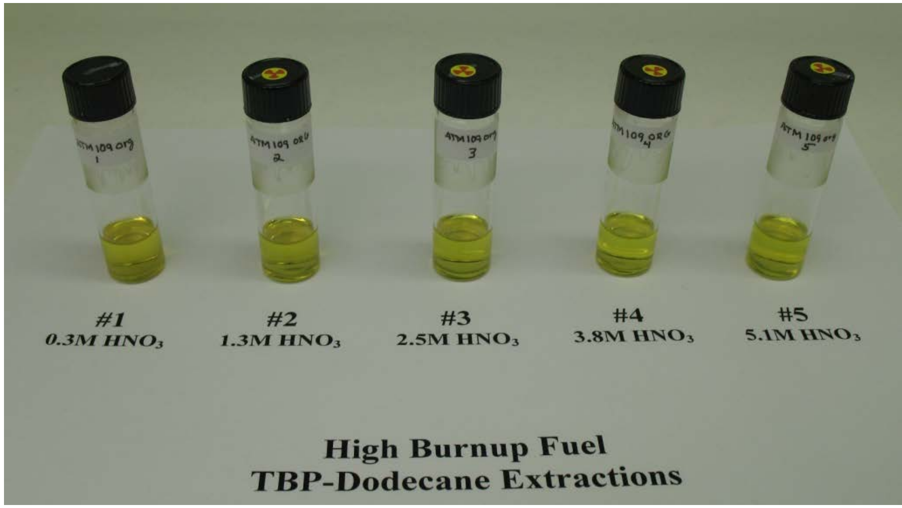
Proof-of-Concept : Applicability of spectroscopic methods for commercial BWR ATM-109 fuel measurements

- **Commercial fuel:** ATM-109, BWR, Quad Cities I reactor; 70 MWd/kg; high burnup
- **Fuel dissolved in HNO_3**
- **Performed batch contact on each aqueous feed with 30 vol% TBP-dodecane**
- **Feed, Organic, Raffinate phases successfully measured by**
  - Raman, Vis-NIR
- **Excellent Agreement of spectroscopic determination with ORIGEN code and ICP measurement**



ATM-109	U	Pu	Np	Nd
burnup code (ORIGEN-ARP)	0.720	7.50E-03	4.60E-04	1.10E-02
ICP-MS	0.721	8.99E-03	4.70E-04	0.84E-02
Spectroscopy	0.719	8.90E-03	4.70E-04	1.10E-02
Spectroscopic / ICP ratio	1.0	0.99	1.0	1.3

Molar units

Bryan et al. Radiochim. Acta, 2011.

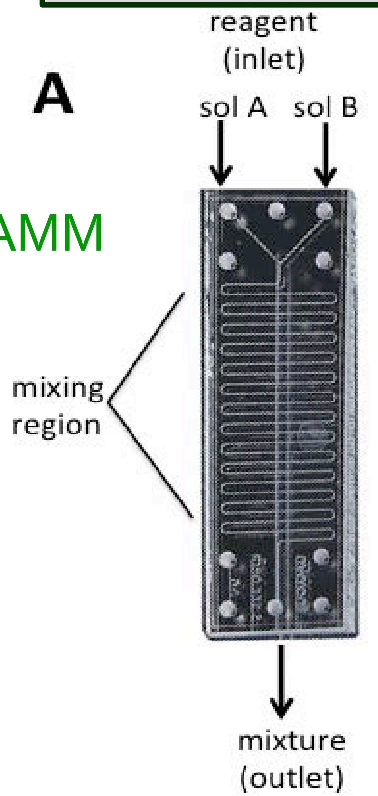
Task objectives FY15/16

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

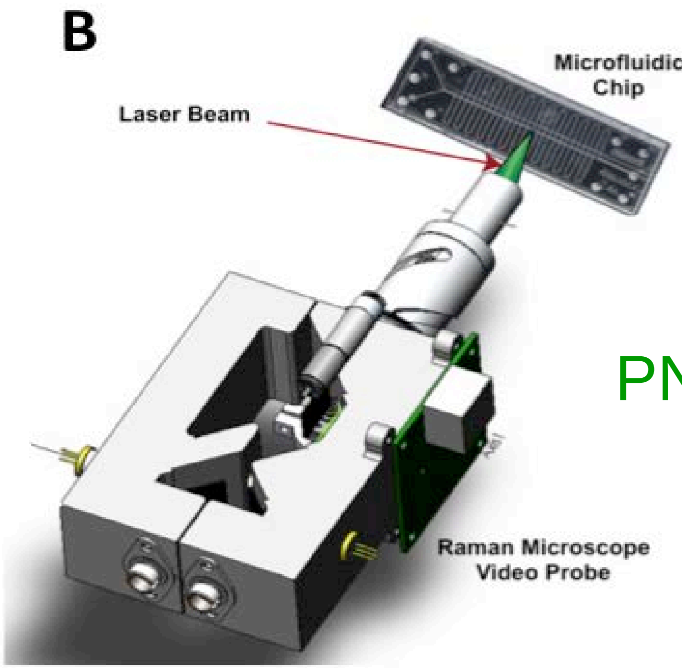
- **CEA-DOE collaboration**
  - demonstrate micro-Raman probe for use on U and HNO_3 measurements
  - interface micro-Raman probe for measurement at the microfluidic scale
- **SBIR Grant: Spectra Solutions, Inc. / PNNL**
  - development of combined Raman/UV-vis probe for use in reprocessing environment
- **Advances in spectroscopic method for weak acid (pH) monitoring, supporting advanced TALSPEAK**
  - Instrumented two phase extraction system for kinetic monitoring
  - Spectroscopic process monitoring for real-time feedback control

Measurement on micro-scale: Schematic of Raman Microprobe

Microprobe for DOE-CEA Collaboration



CEA/LAMM



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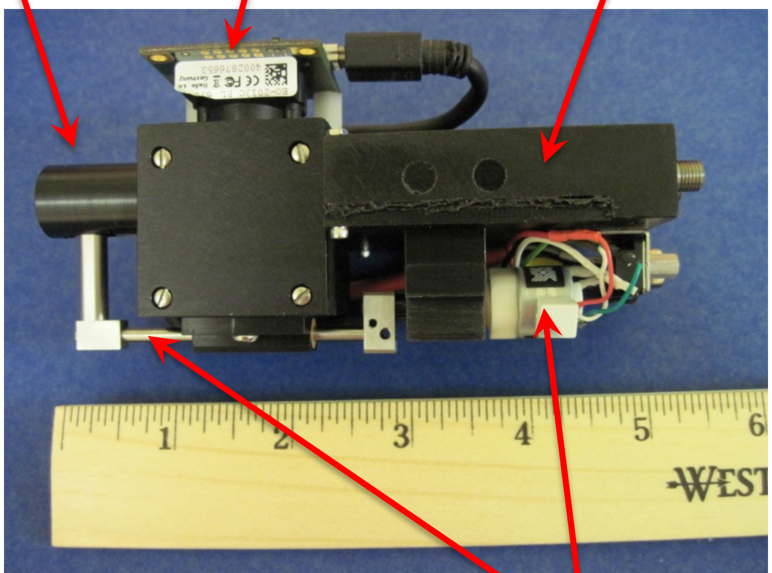
A) Microfluidic mixing chamber showing inlets for reagents (Solution A and B), and outlet for mixture. B) Schematic of the Raman Microscope-video probe adjacent to the microfluidic cell shown with the laser focus within the microchannels of the mixing chamber

Photograph of Micro-Raman Probe Without the External Protective Housing

Focusing Lens

CCD Video Camera

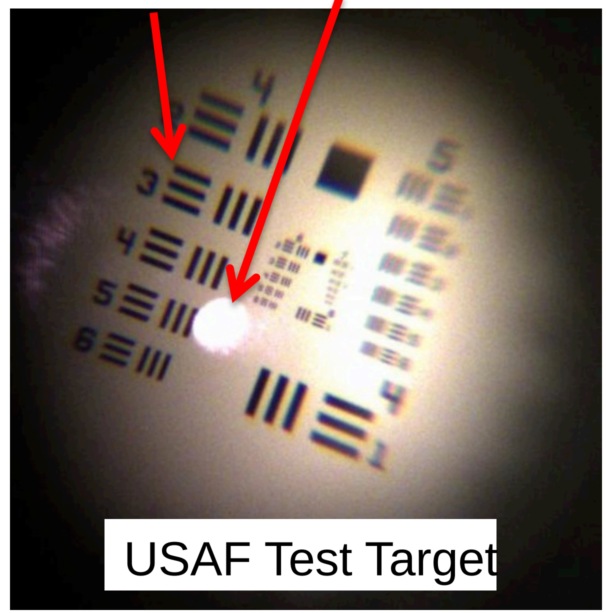
Raman Filter Module



Linear Actuator

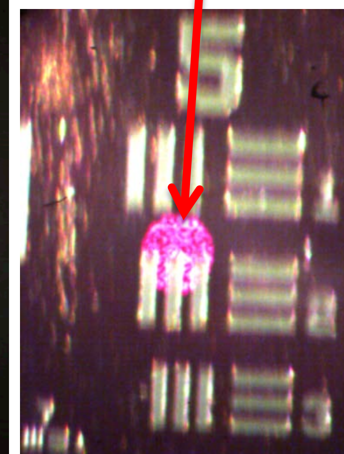
24.8 μm linewidth

Laser spot 124 μm



1st generation probe

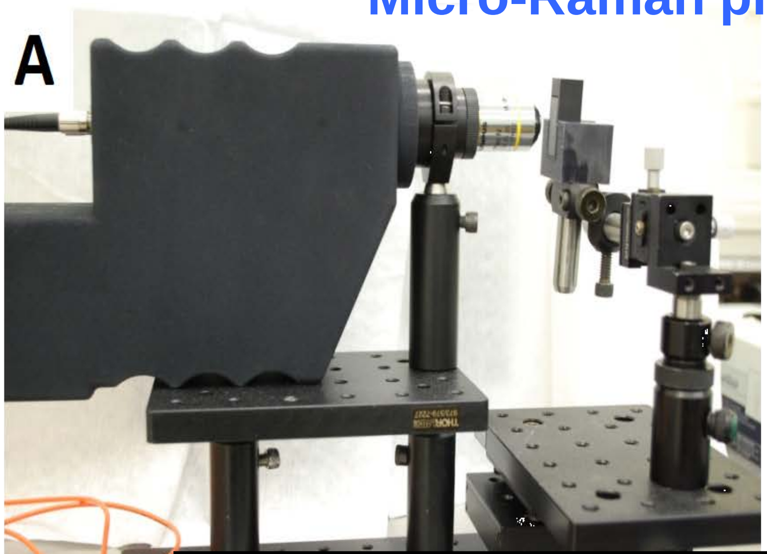
Laser spot ~69 μm

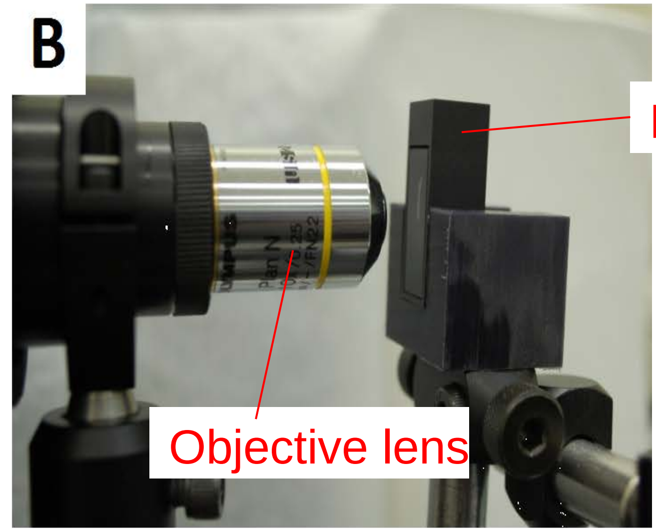


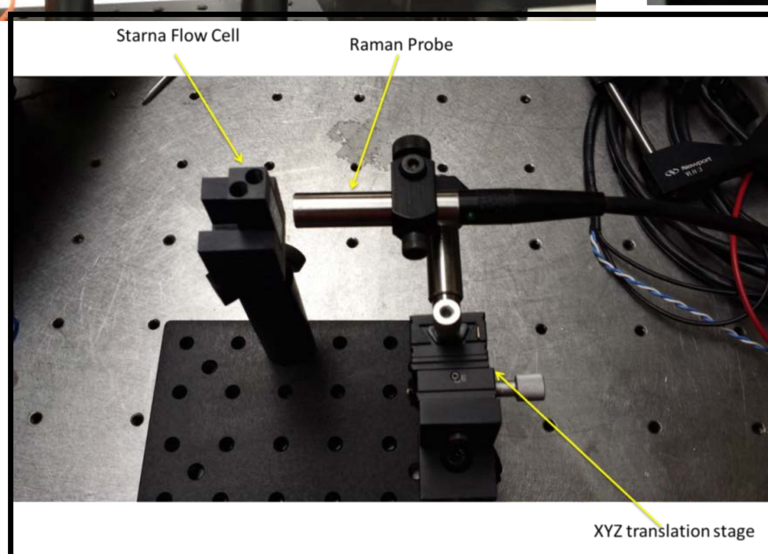
2nd generation

Photograph of MicroRaman Probe Positioned in Front of Flow Cell

Micro-Raman probe



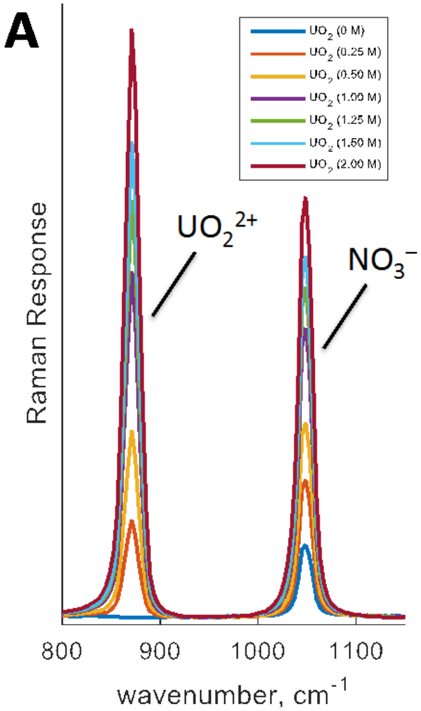




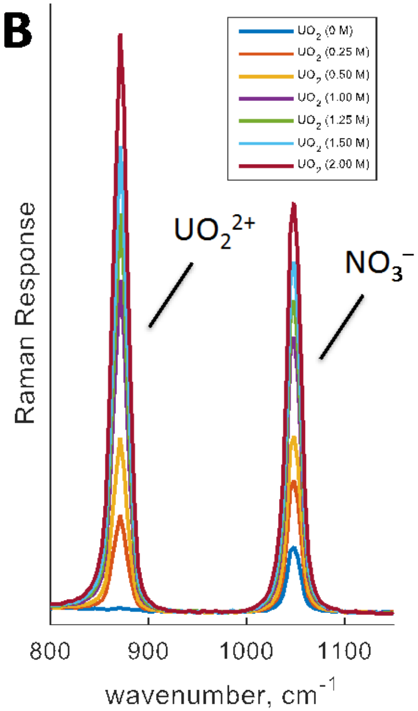
Macro-Raman probe

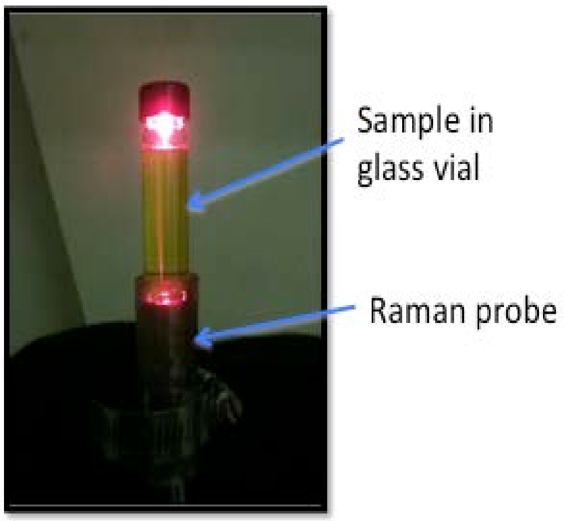
Detection limits for micro-Raman probe

Macro-Raman Probe



Micro-Raman Probe



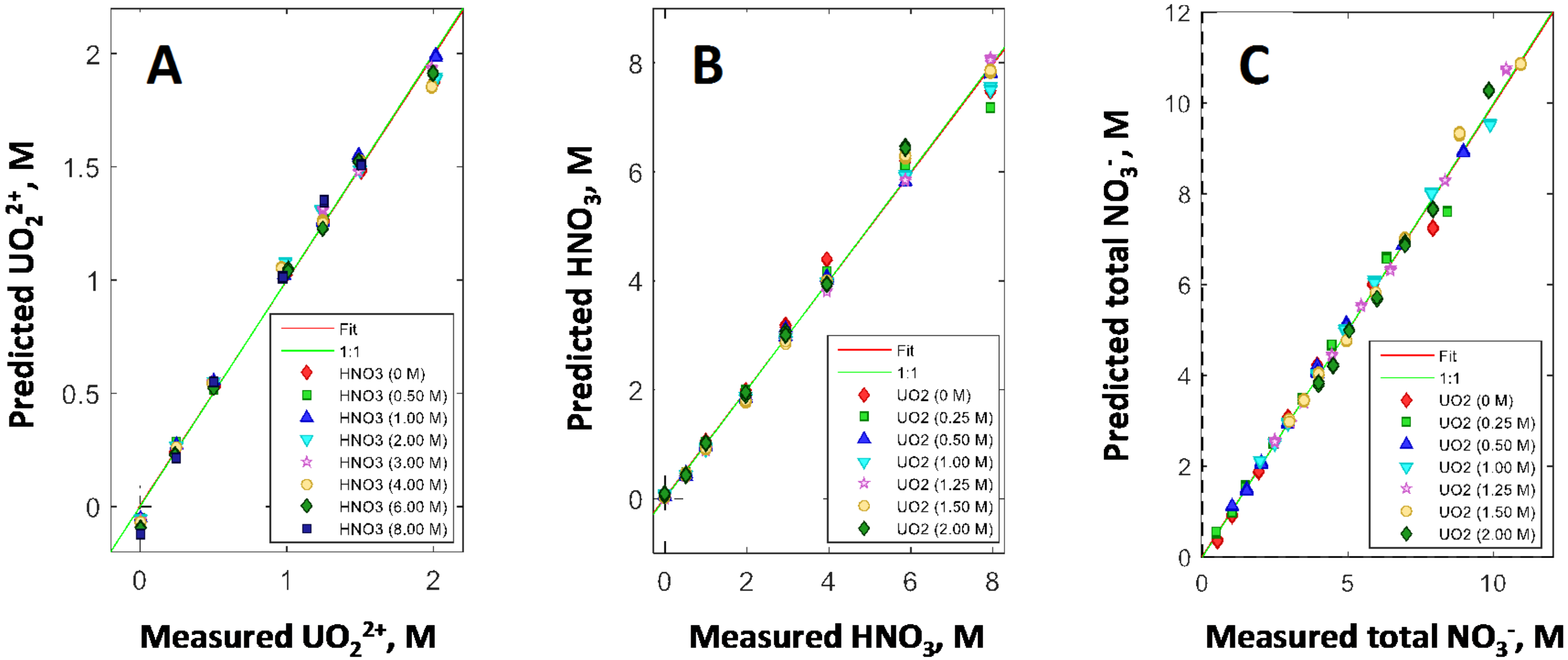


Detection limit, mM	***HNO_3***	***Total Nitrate***	***$UO_2(NO_3)_2$***
macro-Raman Probe	*5.7*	*5.5*	*2.9*
micro-Raman Probe	*6.8*	*6.7*	*4.5*

Model predictions for $UO_2(NO_3)_2$, HNO_3, and total nitrate using the Micro-Raman Probe

PLS predictions using micro-Raman probe

U(VI) model HNO$_3$ model total NO$_3$ model



Solution composition mixtures of $UO_2(NO_3)_2$ (0 – 2M) and HNO_3 (0 – 8M)

Raman Spectra as a Function of Time for Varying Nitric Acid Solutions in 8 μL cell

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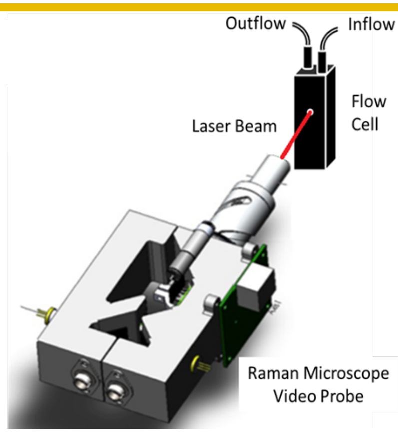
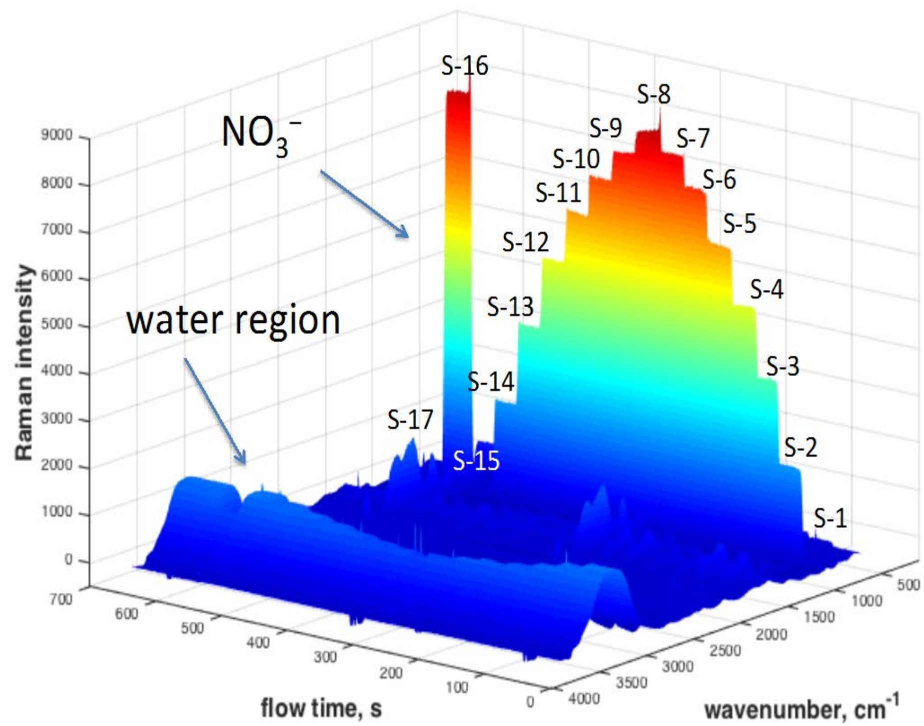


Micro-Raman probe with 8 μL cell

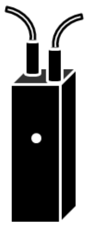
Soln ID	HNO_3		Soln ID	HNO_3
S-1	0		S-9	6.0
S-2	1.0		S-10	5.0
S-3	2.0		S11	4.0
S-4	3.0		S-12	3.0
S-5	4.0		S-13	2.0
S-6	5.0		S14	1.0
S-7	6.0		S-15	0
S-8	8.0		S16	8.0
			S-17	0

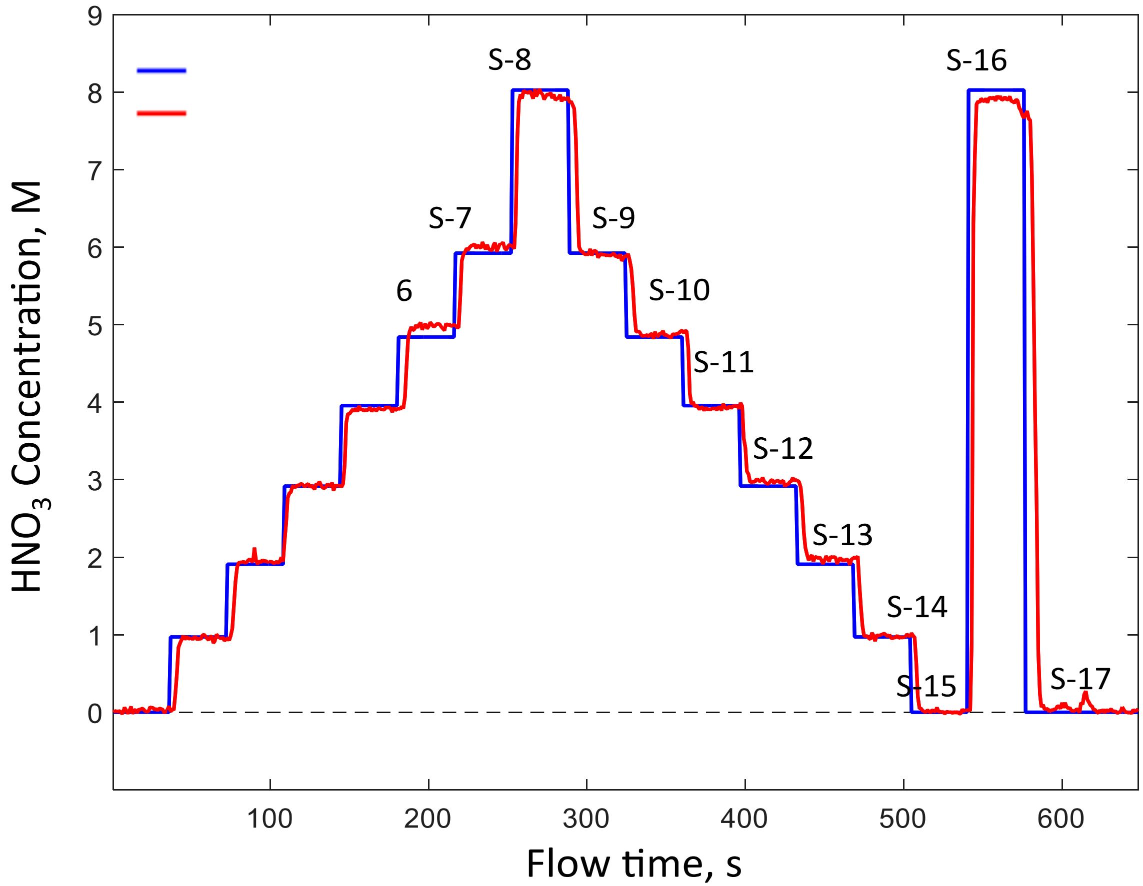


Flow rate: 1 mL/min

Raman Spectra as a Function of Time for Varying Nitric Acid Solutions in 8 μL cell

Micro-Raman probe with 8 μL cell





Flow rate: 1 mL/min

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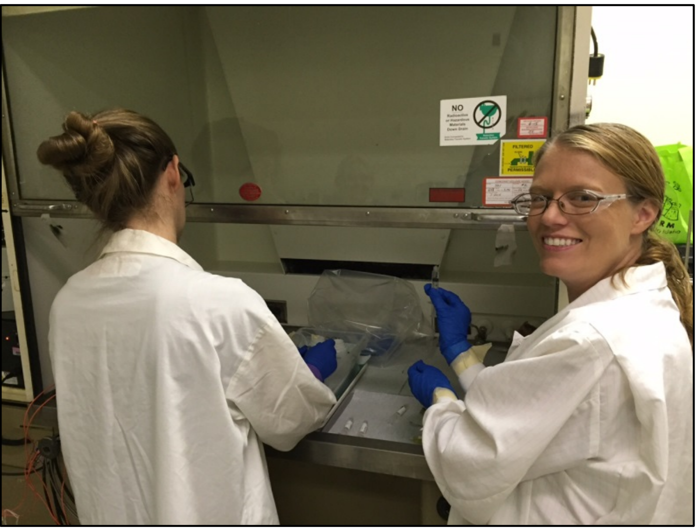
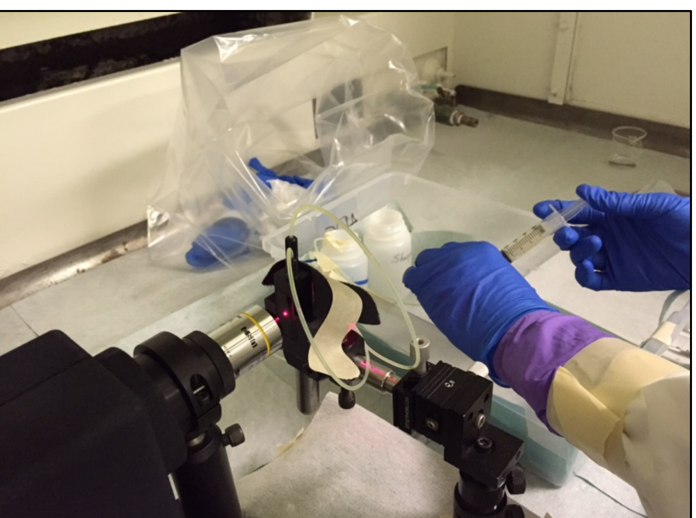
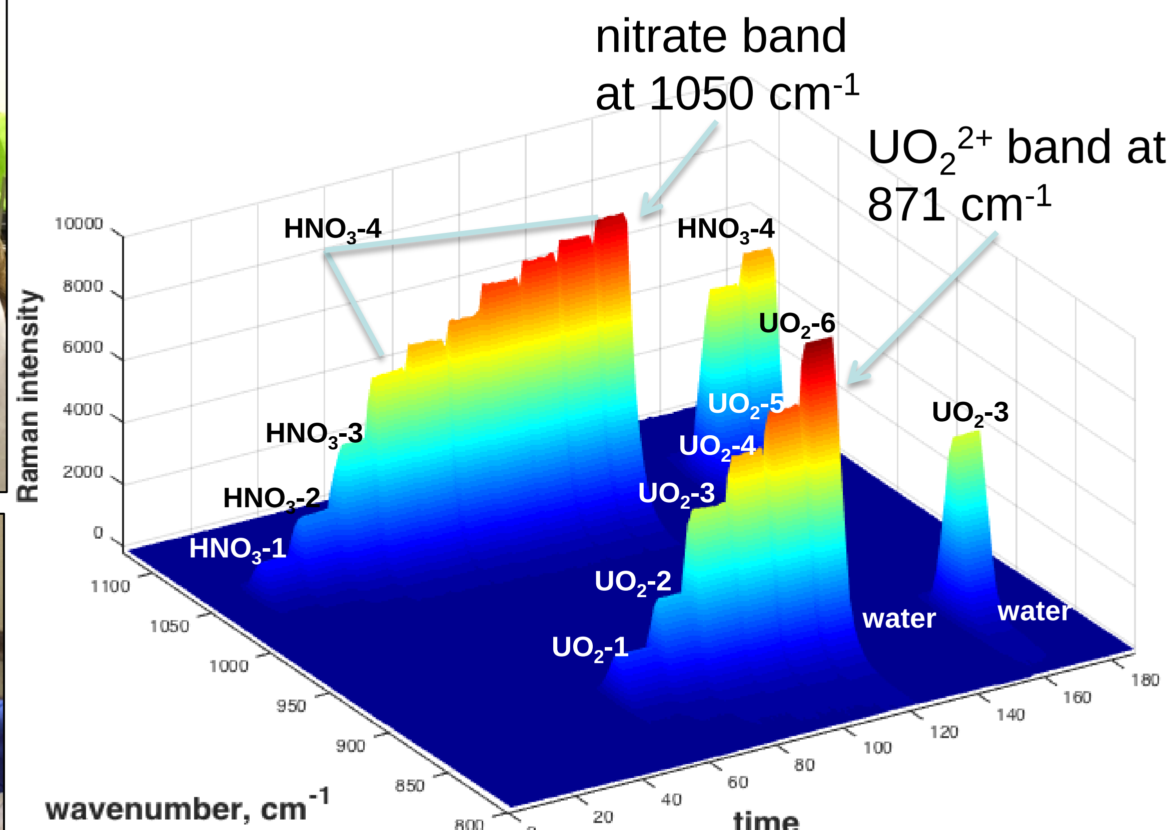
MicroRaman spectra as a function of time for varying $UO_2(NO_3)_2$ and nitric acid Solutions in 8 μL cell





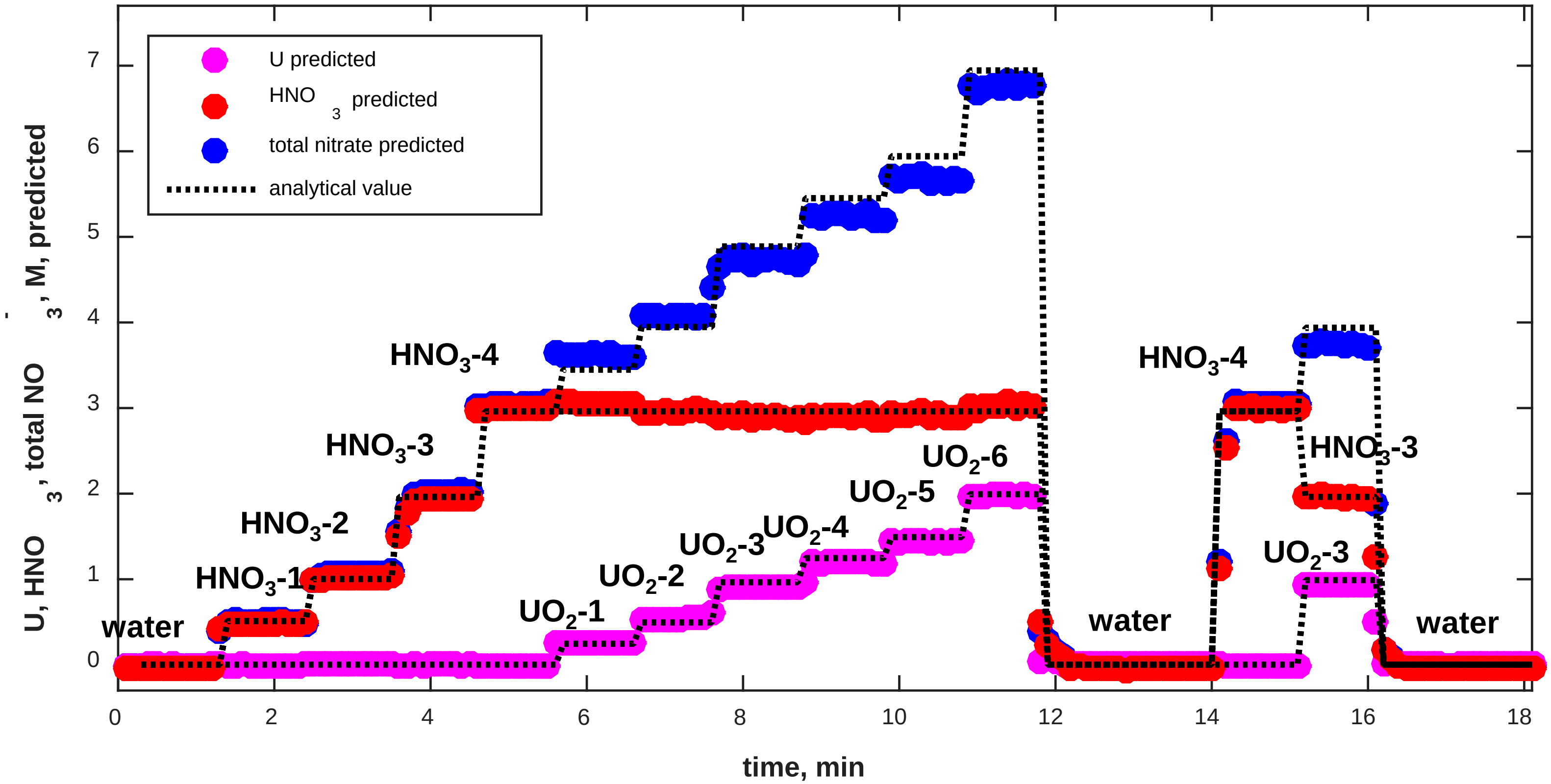


Nitric acid range: 0 – 3M

$UO_2(NO_3)_2$ range: 0 – 2M

total nitrate range: 0 – 7M

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



SBIR collaboration grant: Spectra Solutions, Inc. / PNNL

"Industrial Scale Accounting Control and Process Monitoring Spectroscopic System for Nuclear Material Recovery Process"

- Hardened, combined UV-vis/Raman, process monitoring system for use in commercial reprocessing environment

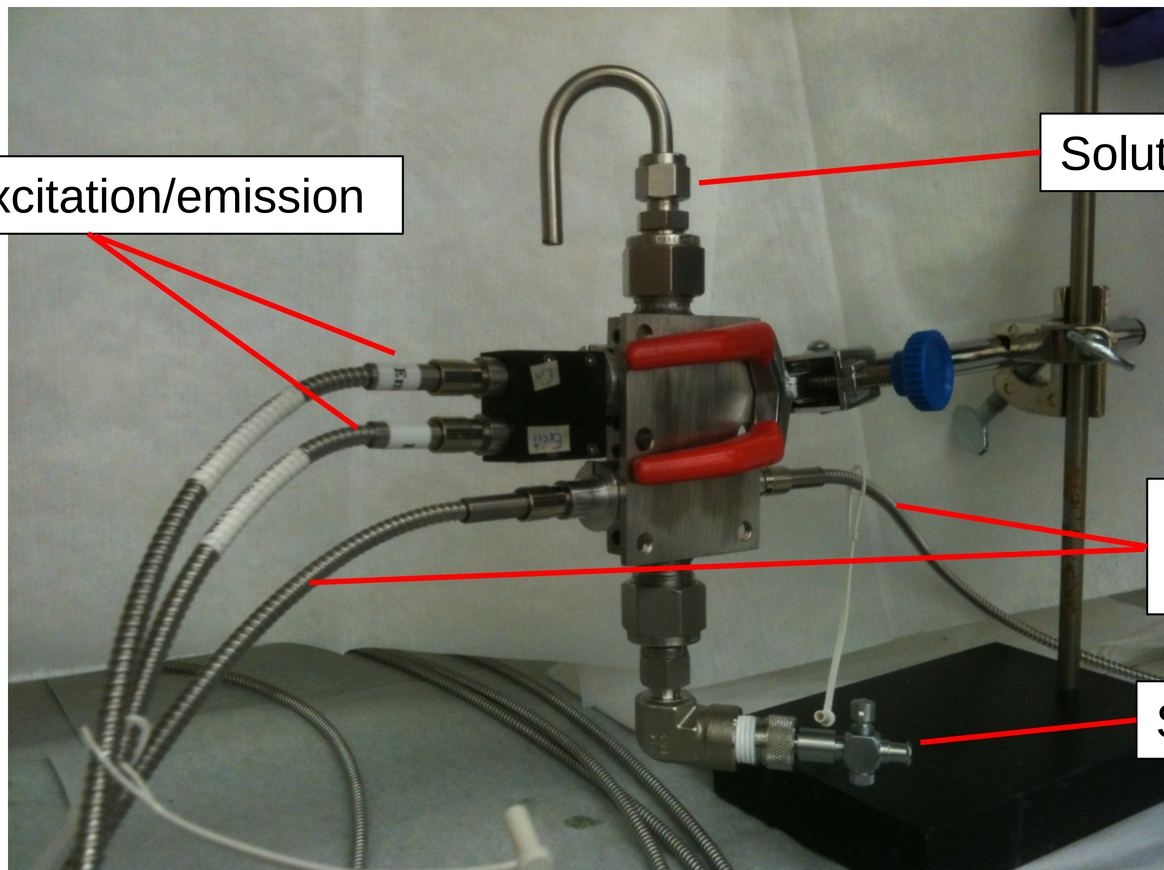
- **Phase 1: Funded May 2015. (May 2015 - Jan 2016)**
  - fabricate and demonstrate utility of combined UV-vis/Raman Probe

- **Goal: to coordinate hardware development/demonstration under SBIR with deployment under FCRD**

- **Related FCRD activity**
  - Planning for H-Canyon process monitoring demonstration

SBIR Phase 1 grant: combined UV-vis/Raman probe

SBIR Grant: An Industrial Scale Accounting Control and Process Monitoring Spectroscopic System for Nuclear Material Recovery Process
PNNL/ Spectra Solutions, Inc.



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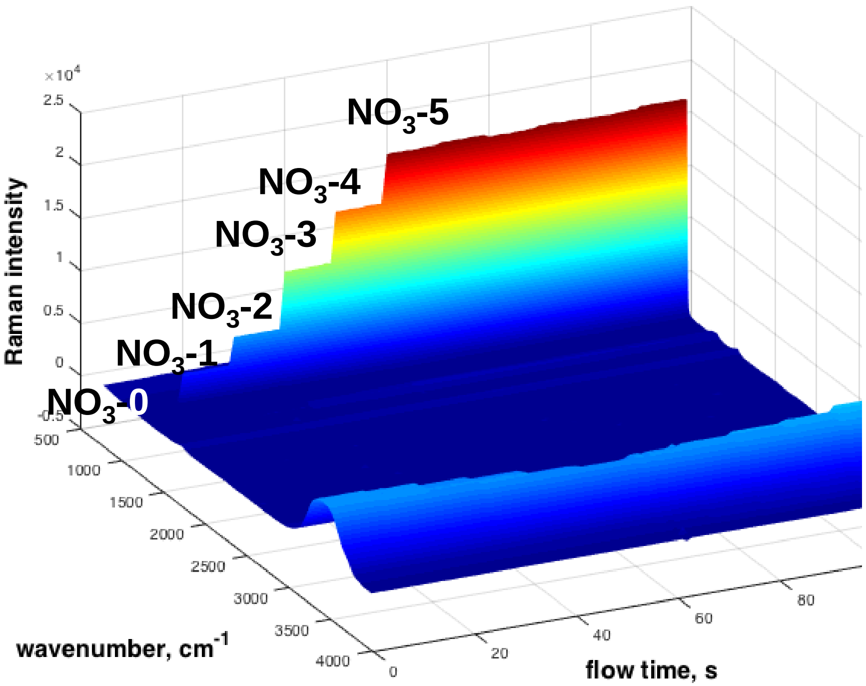
SBIR combined UV-vis/Raman probe

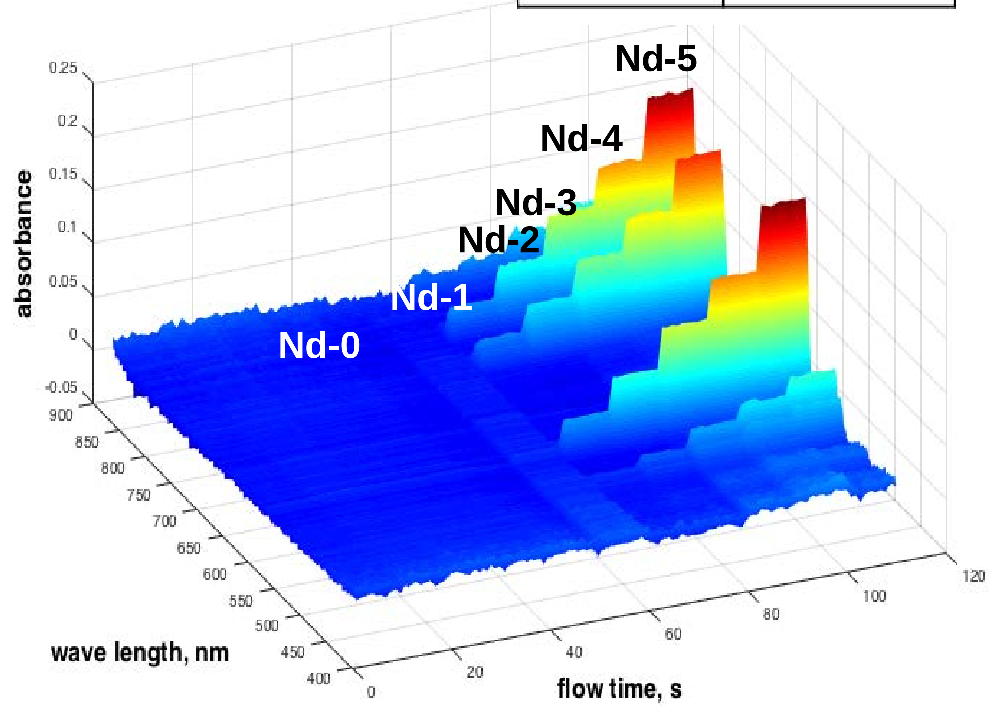
$NaNO_3$, M	$Nd(NO_3)_3$, mM
0.00	0
0.50	0
1.00	0
2.00	0
3.00	0
4.00	0
4.00	5.0
4.00	10.0
4.00	15.0
4.00	20.0
4.00	30.0

Raman

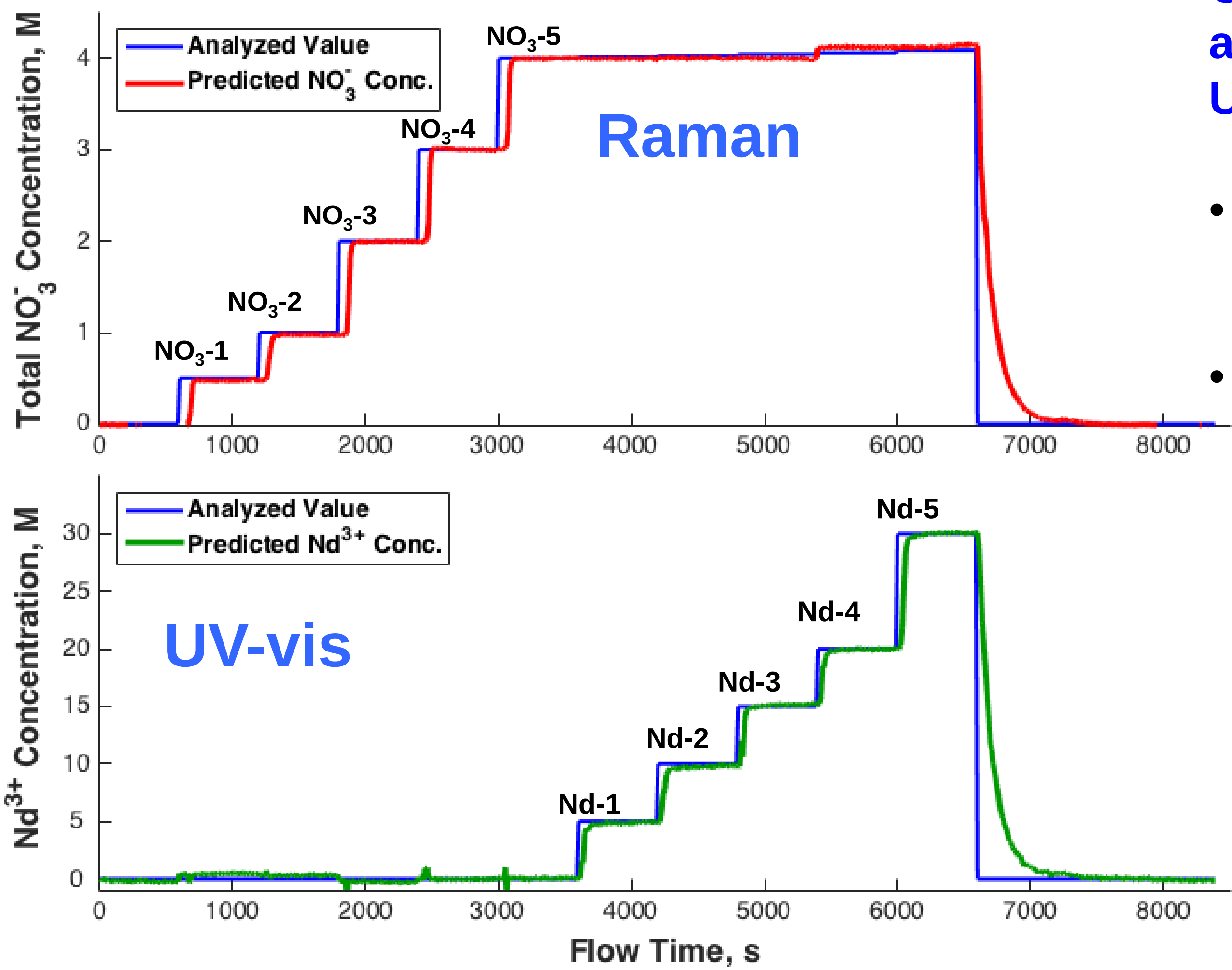
Training set



UV-vis



Concentration profile of Nitrate and Nd^{3+} during flow experiment



Chemometric (PLS) analysis of Raman and UV-vis spectra

- Nitrate determined by Raman
- Nd^{3+} determined by UV-vis

$NaNO_3$, M	$Nd(NO_3)_3$, mM
0.00	0
0.50	0
1.00	0
2.00	0
3.00	0
4.00	0
4.00	5.0
4.00	10.0
4.00	15.0
4.00	20.0
4.00	30.0
0.00	0

SBIR summary and planning

- **Demonstrated utility of integrated UV-vis/Raman probe design using non-rad $NaNO_3/Nd(NO_3)_3$ solutions**

- **Phase 2: Funding FY 2016 (TBD)**
  - Goal to fabricate and demonstrate hardened combined UV-vis/Raman probe and spectrometer system.

- **Experiments planned under Phase 2 funding**
  - U, Pu, Np, variable HNO_3 measurements with combined probe
    - Demonstration purposes
    - Generate database for eventual deployment

Conclusions

- **Using simulants and BWR Spent Fuel**
  - Demonstrated quantitative spectroscopic measurement on actual commercial fuel samples under fuel reprocessing conditions
    - 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
- **Future plans for on-line process monitoring**
  - Collaborative demonstration on commercial (larger) scale

Acknowledgement

- U.S. Department of Energy (DOE) : Fuel Cycle Research and Development (FCR&D), Separations Campaign (NE)
- Human Capital Development project under the Next Generation Safeguards Initiative (NGSI), Office of Nonproliferation and Arms Control (NA-24)
- U.S. DOE; Visiting Faculty Program (VFP), Office of Science (SC)
- Small Business Innovative Research (SBIR) Grant, Office of Science (SC)
- FCRD young investigator of the year awardee (Amanda Casella)