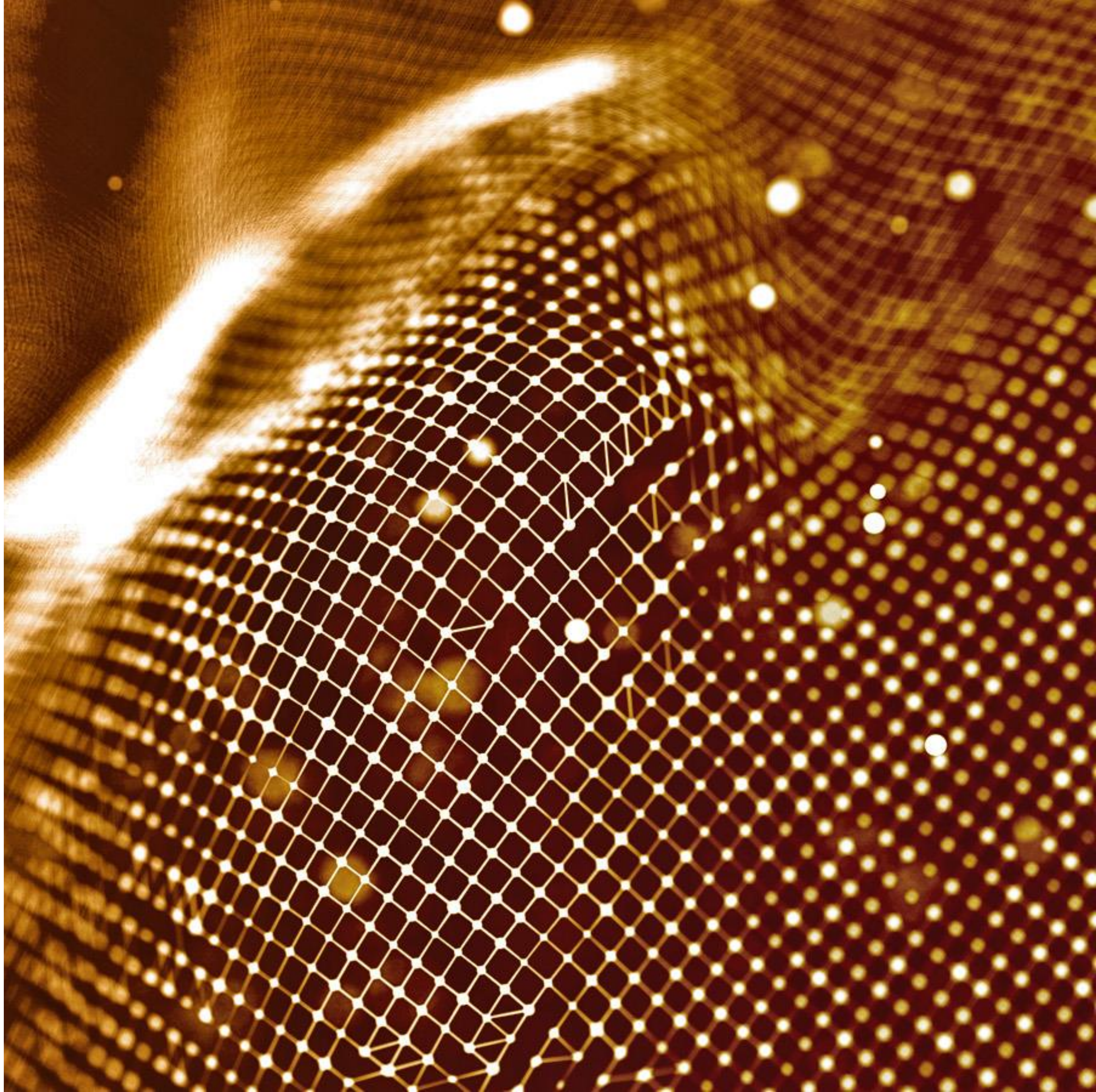
Pacific Northwest NATIONAL LABORATORY

On-line, Real-time Monitoring of Chemical Composition: Process Control and Optimization

May, 15, 2019

Amanda Lines and Samuel A, Bryan



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Contributing team members

PNNL Team:

Sam Bryan
Amanda Lines
Gregg Lumetta
Shirmir Branch
Gabe Hall
Jarrod Allred
Heather Felmy
Adan Schafer
Amanda Casella
Forrest Heller
Susan Adami
Brian Riley
Susan Asmussen

Industry Partners:

Job Bello/Spectra Solutions

Students/visiting faculty:

Gilbert Nelson
Hope Lackey
Jen Wilson
PoKi Tse

ORNL Team:

Hunter Andrews
Shay Chapel
Bill Del Cul
Dianne Ezell
Alex Hackett
David Holcomb
Joanna McFarlane
Kristian Myhre

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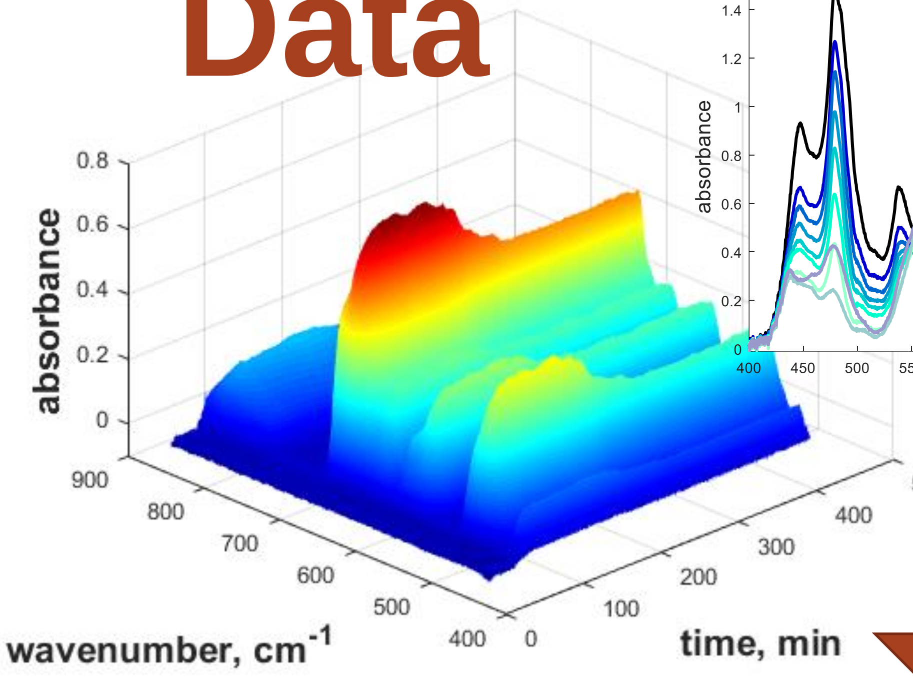
What On-Line Monitoring Provides

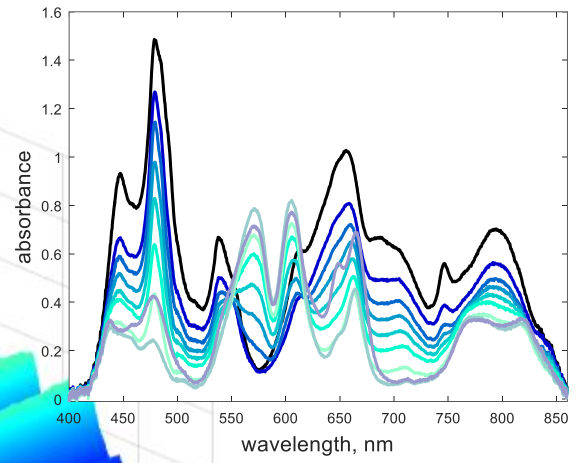
Enabling real-time process characterization to supply essential process information

- Design phase
  - Informed and optimized R&D

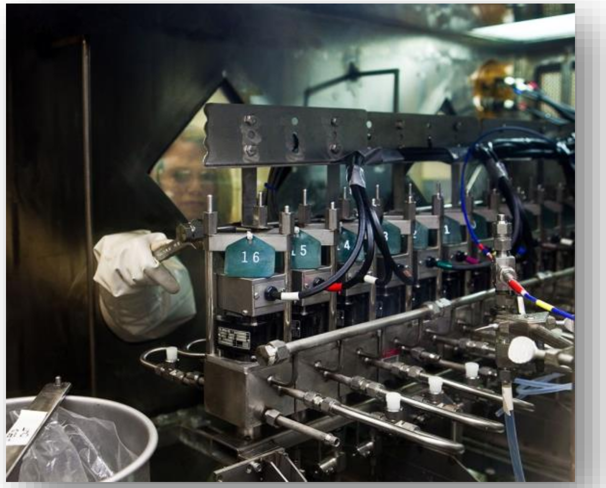
- Deployment phase
  - Process optimization
  - Process control
  - Real-time characterization

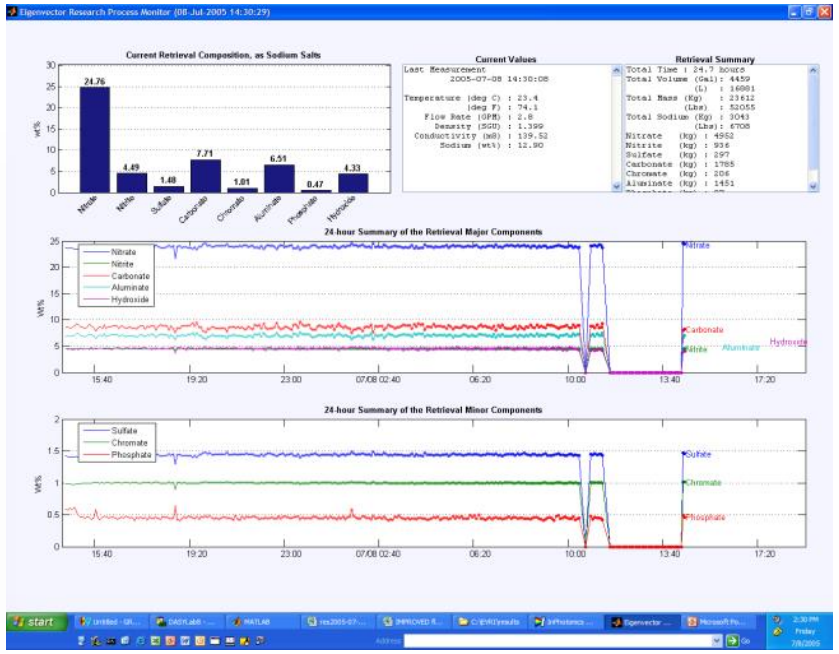
Data





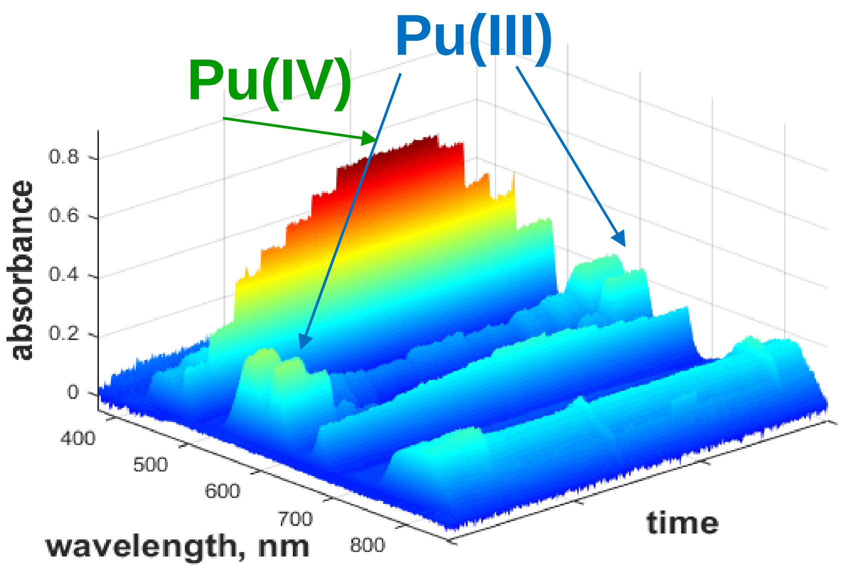
Information

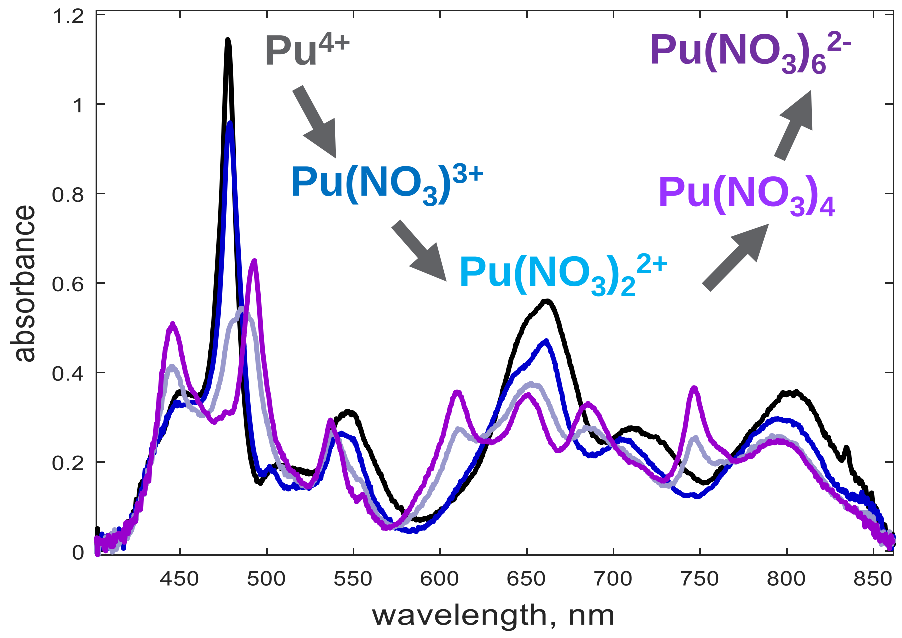




Chemical characterization: Optical spectroscopy

- Provides chemical information
  - Identification and quantification
  - Oxidation State
    - Essential information for control of systems
  - Molecular and elemental species
    - Essential information to understand/control separation efficiency or general system behavior
- Fast
- Robust
- Versatile



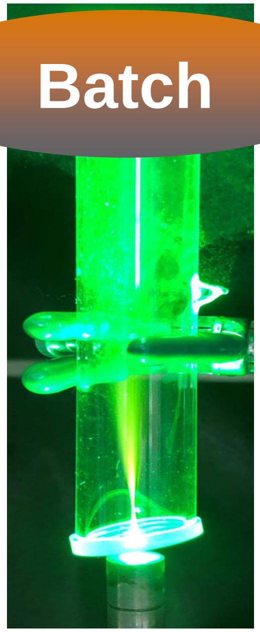


U(III)
U(IV)
U(VI)
Pu(III)
Pu(IV)
Np
Cr
Lns

Optical Spectroscopy: Highly Versatile in Application

System Method

Batch



Continuous

System Matrix

Solid

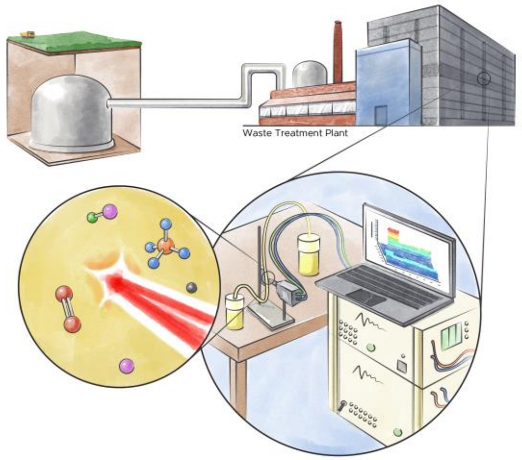
Liquid

Gas

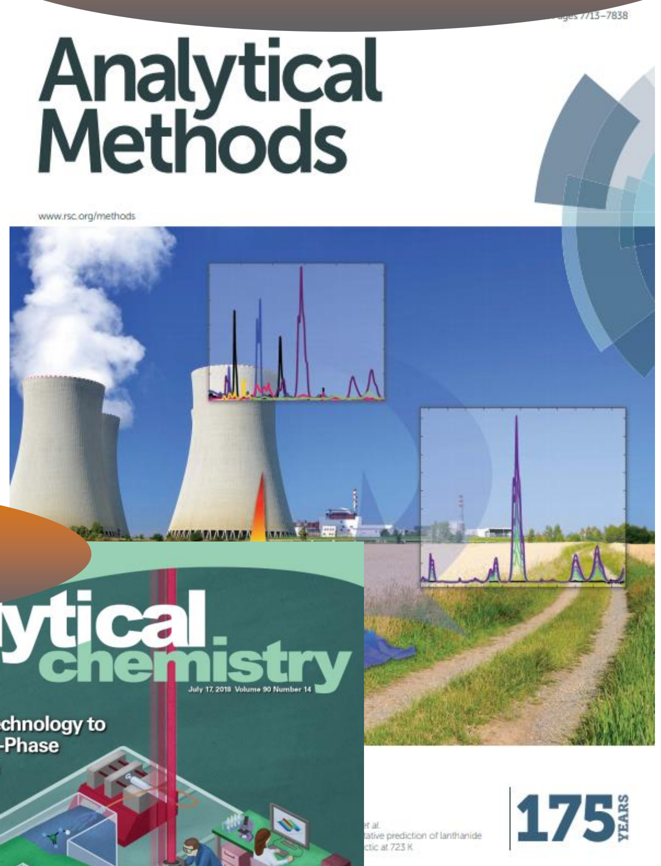
Molten salt

System scale

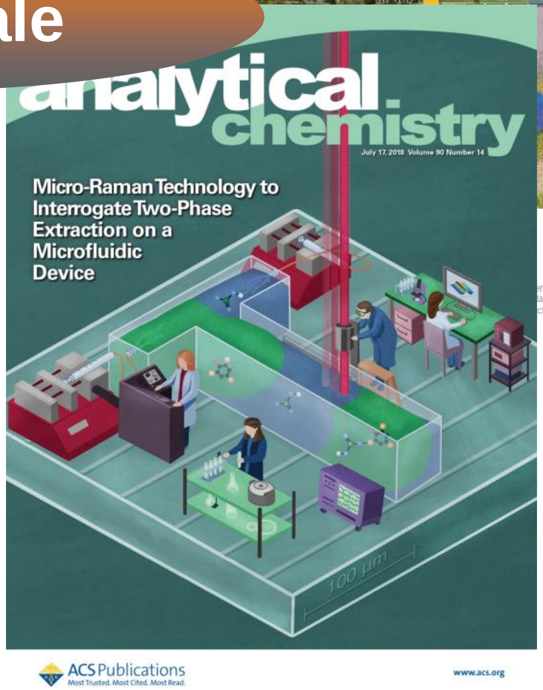
Commercial Scale



Design Scale



Microscale



Optical Spectroscopy: Widely Applicable to Analytes

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

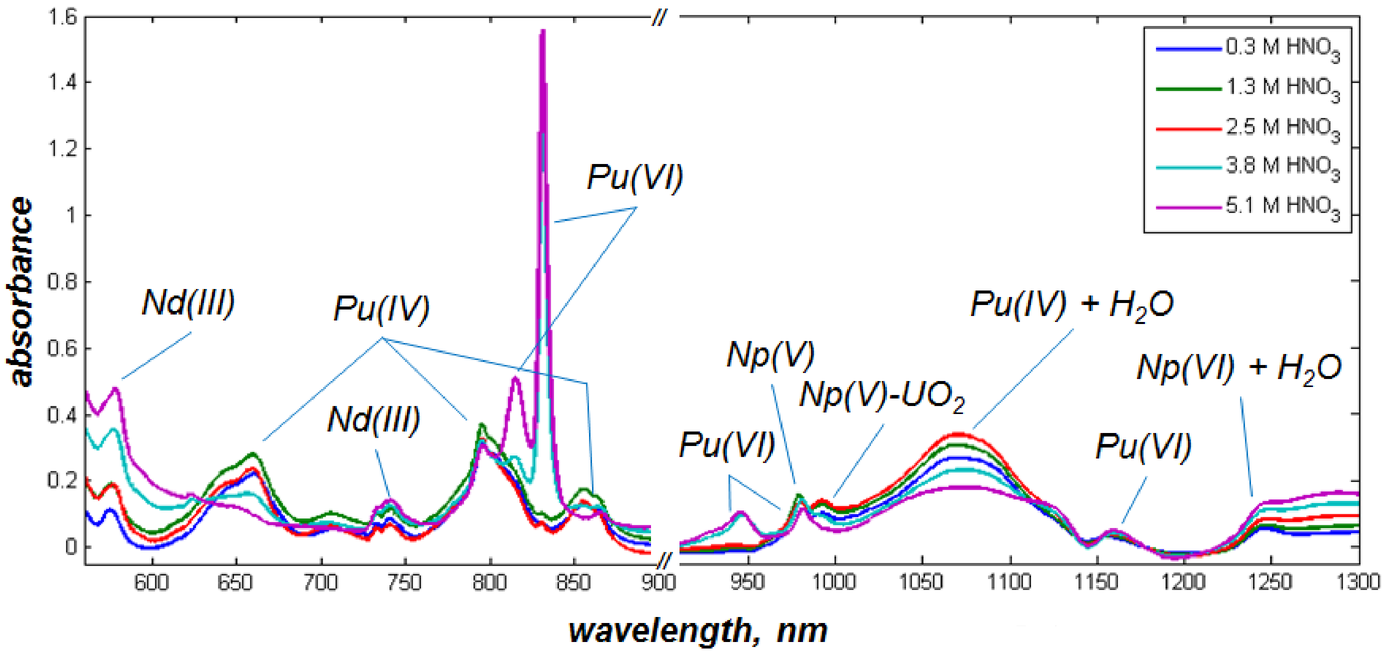
UV-vis-NIR absorption

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

Several other options

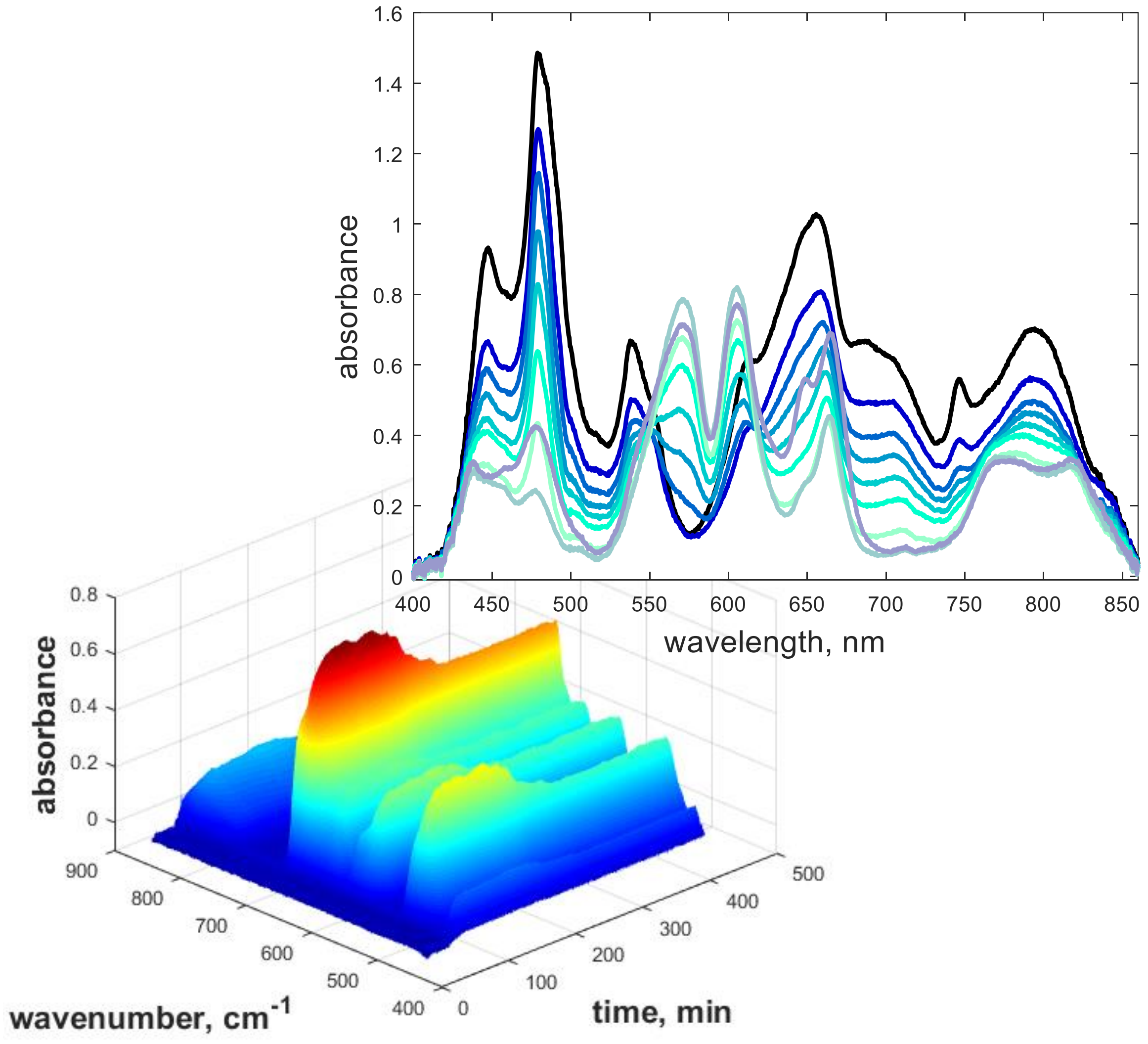
- **FTIR**
  - Organic complexants
- **Light scatter**
  - turbidity
- **Optical density**
  - Formation of complexes

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

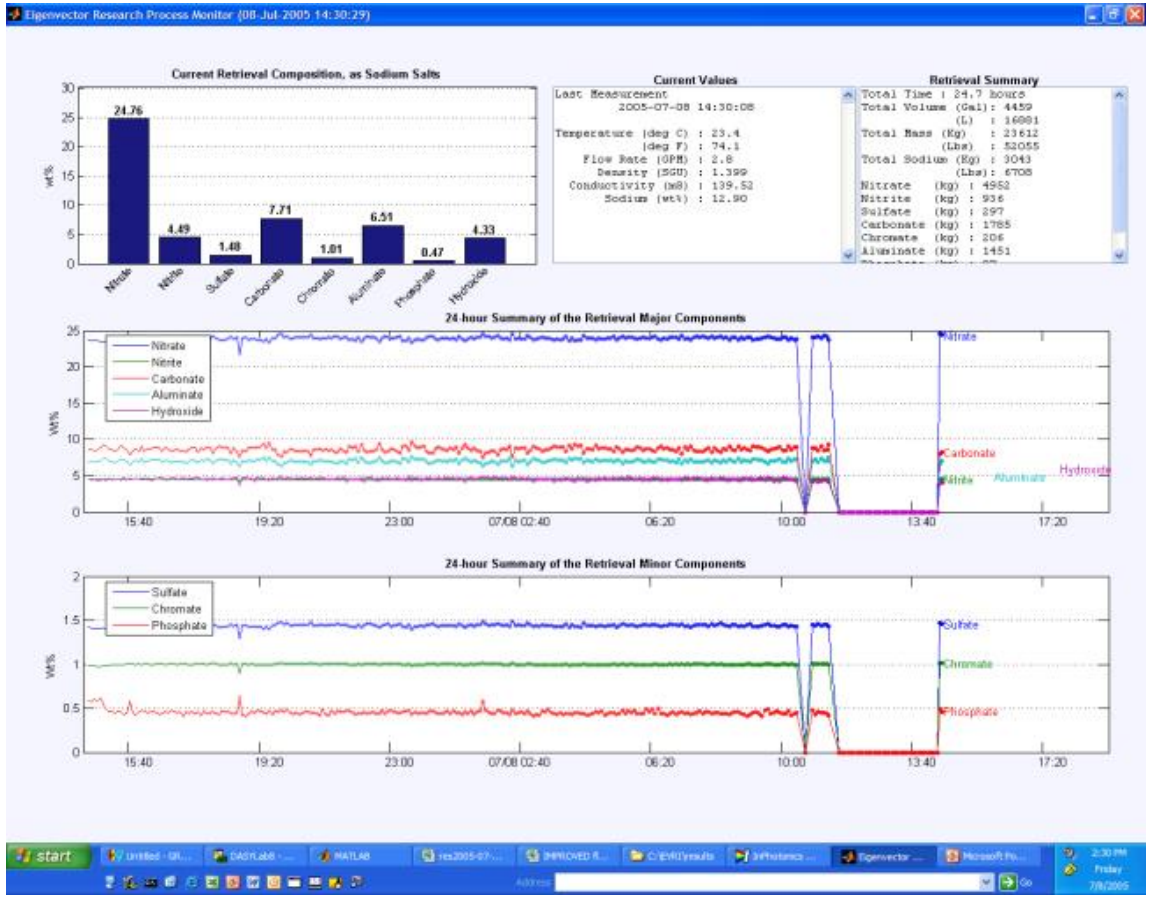


Primary analytical challenge

Data

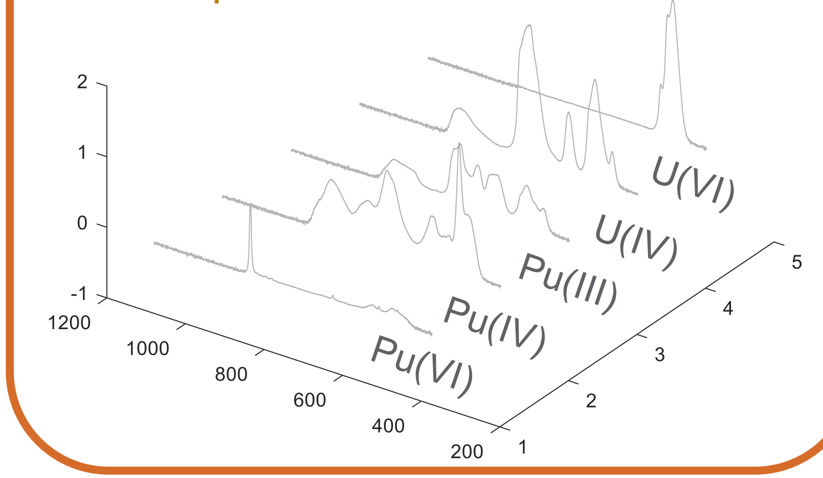


Information

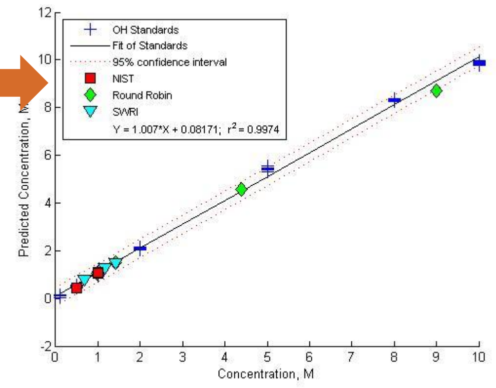


Development of on-line, real-time analysis systems

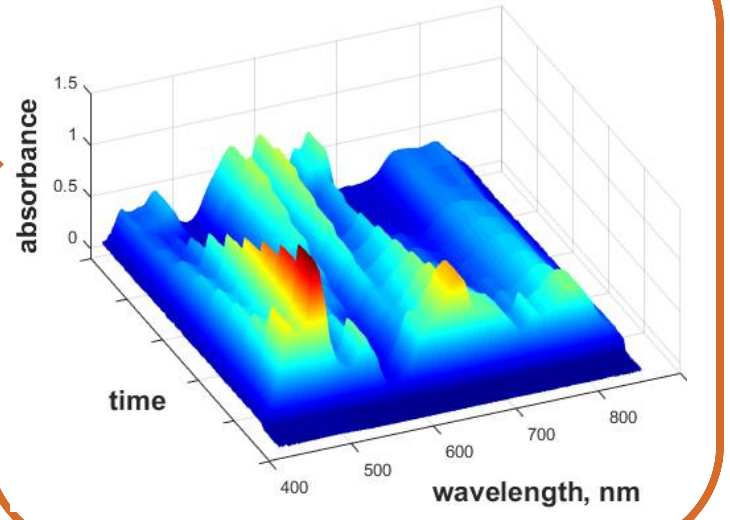
Identify target analytes and collect representative training set



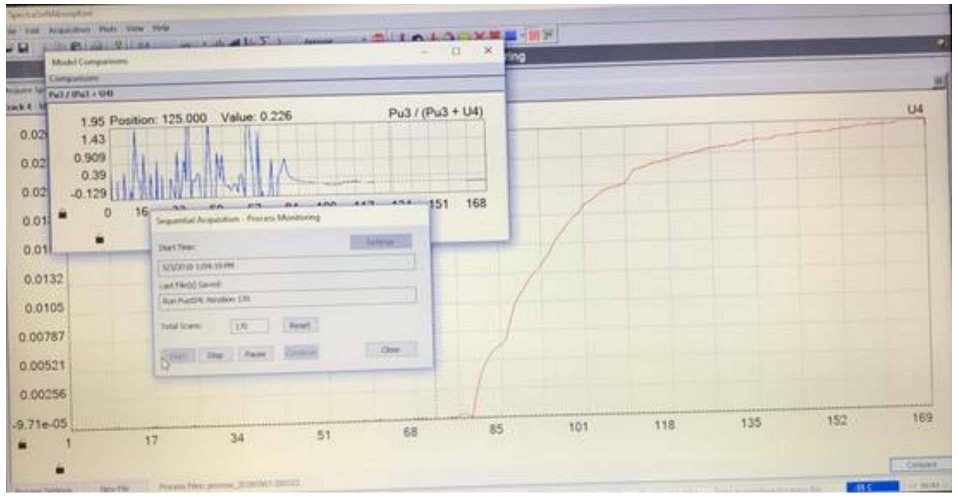
Build chemometric models



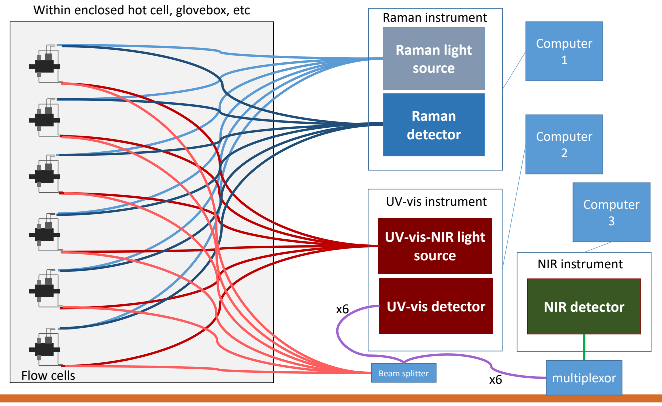
On-line monitoring validation



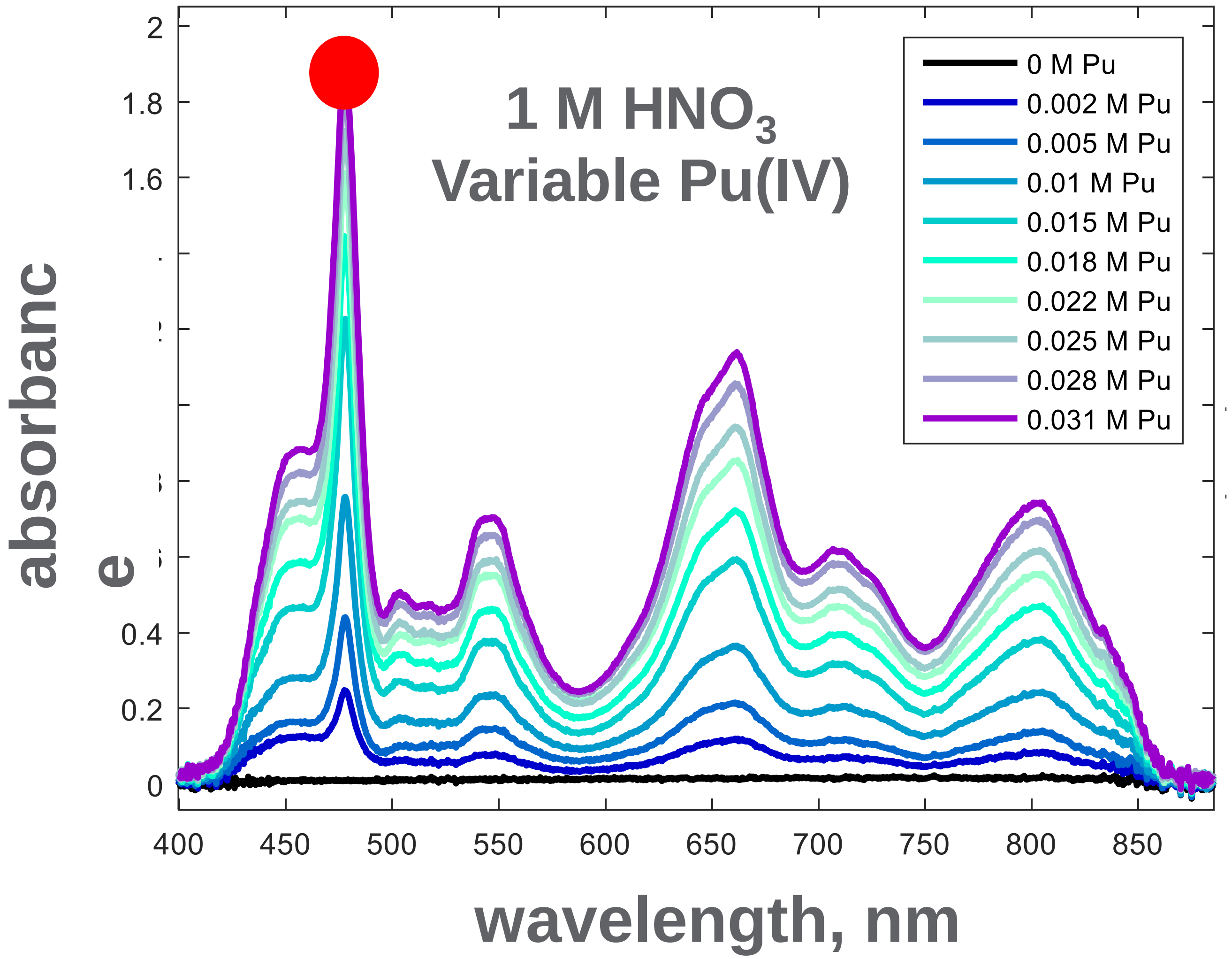
Real-time analysis: turning data into information

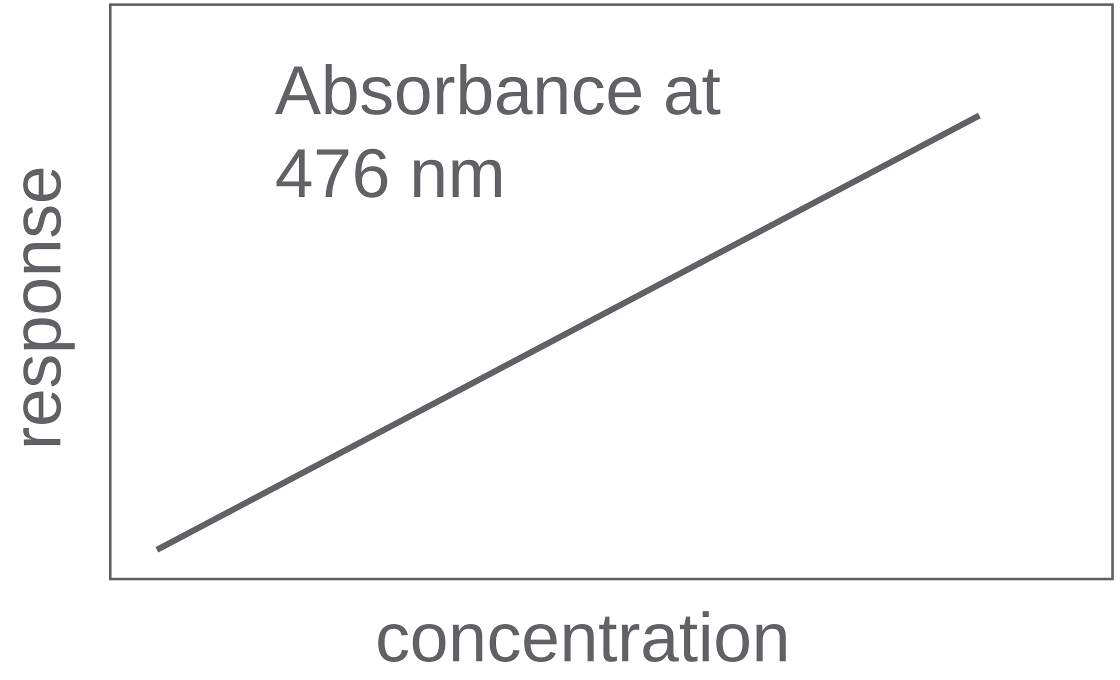


Deployment of instrumentation

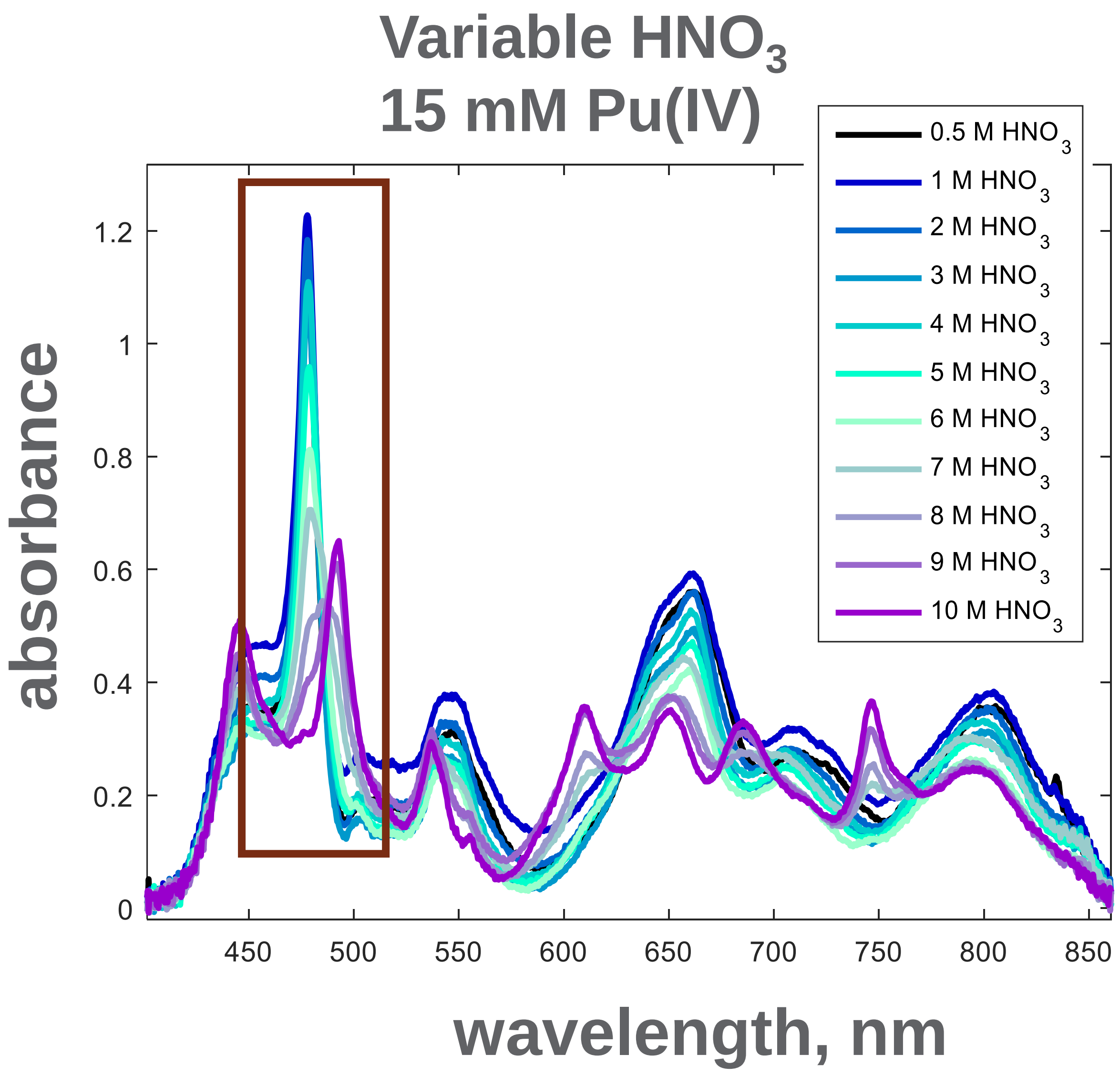


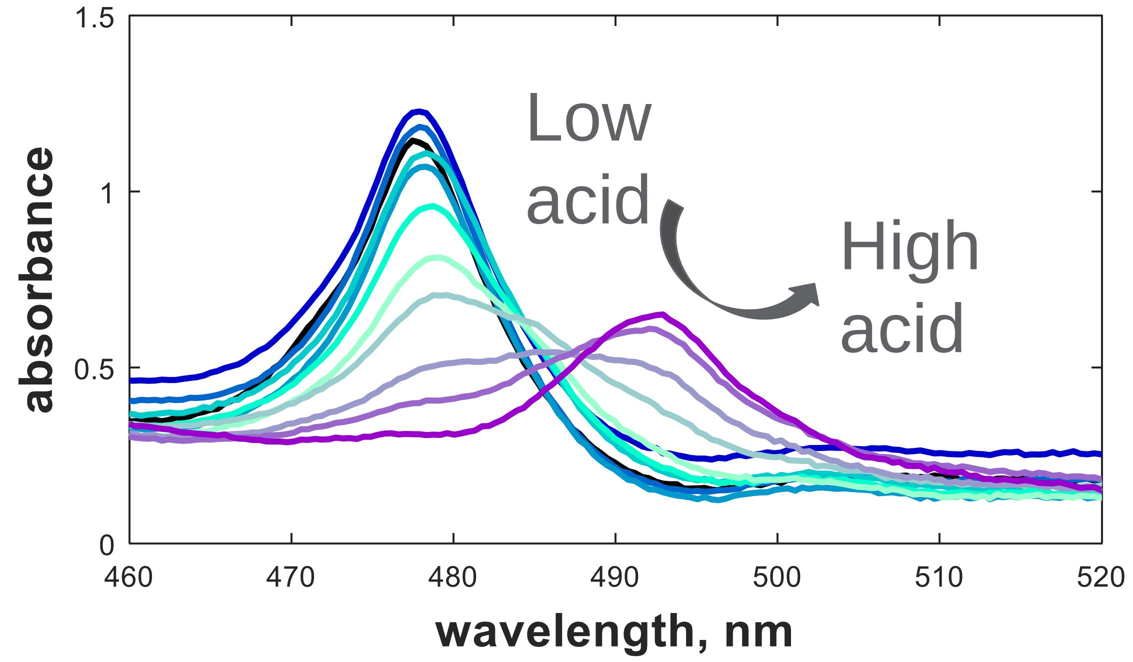
Developing chemometric models to enable on-line monitoring

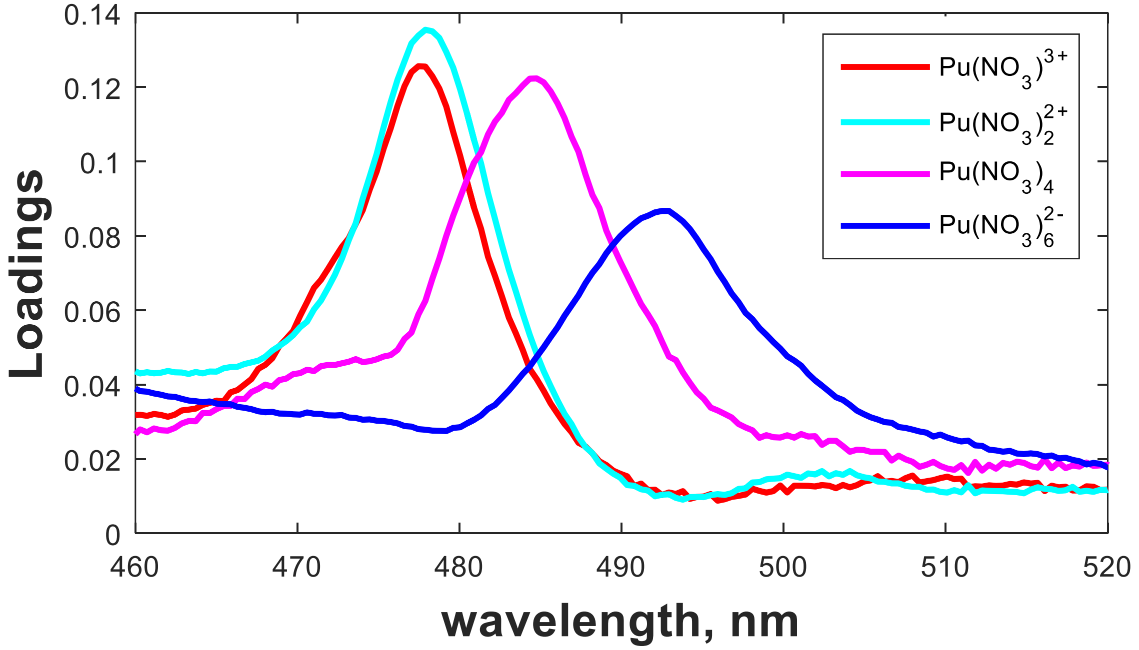




Developing chemometric models to enable on-line monitoring





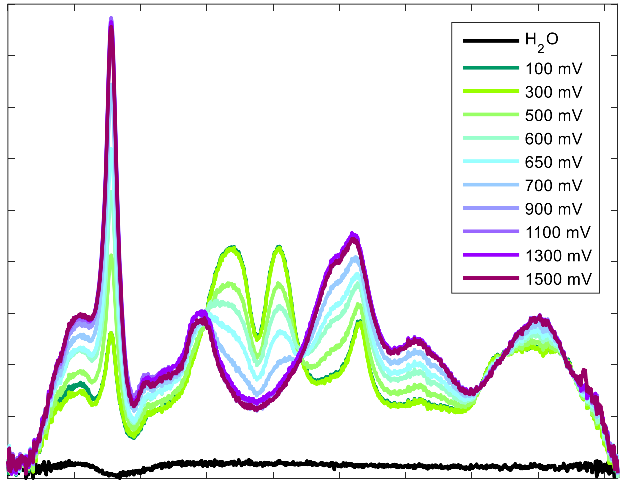


Lines, Adami, Sinkov, Lumetta, Bryan. Multivariate Analysis for Quantification of Plutonium(IV) in Nitric Acid Based on Absorption Spectra. *Anal Chem.* 2017

Wide Range of Applications

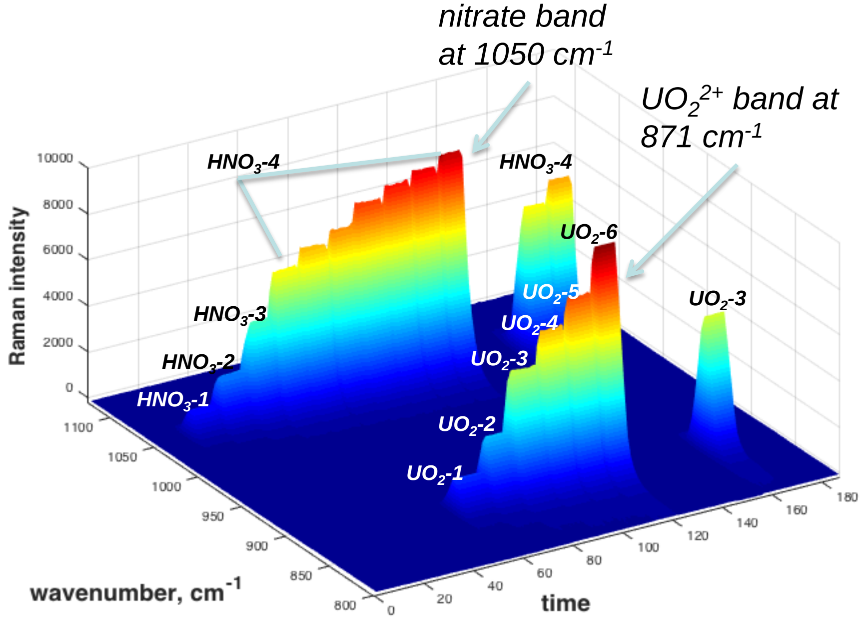
Lines, A.M., S.R. Adami, S.I. Sinkov, G.J. Lumetta, and S.A. Bryan. 2017. “Multivariate analysis for quantification of plutonium (IV) in nitric acid based on absorption spectra.” Anal. Chem., 89(14):9354-9359, DOI: 10.1021/acs.analchem.7b02161.

Measurement of Pu in multiple oxidation states



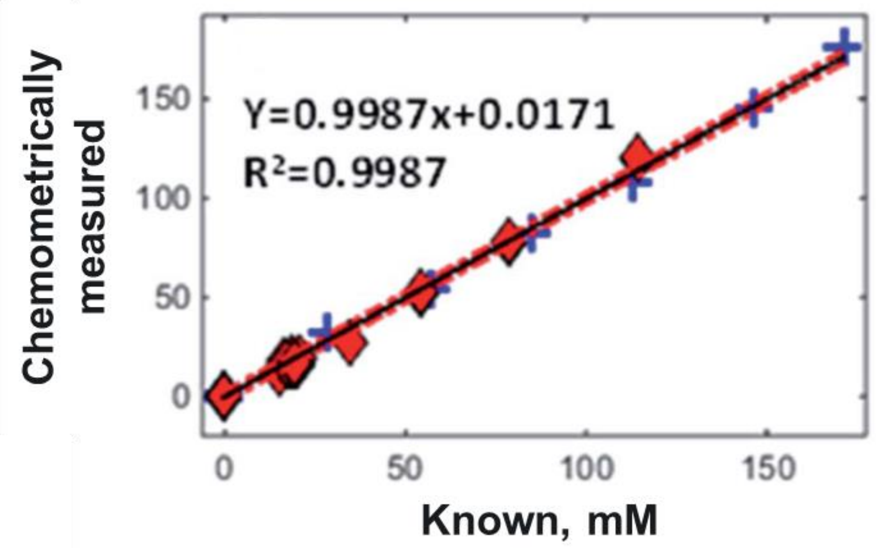
Lines, Adami, Casella, Sinkov, Lumetta, Bryan. Electrochemistry and Spectroelectrochemistry of the Pu(III/IV) and (IV/VI) couples in Nitric Acid Systems. *Electroanalysis.* 2017

Quantification in presence of direct interferents



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

Quantification in complex and harsh environments



Schroll, C. A., et al. (2016). "Absorption spectroscopy for the quantitative prediction of lanthanide concentrations in the 3LiCl–2CsCl eutectic at 723 K." Analytical Methods 8(43): 7731-7738.

Applications

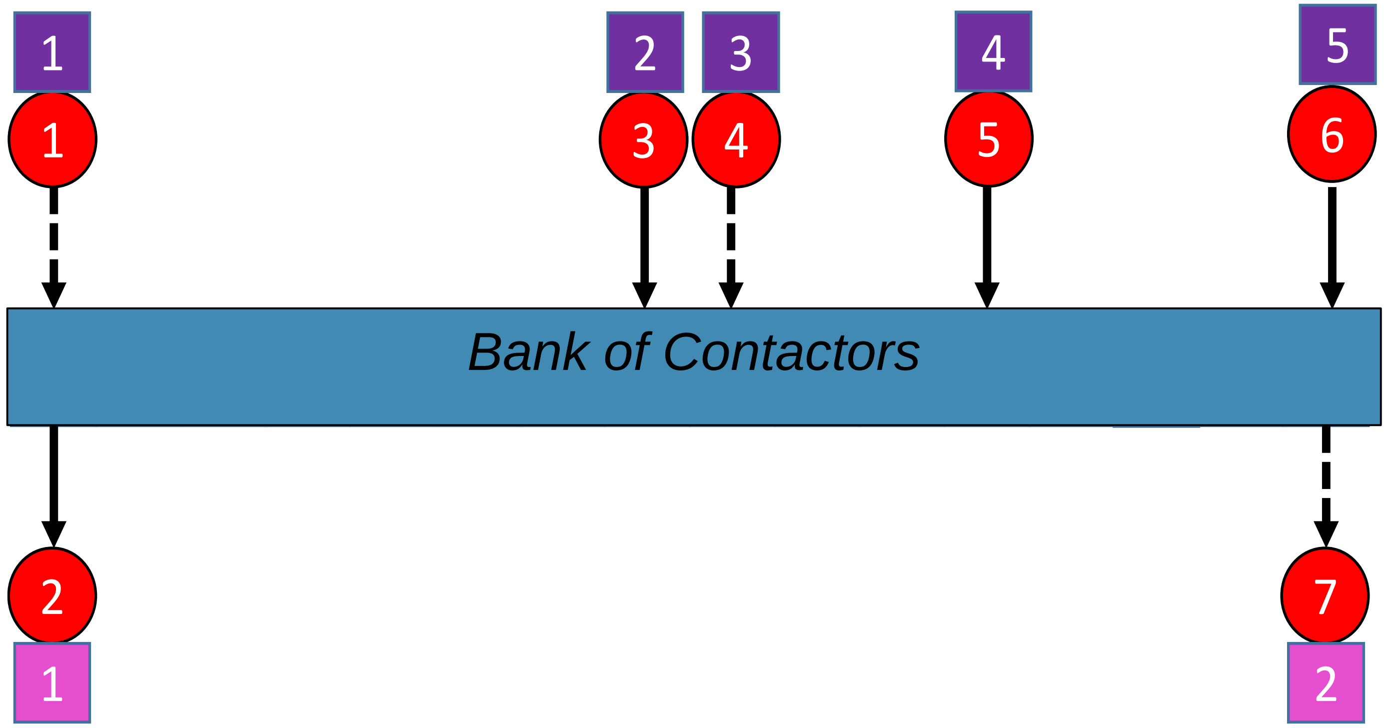
- DOE NE
  - CoDCon (Co-decontamination)
  - Microfluidics, collaboration with CEA, SBIR
  - MSR off-gas treatment
- EM
  - Hanford tank waste processing
  - Off-gas condensate from waste processing
  - In-situ characterization of tank solids
- LDRD
  - Molten salt characterizations
  - Development of fieldable MSR probes

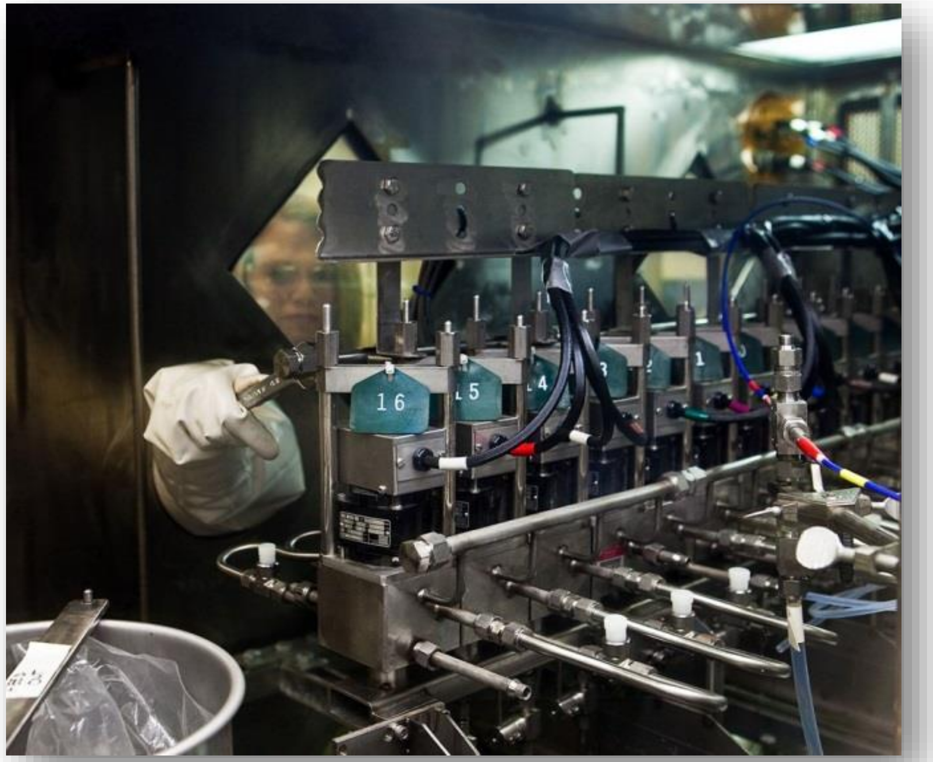
- used nuclear fuel simulant (complex signals)
- aqueous and non-aqueous streams
- Micro and lab scale applications
- Process control

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

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

CoDCon Demonstration





Aqueous stream

Organic stream

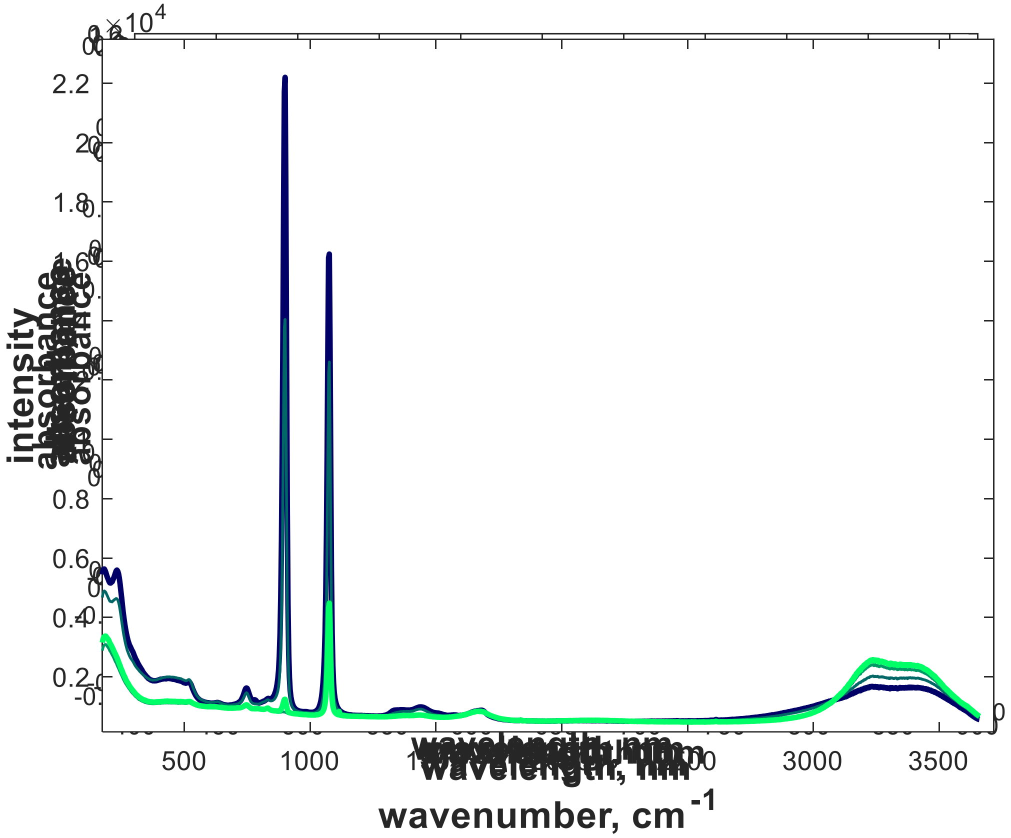
Spectroscopic measurement: U, Pu, and HNO3

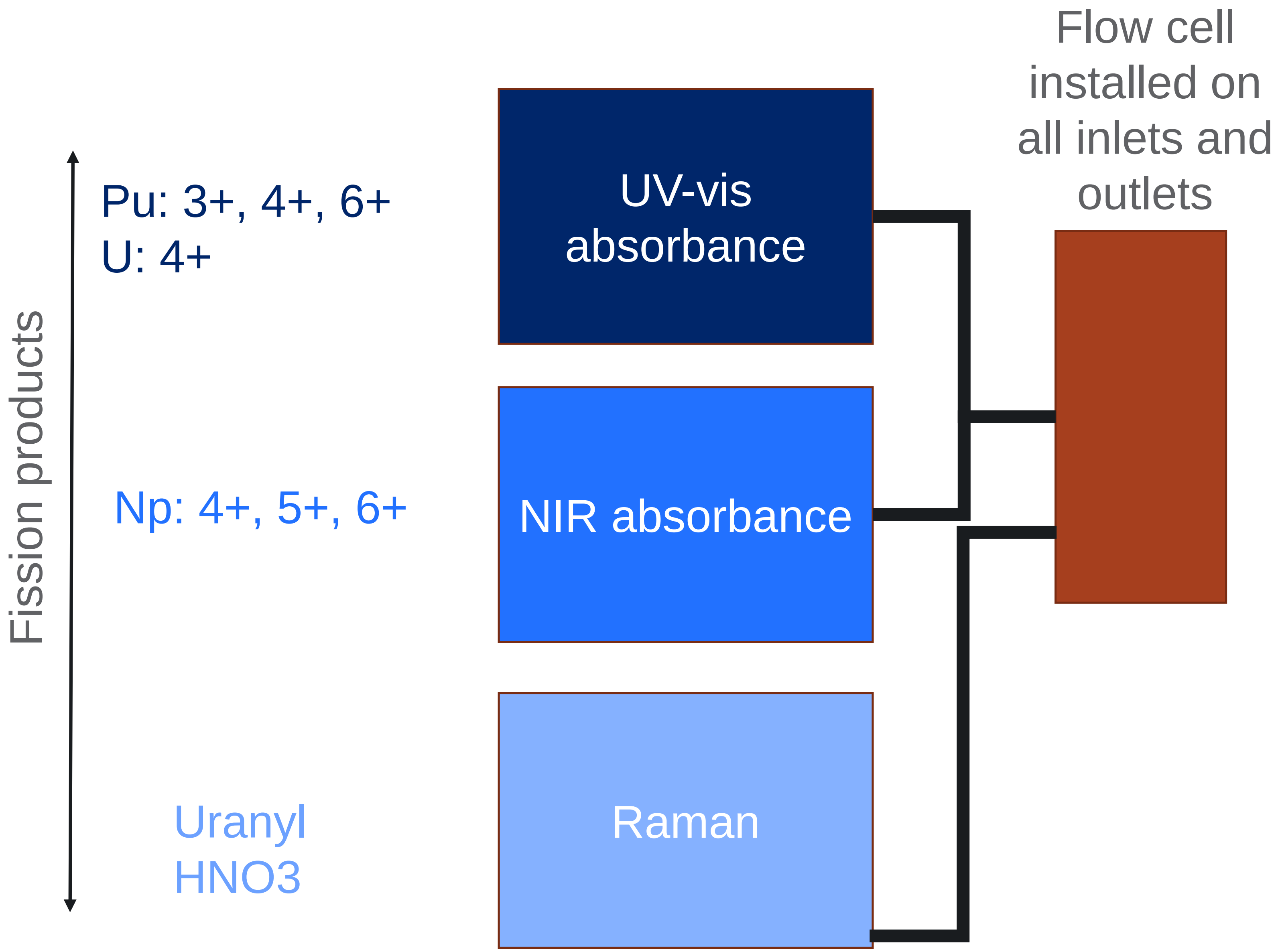
Flowrate/density measurement, Coriolis meter

Flowrate/mass measurement, time collection and scales

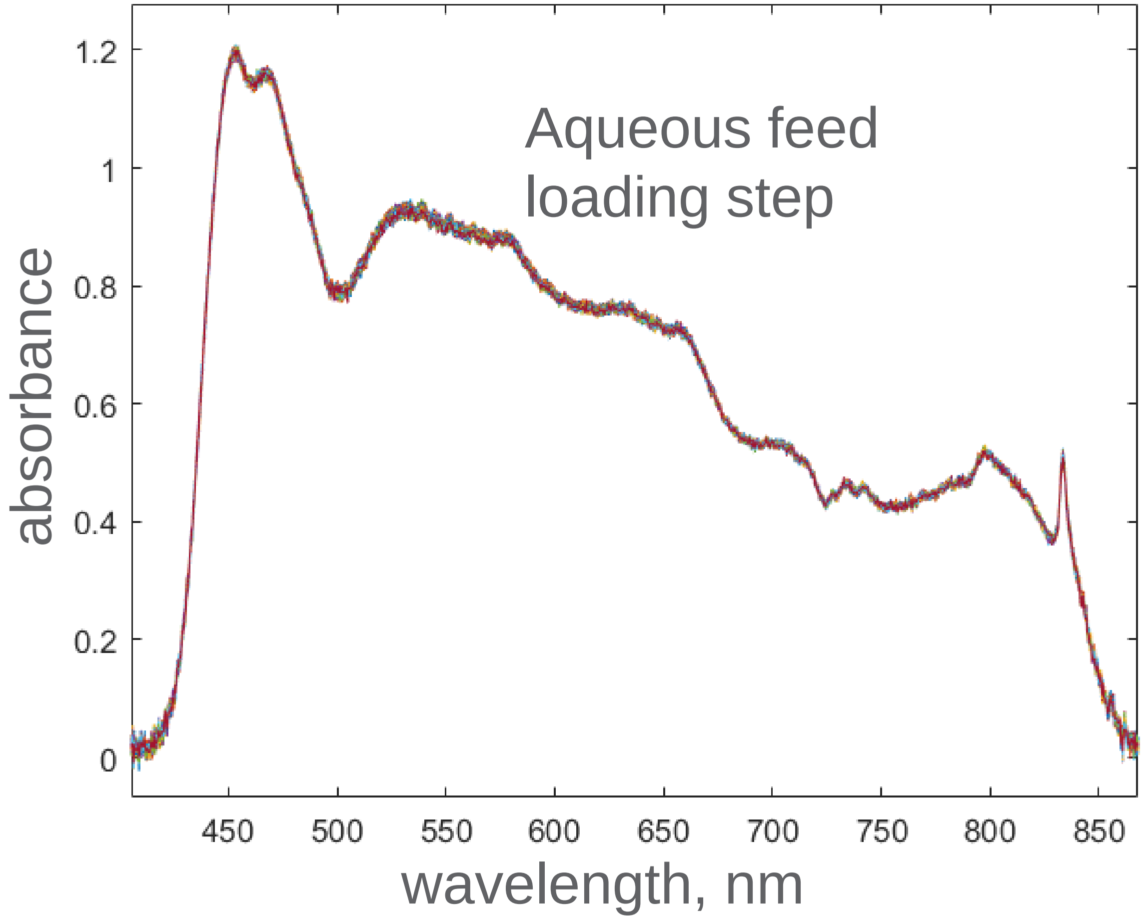
CoDCon on-line monitoring system design

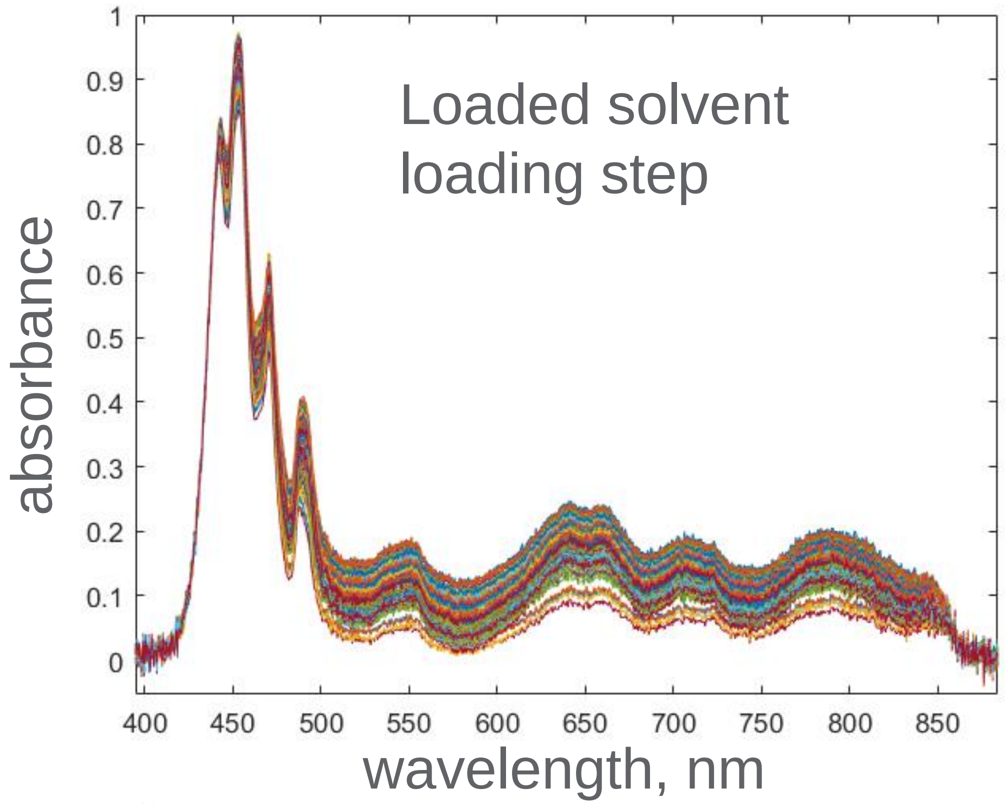
Raman

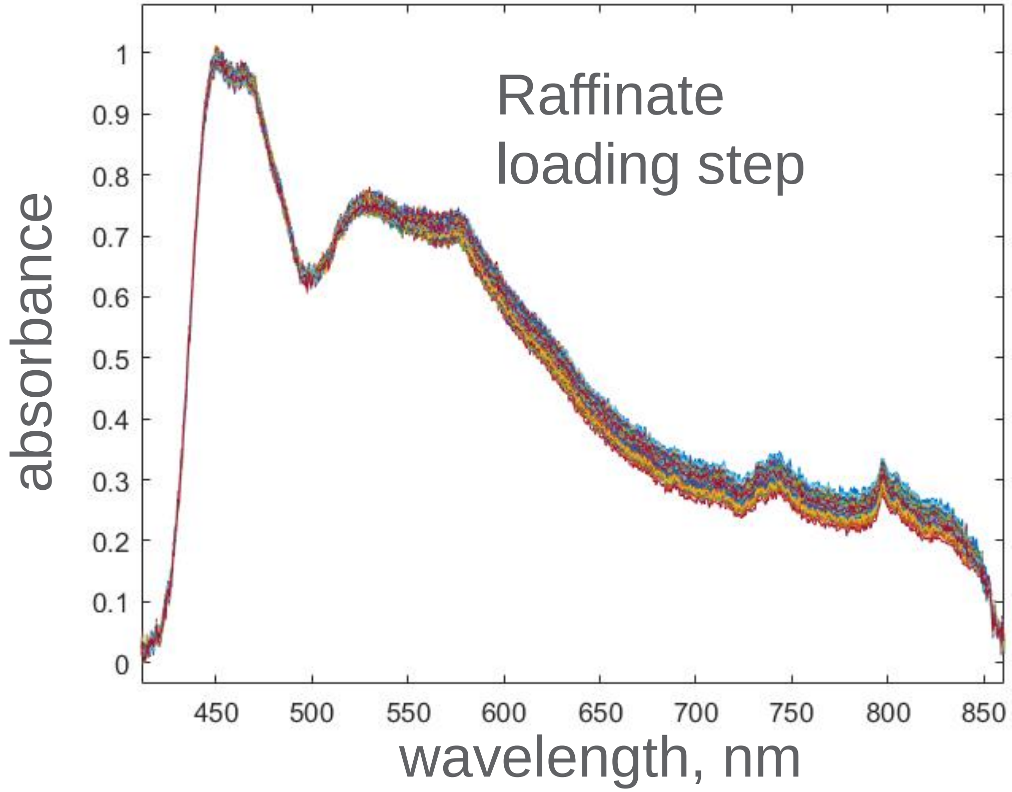




Monitoring all inlets and outlets







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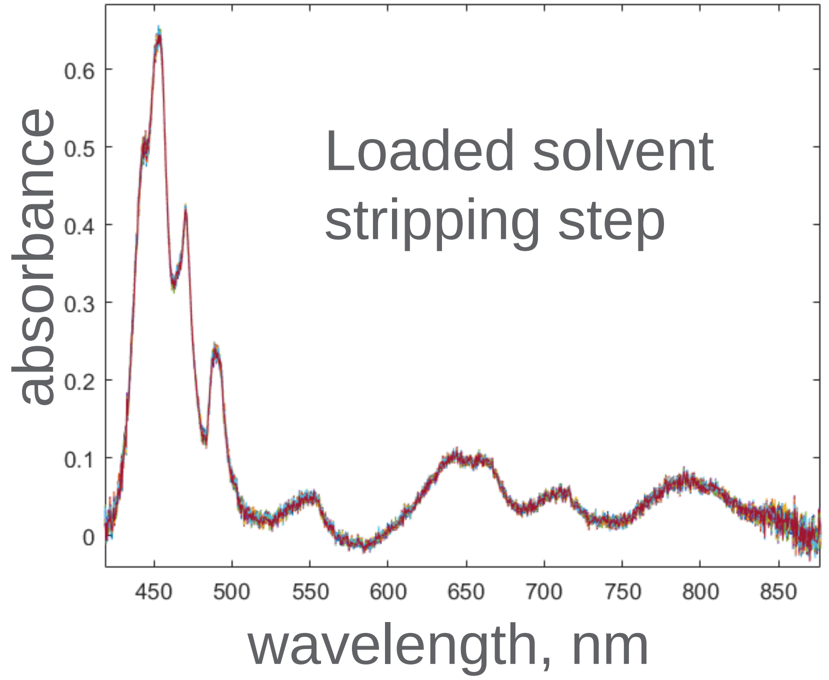
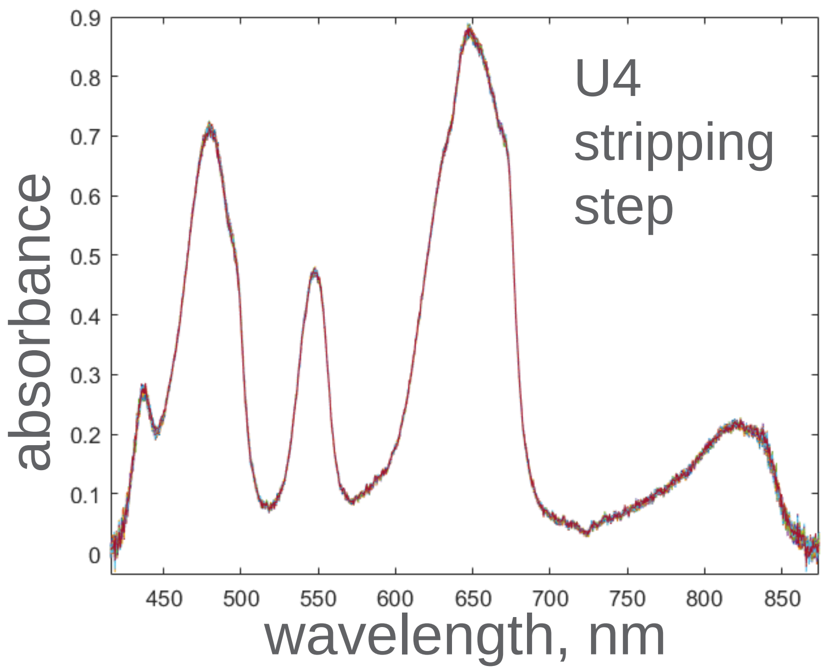
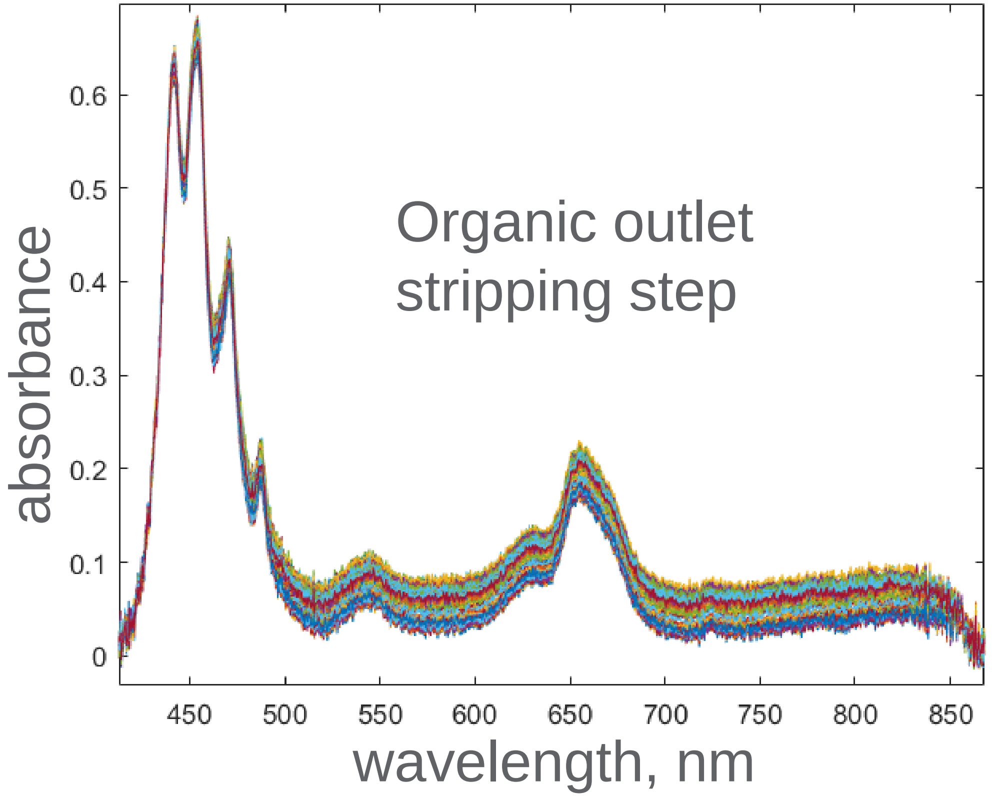
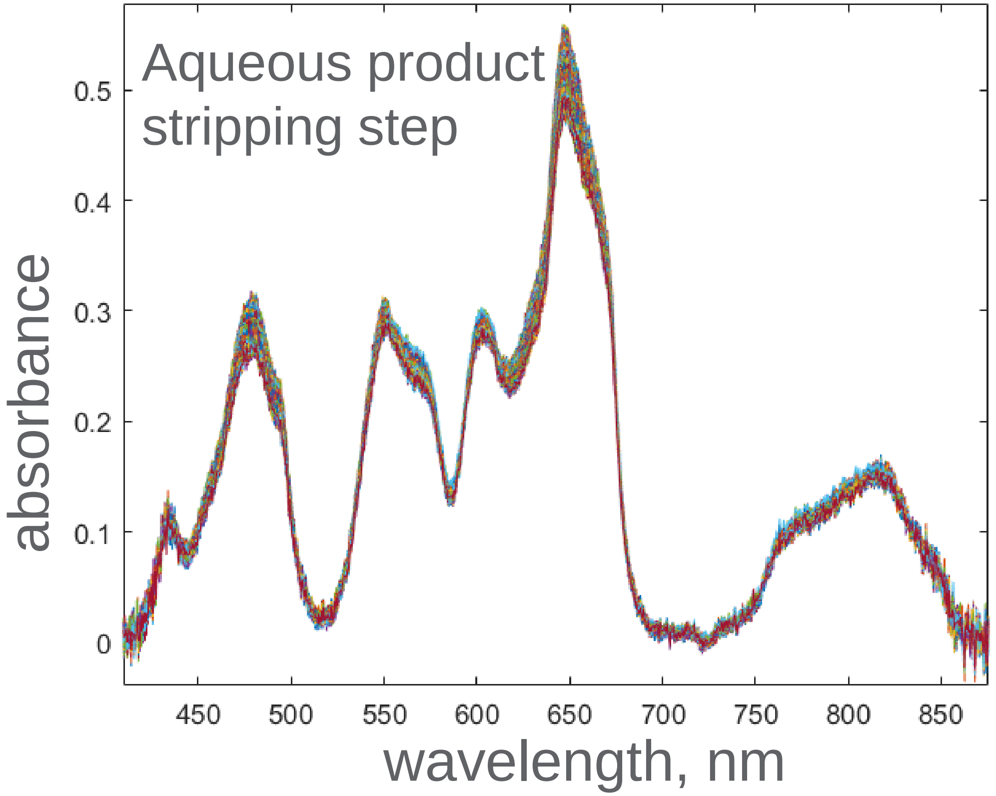


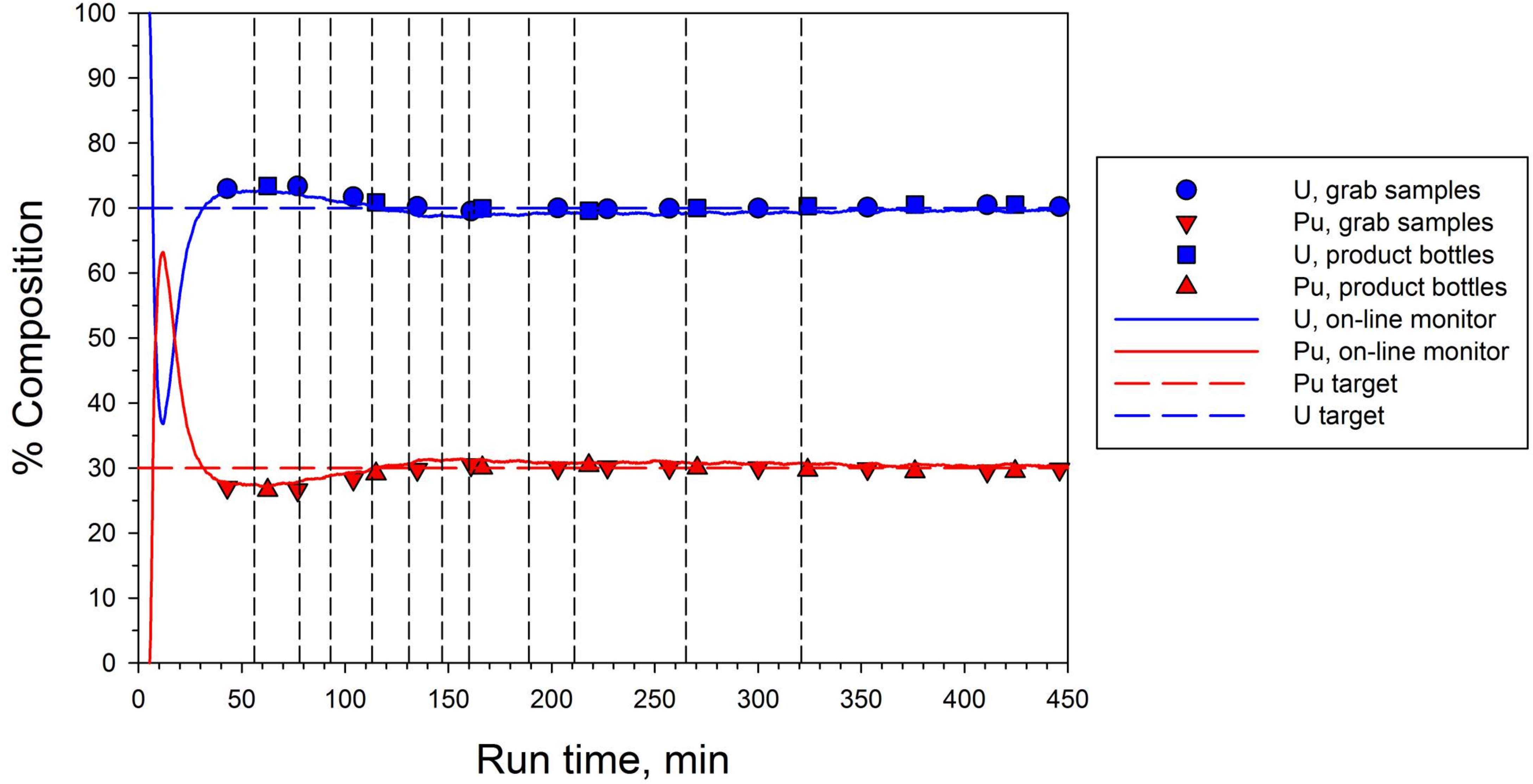






CoDCon demonstration: Enabling Real-Time Process Control

Run 3

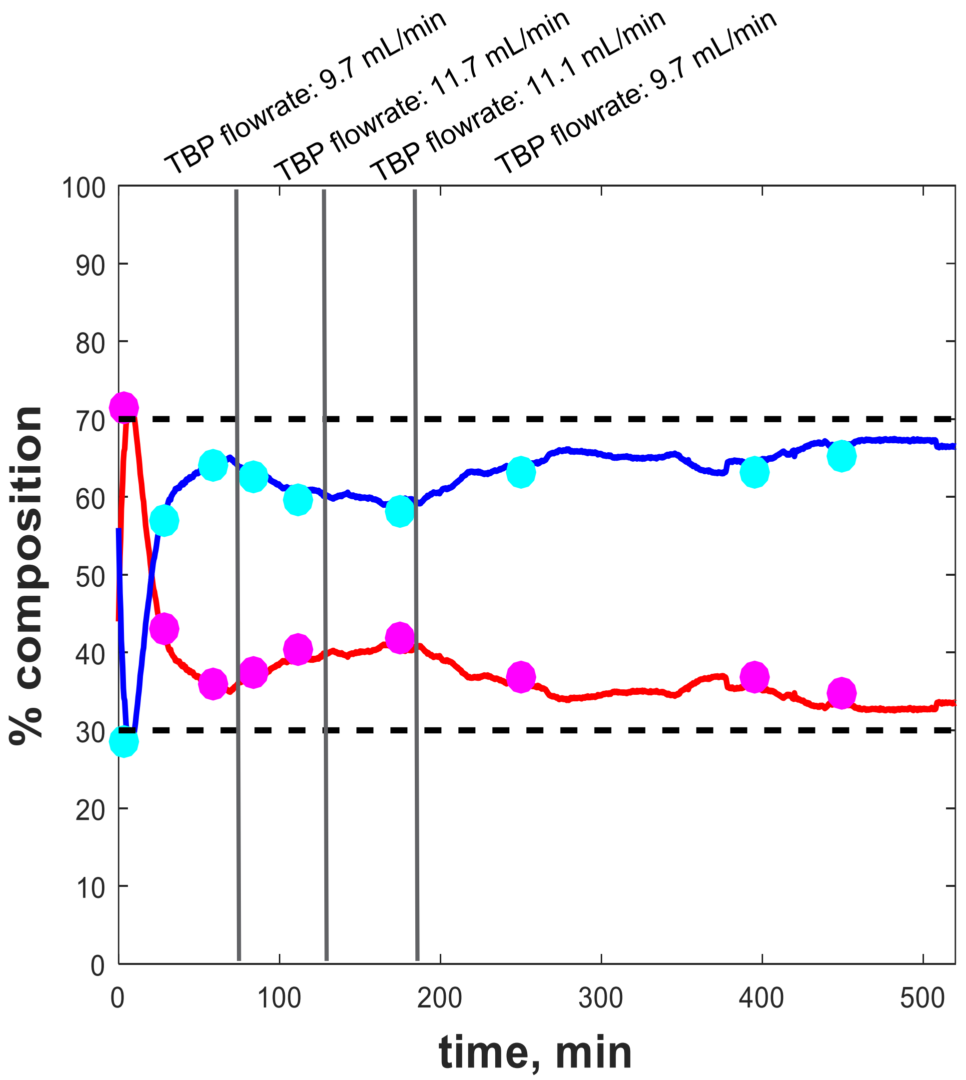


CoDCon Run3.JNB

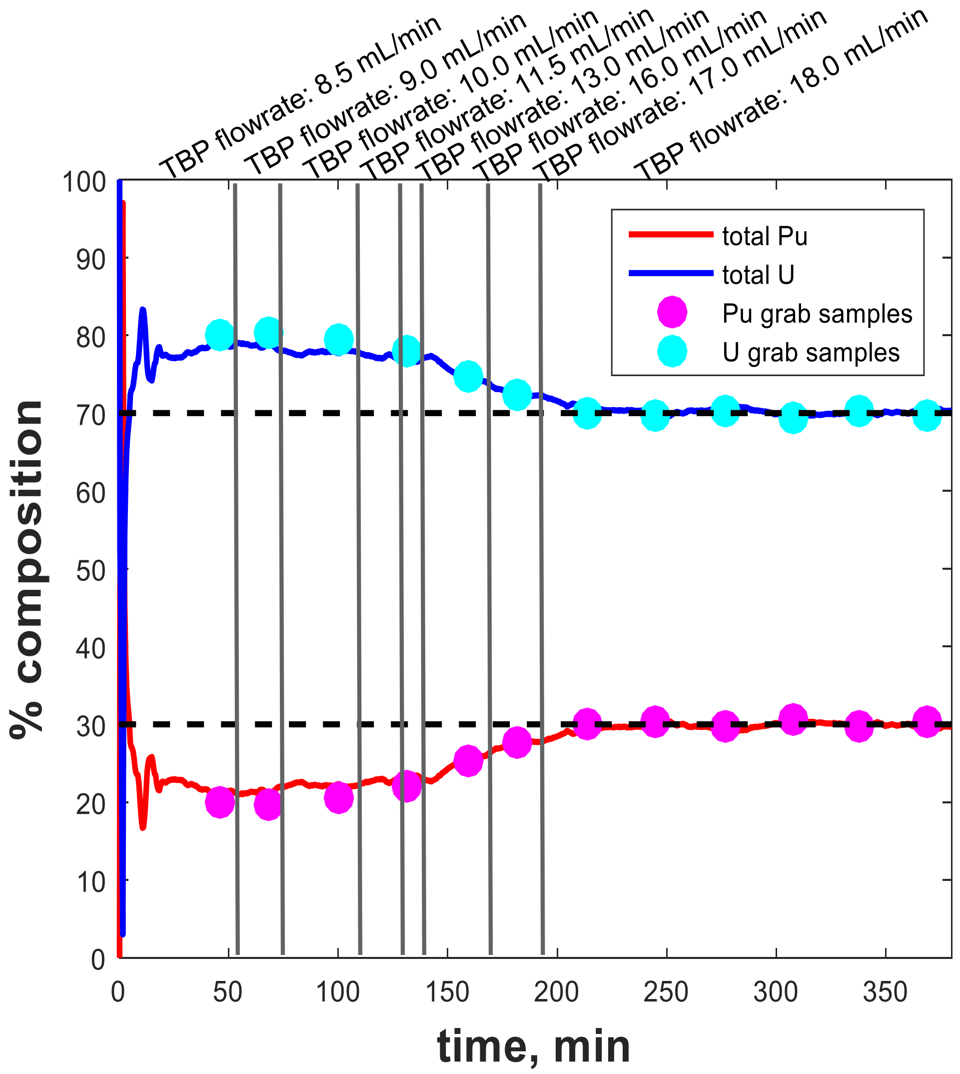
Other benefits of on-line monitoring: Identifying Process Equipment Failures

- Identification of unexpected separation system behavior

Run 1



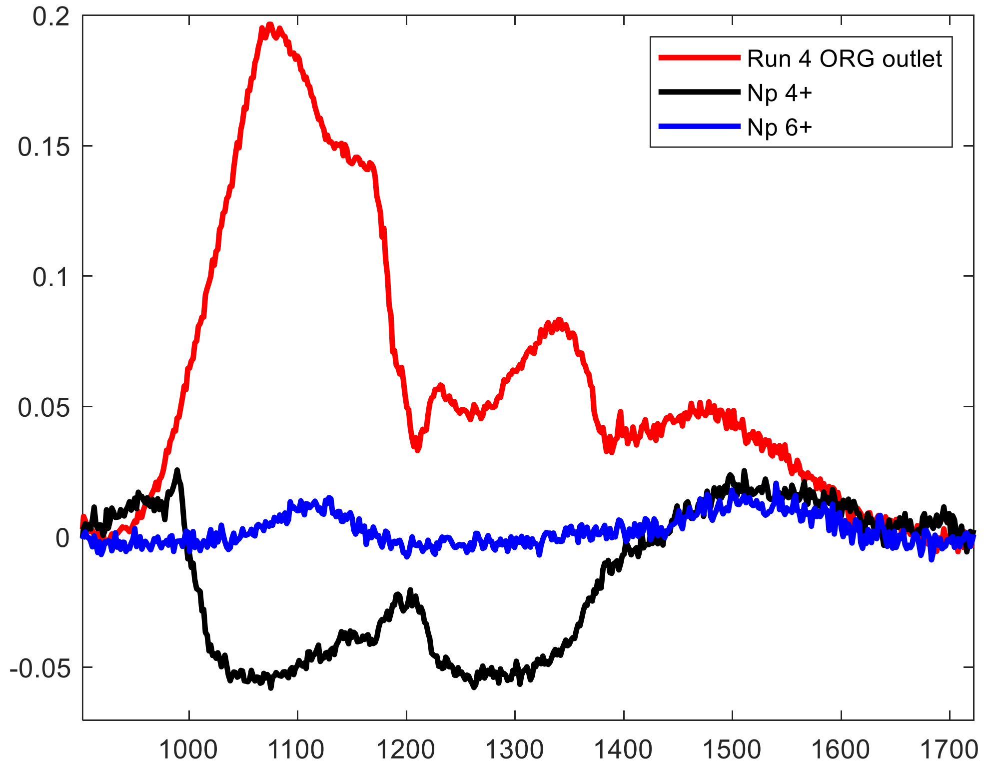
Run 2



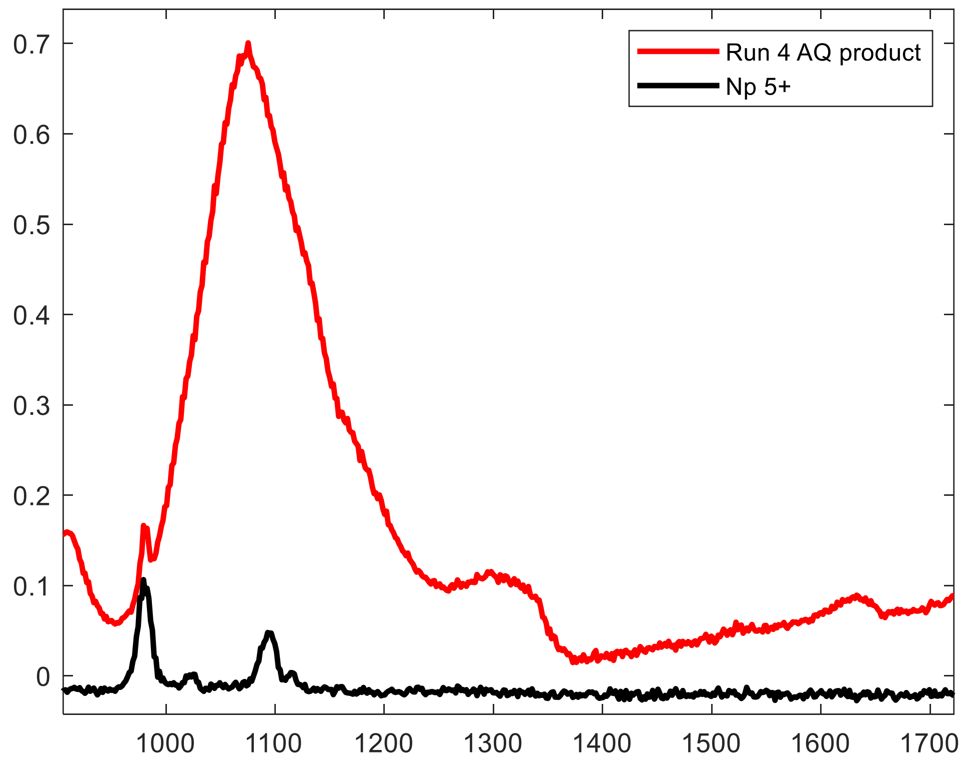
Other benefits of on-line monitoring: Improving Our Fundamental Understanding

- Immediate interrogation of stream allows for capture of short lived species

Run 4
ORG outlet

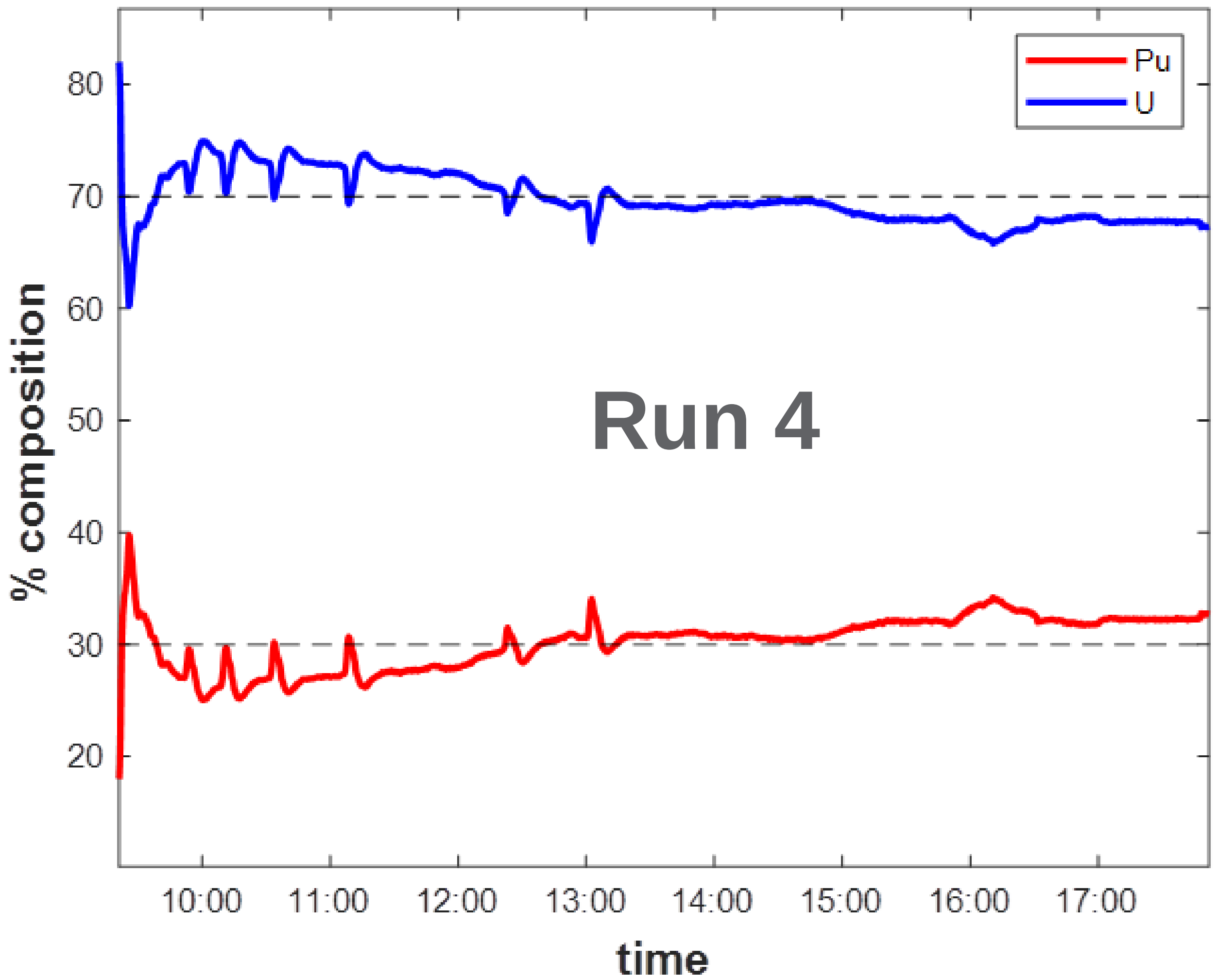


Run 4
AQ product



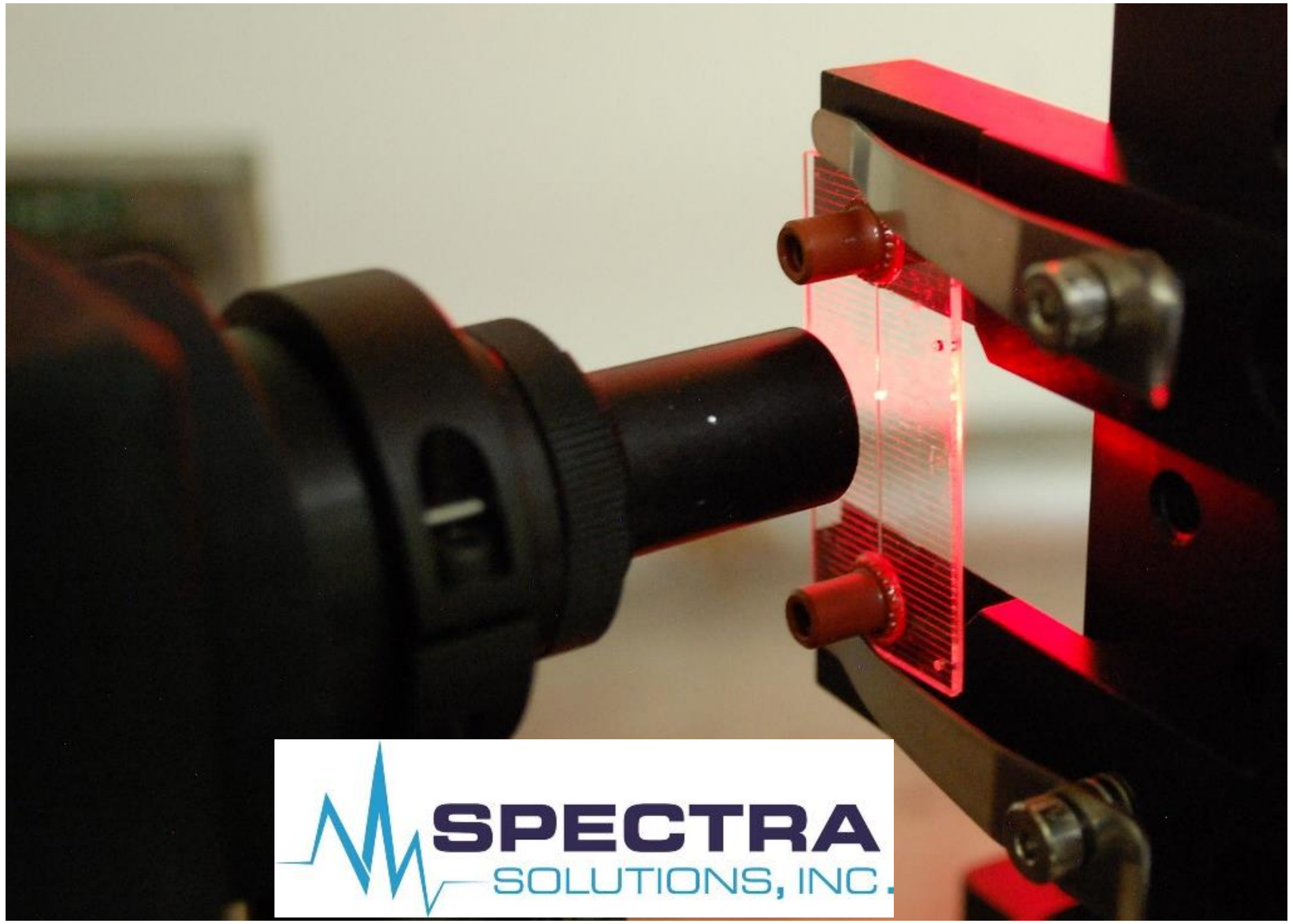
Other benefits of on-line monitoring: Expanding Understanding of Equipment Behavior

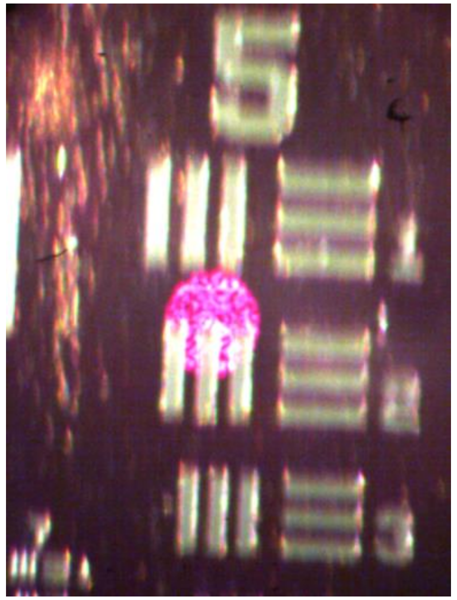
- Catching system deviations that may not be identified via grab sample collection or gross product characterization

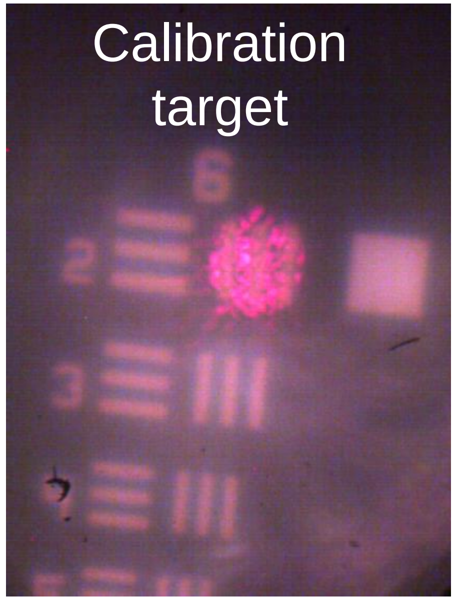


Microfluidics: Leveraging SBIR and CEA Collaborations

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



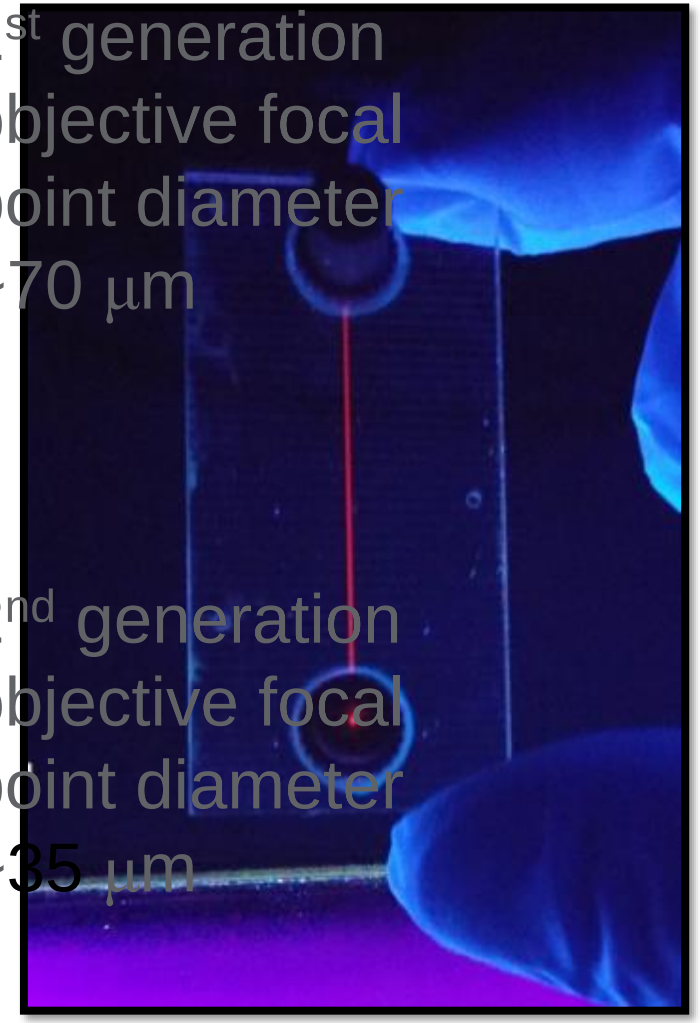




Calibration target

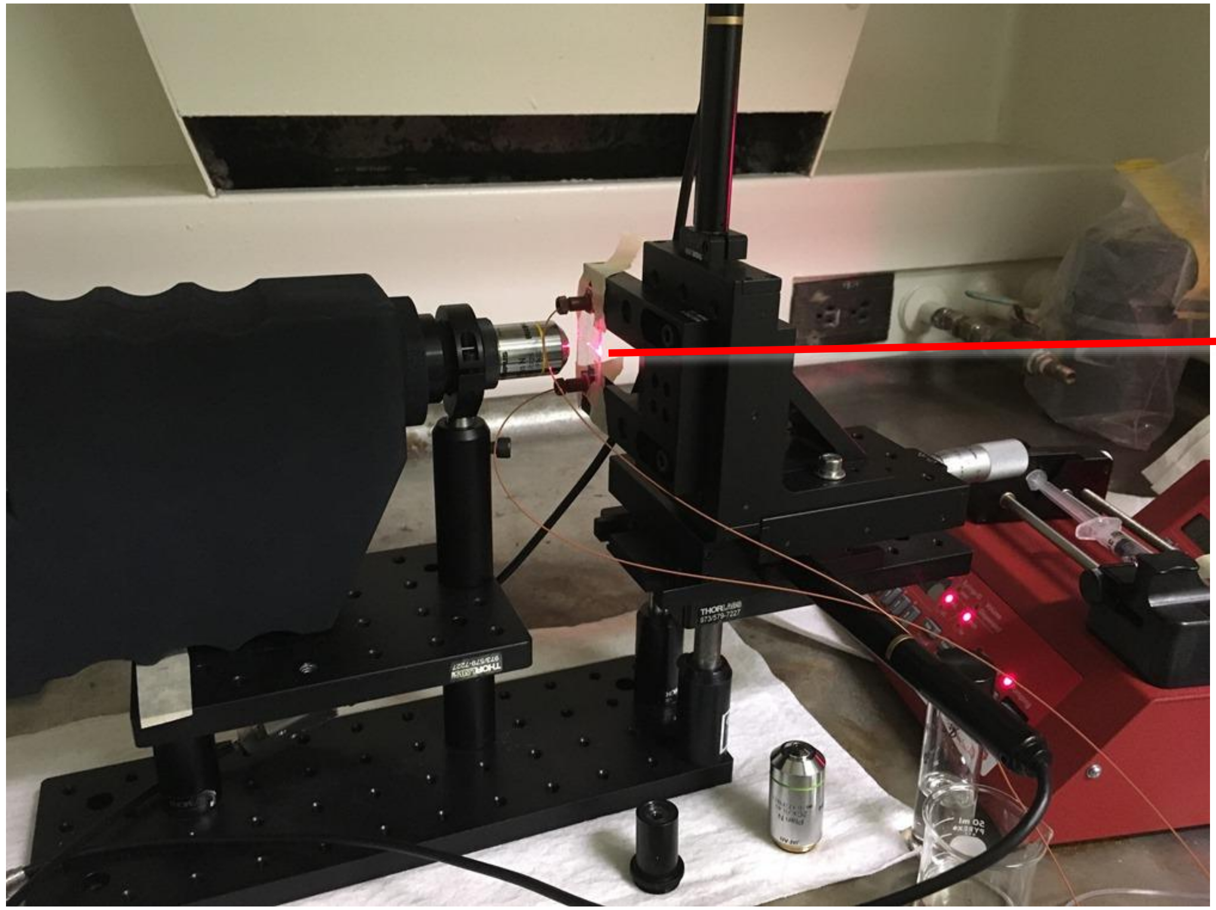
1st generation objective focal point diameter ~70 μm

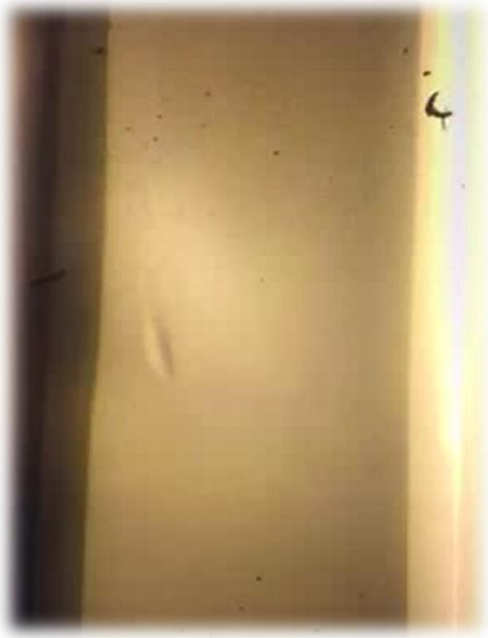
2nd generation objective focal point diameter ~35 μm



Solvent Extraction Monitoring in Microfluidics: simultaneous two-phase measurement

- Two Phase system: 30% TBP-dodecane / nitric acid (HNO_3)
- Simultaneous monitoring of aqueous and organic phases under dynamic flow

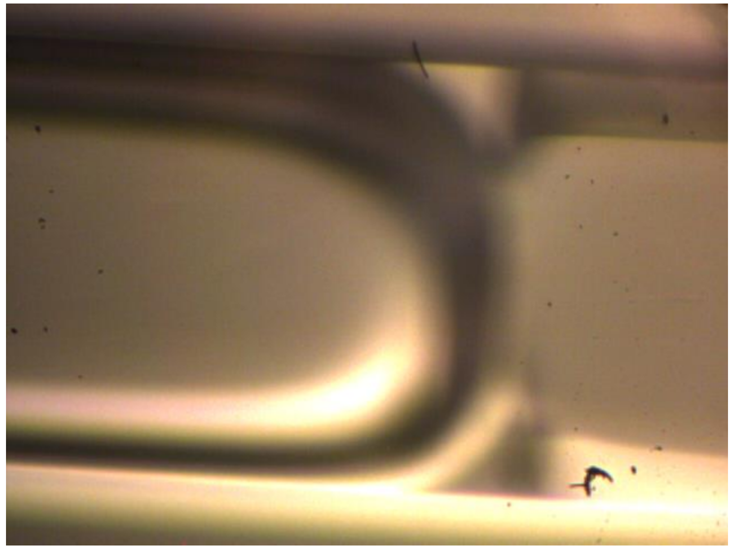


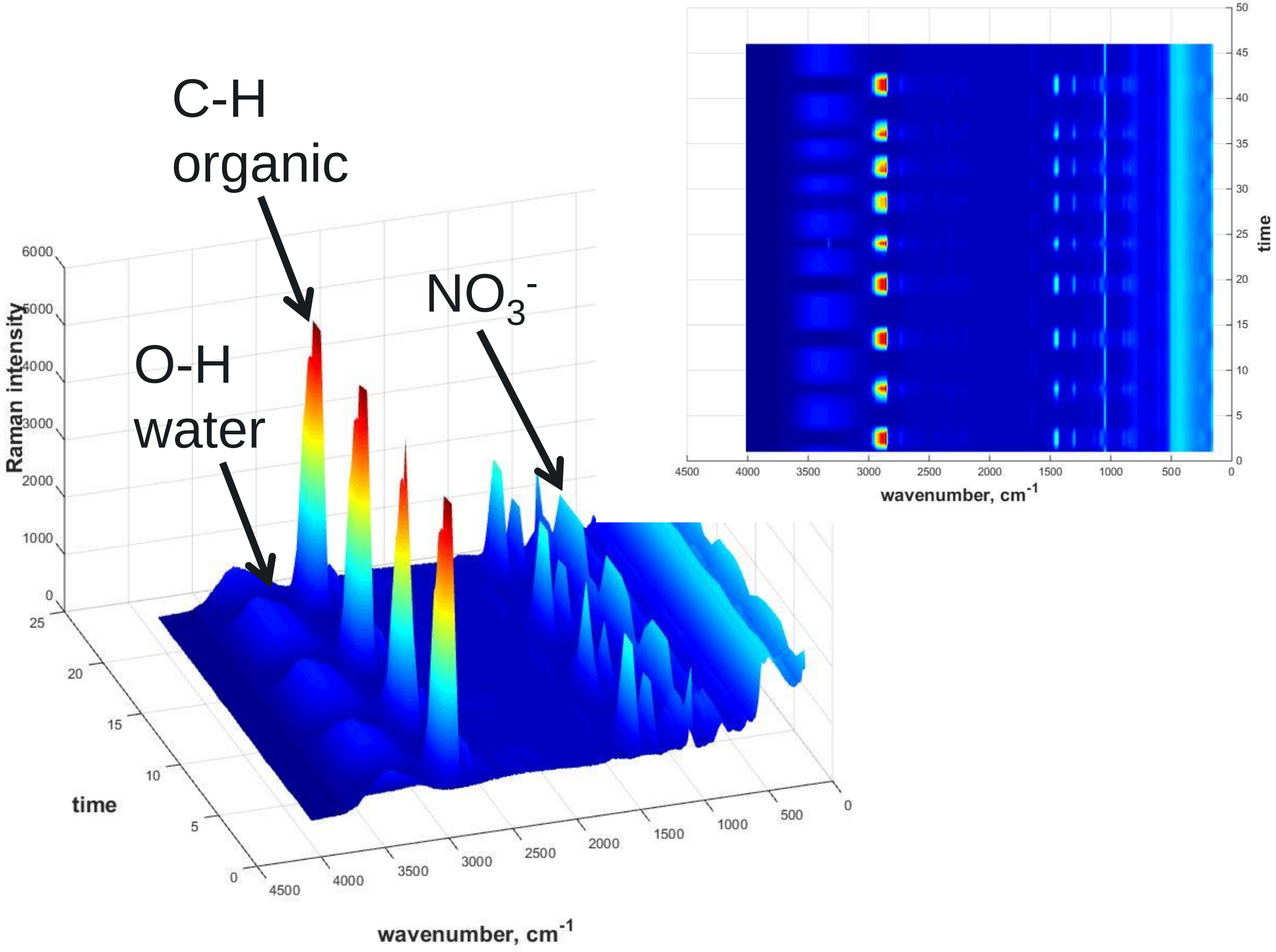


On board camera focused on microfluidic channel

Solvent Extraction Monitoring in Microfluidics: simultaneous two-phase measurement

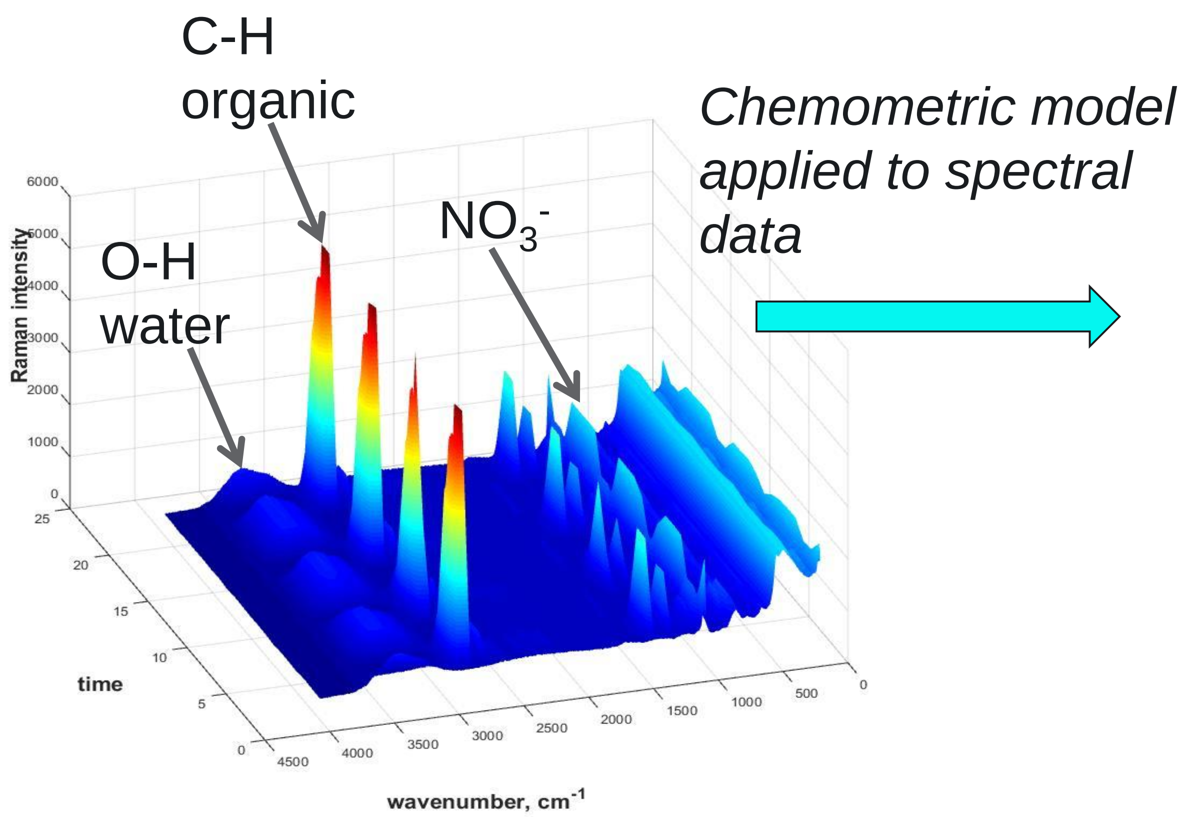
Archetypal binning coupled with chemometric modeling used to simultaneously analyze both phases

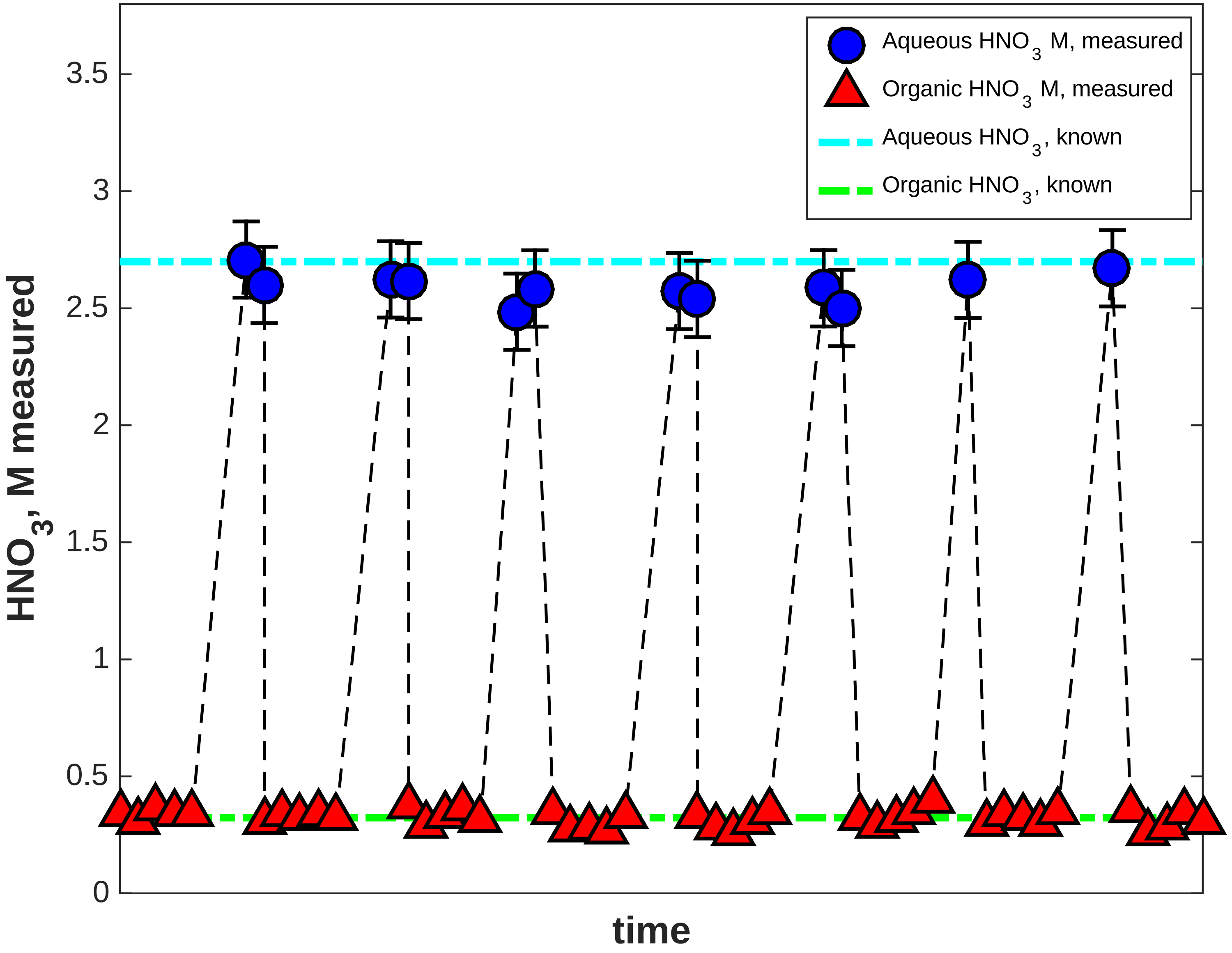




Solvent extraction monitoring in microfluidics: two-phase measurement

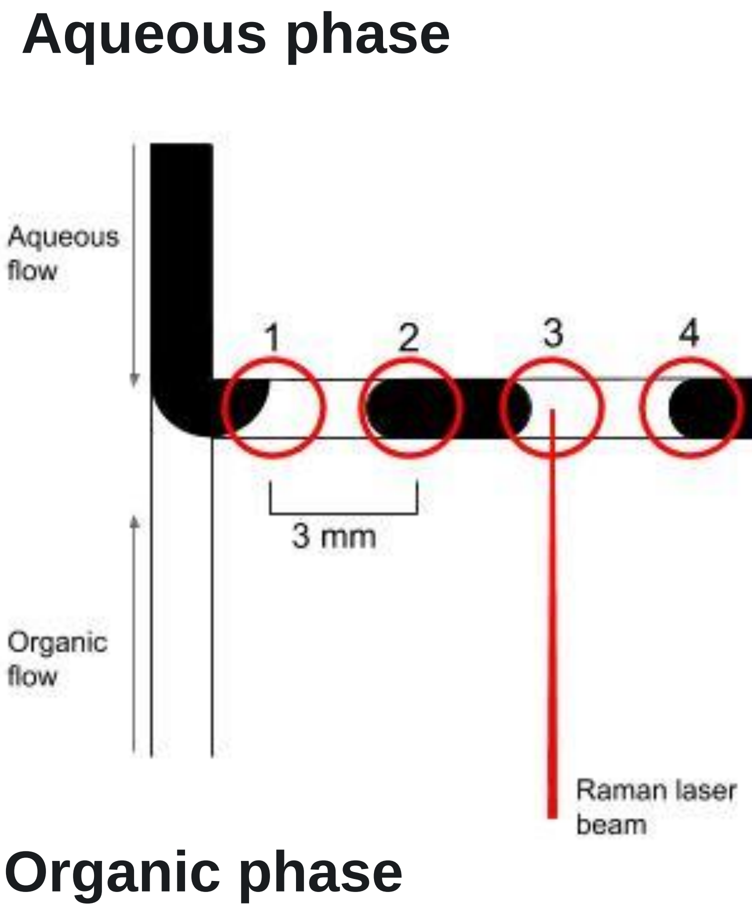
real-time measurement of HNO_3 in aqueous *and* organic phases within microfluidic channel

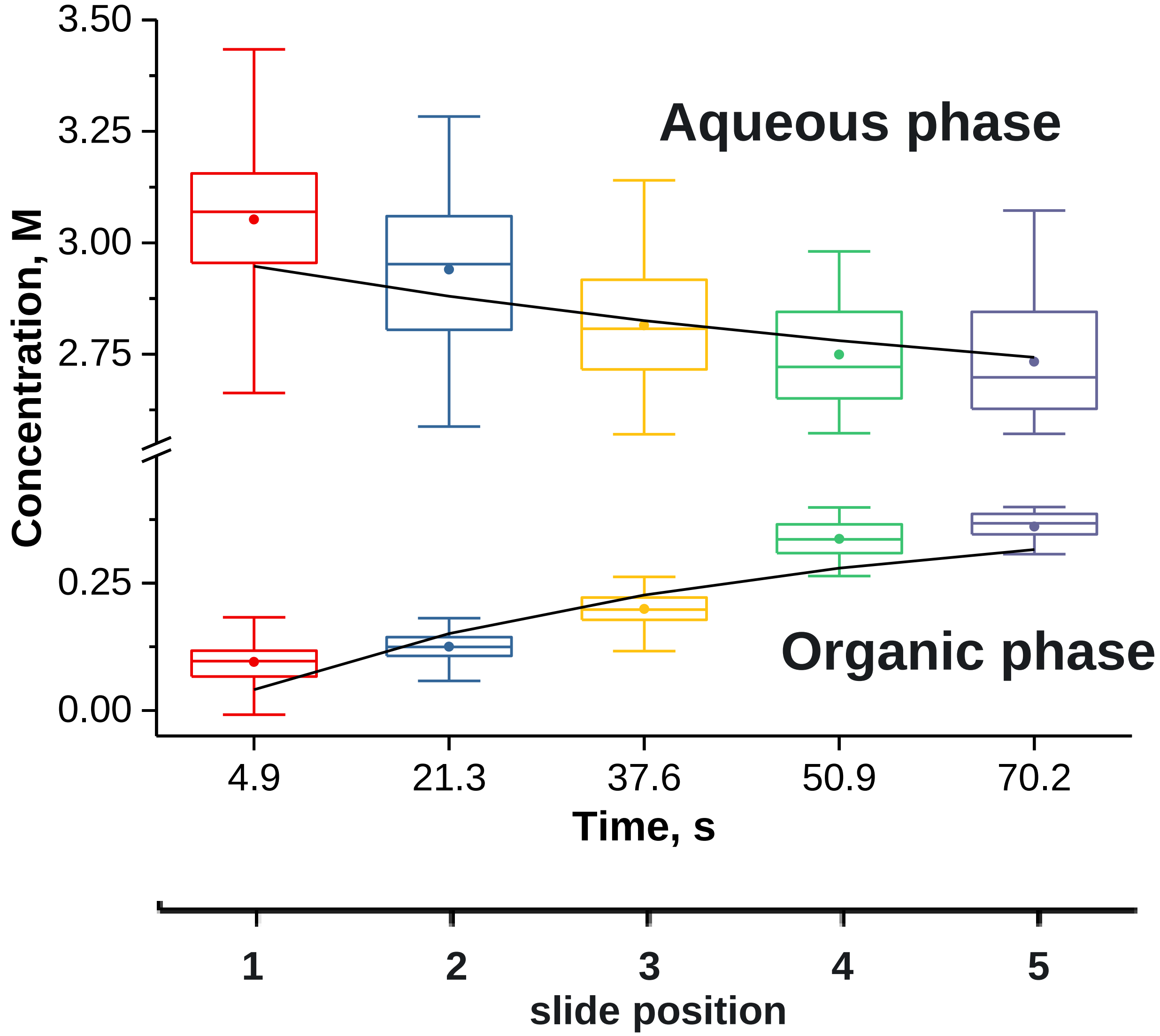




Archetypal binning coupled with chemometric modeling used to simultaneously analyze both phases

Solvent extraction monitoring in microfluidics: kinetics of two-phase extraction

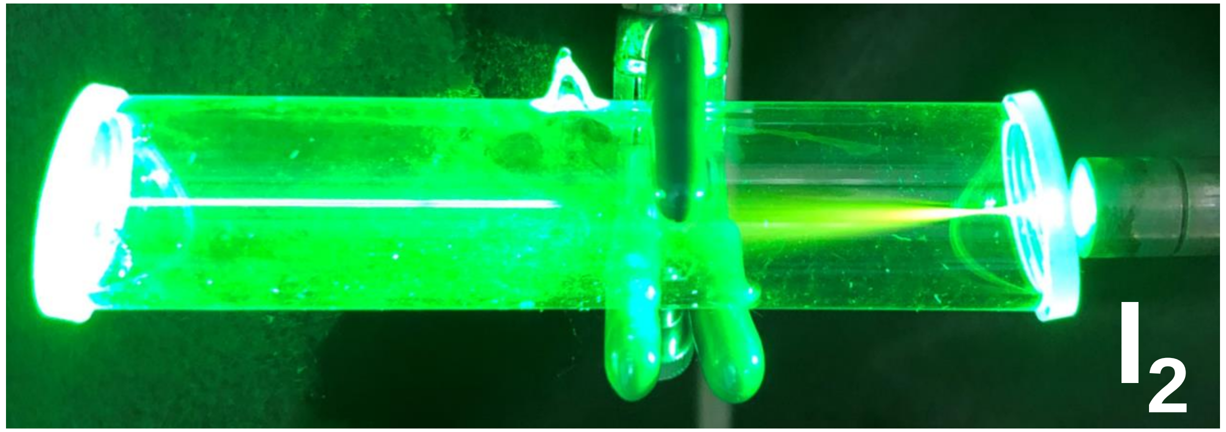


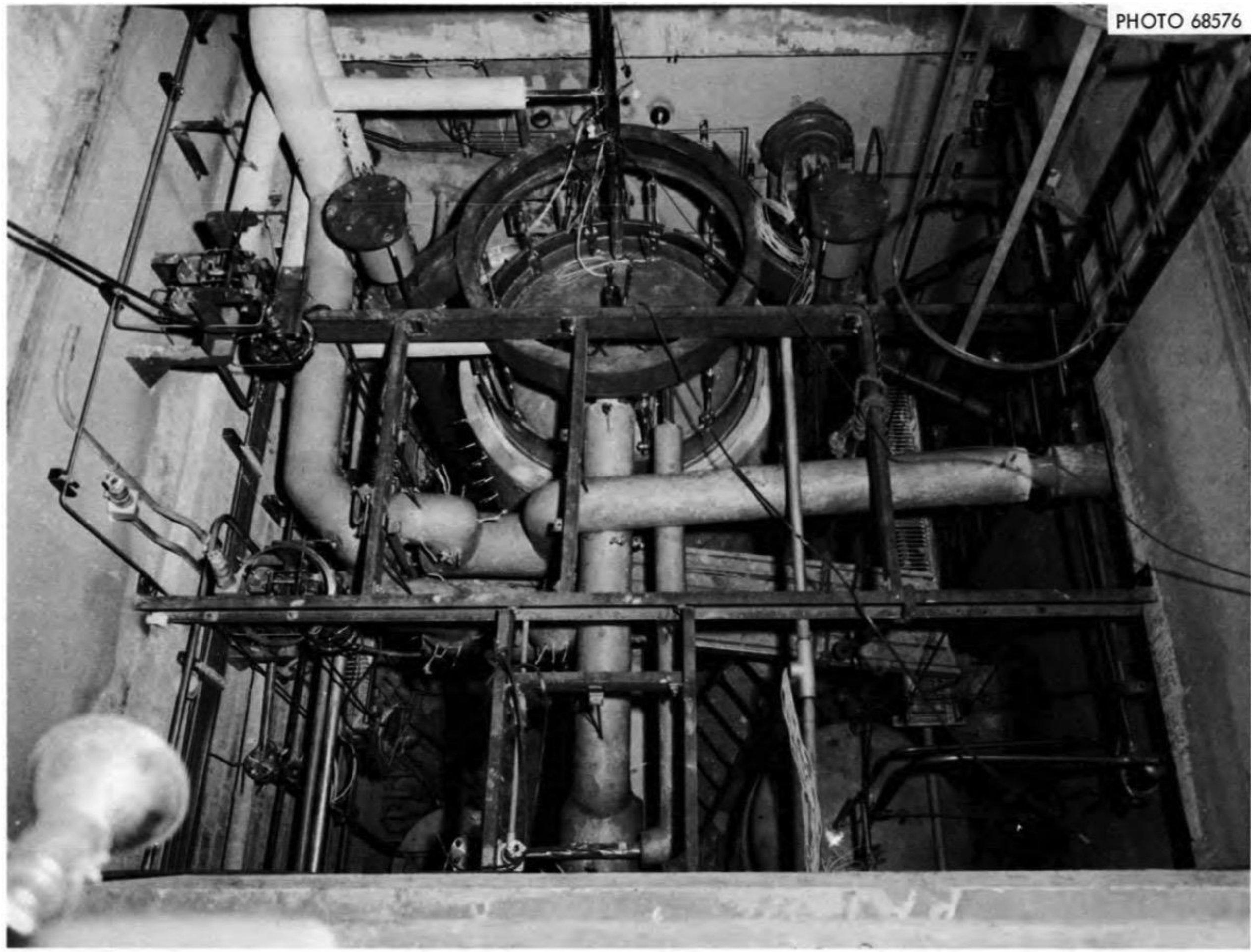


Anal. Chem., 2018, (90), 8345–8353.

Molten Salt Reactor Off-gas Treatment
On-line Monitoring to quantify Iodine Species

- Collaboration with ORNL
- Building off-gas treatment systems and integrating on-line monitoring
- Duel methods
  - LIBS at ORNL
  - Raman at PNNL

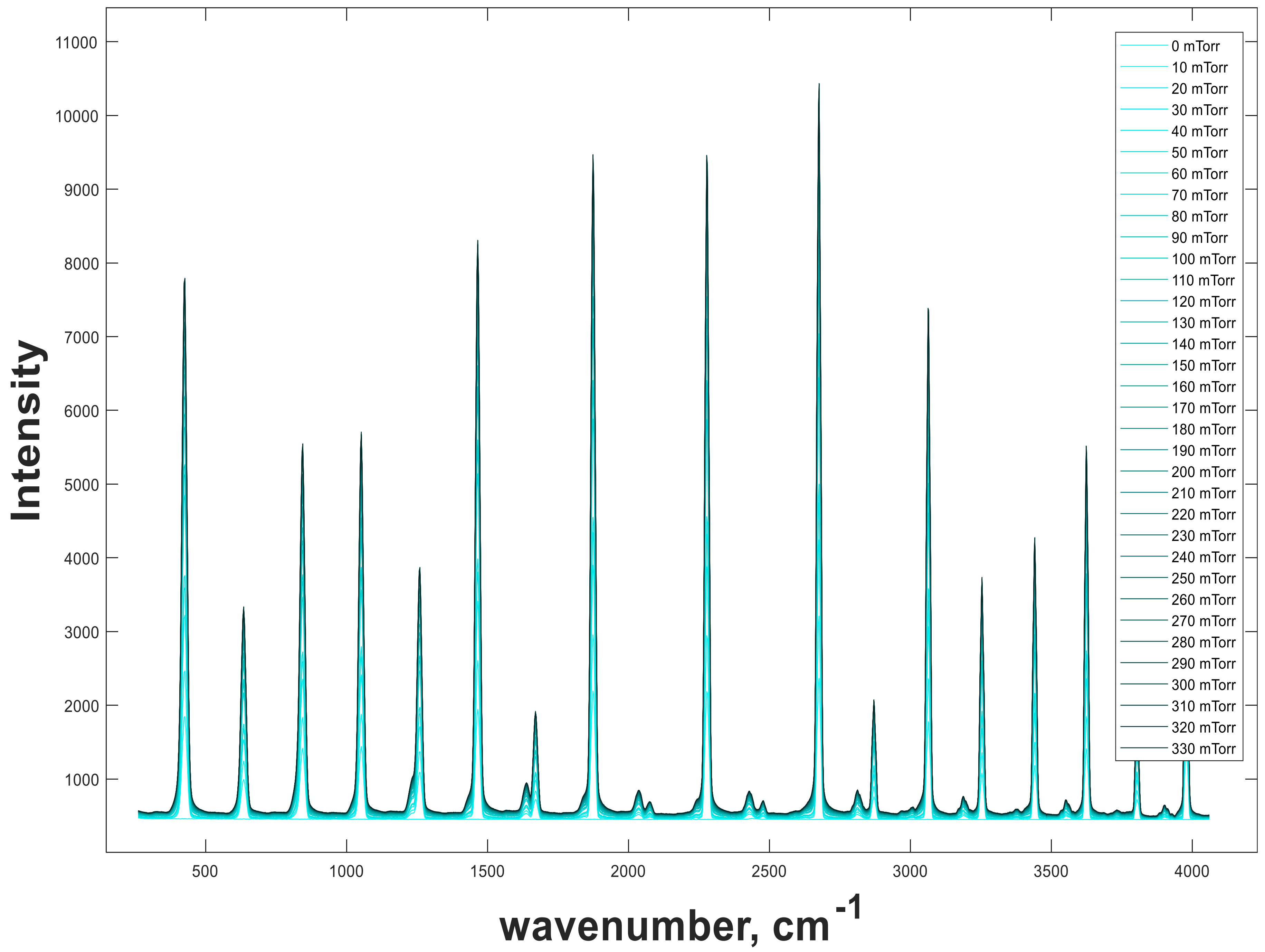




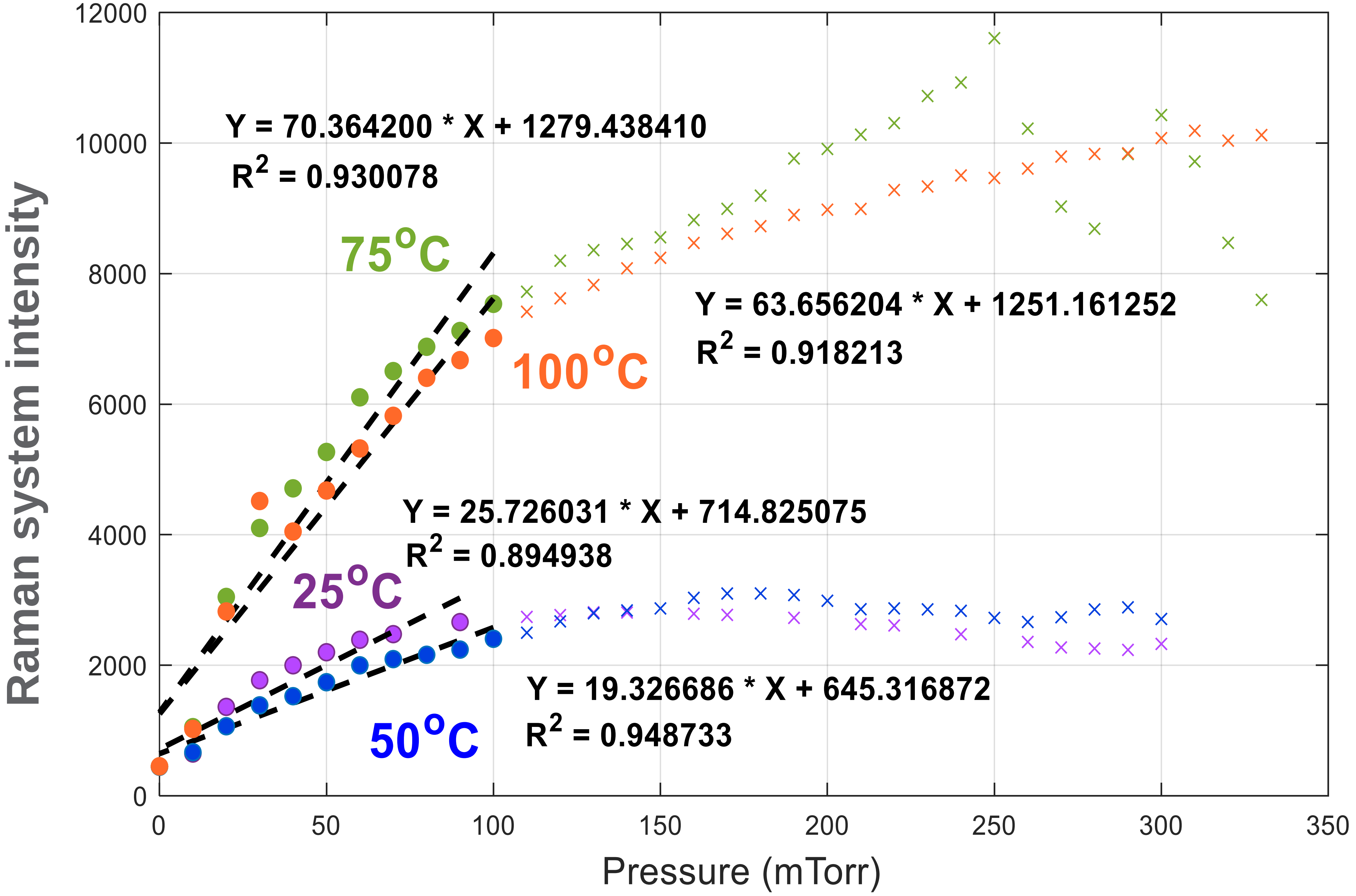
MSRE fuel processing hot cell.
R.B. Lindauer, ORNL-TM-2578 (1969)

Analysis of I_2 fingerprints:
variable pressure

- I_2 exhibits strong and unique fingerprint
- Data shows excellent correlation between signal intensity and I_2 partial pressure

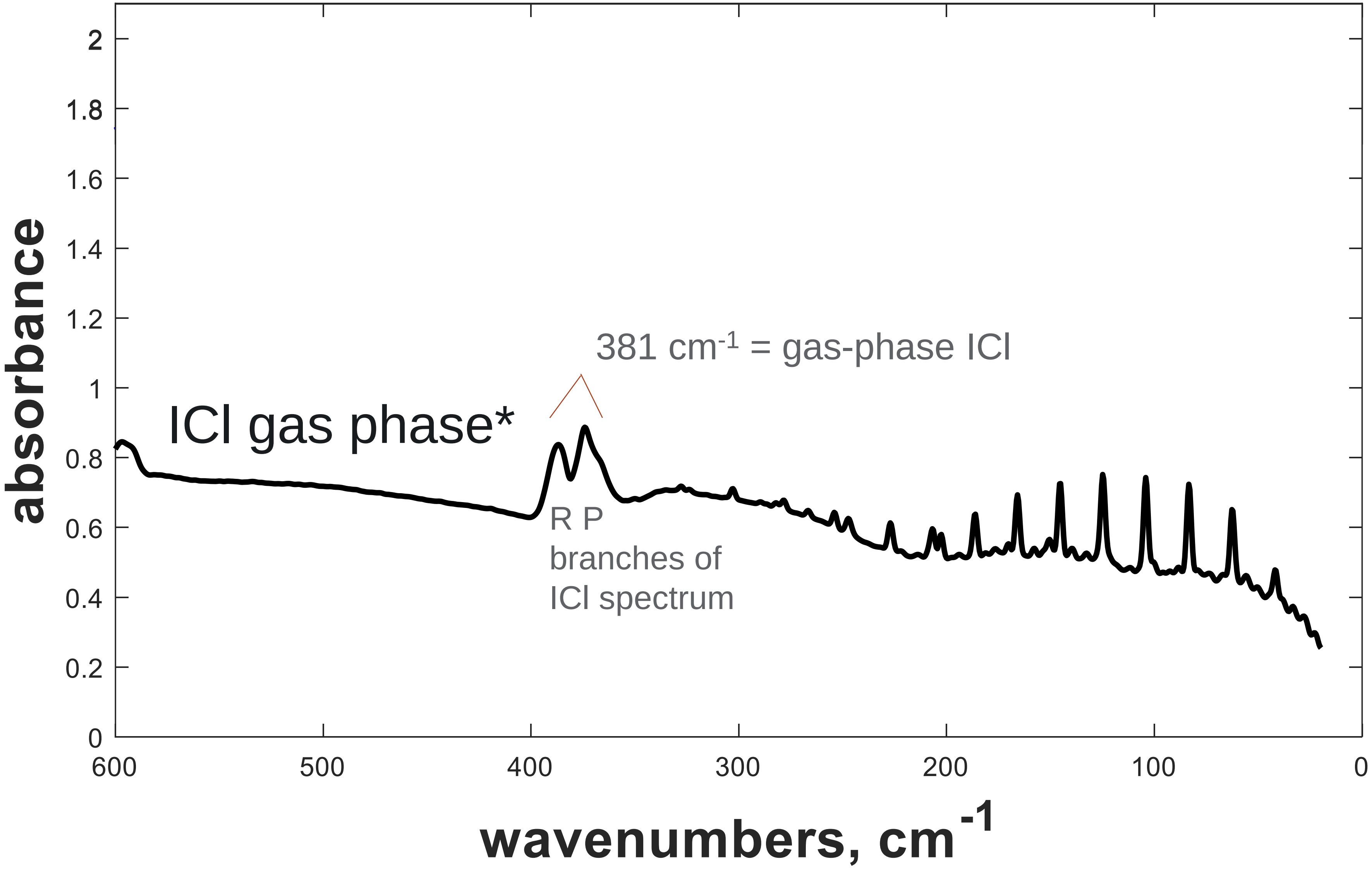


Analysis of I_2 fingerprints:
As a function of temperature and pressure



FTIR analysis of ICl fingerprints

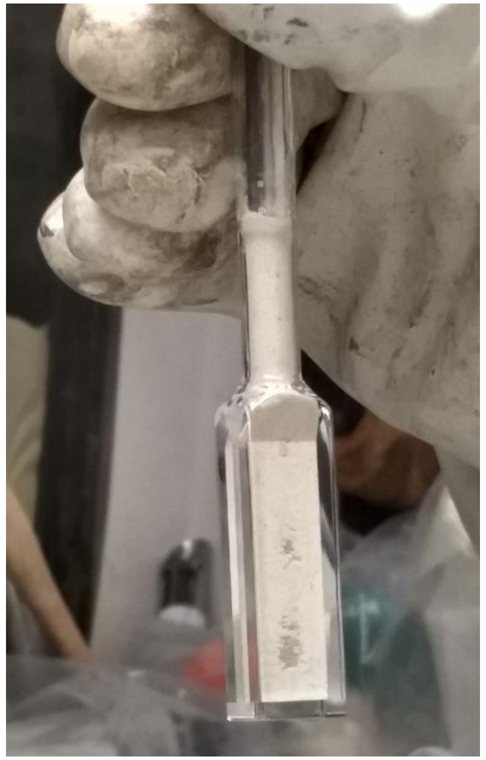
- ICl can also be identified via FTIR
- Sensor fusion of Raman and FTIR additional benefits
  - Multiple methods of detecting HCl, HF, etc
  - Potential to measure temperature of gas based on spectral fingerprint

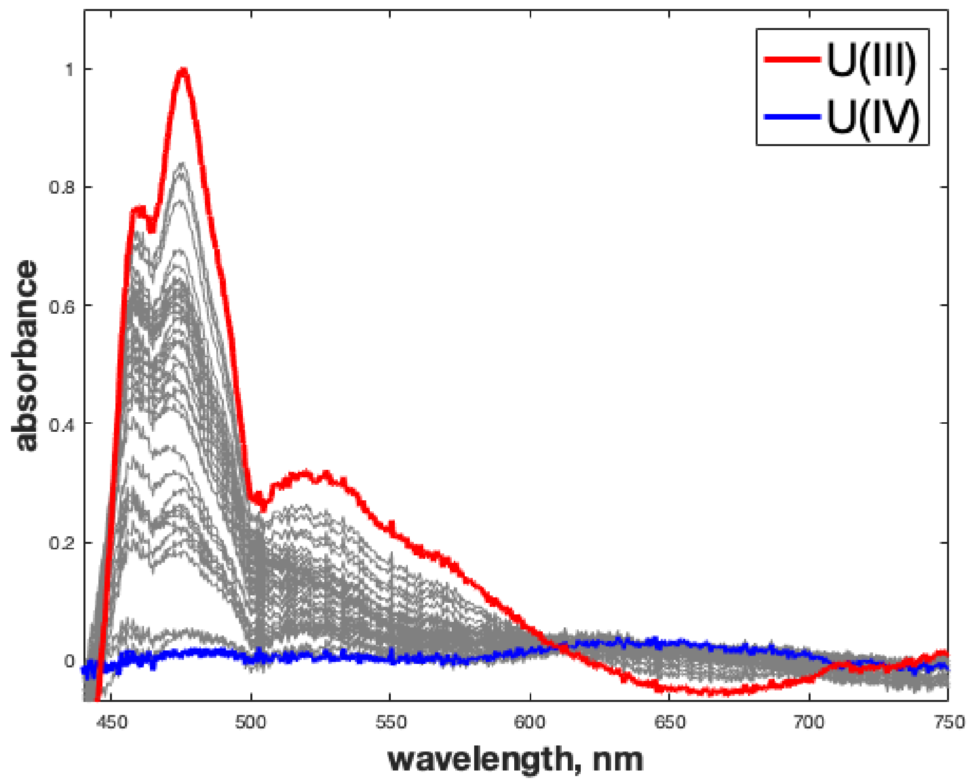


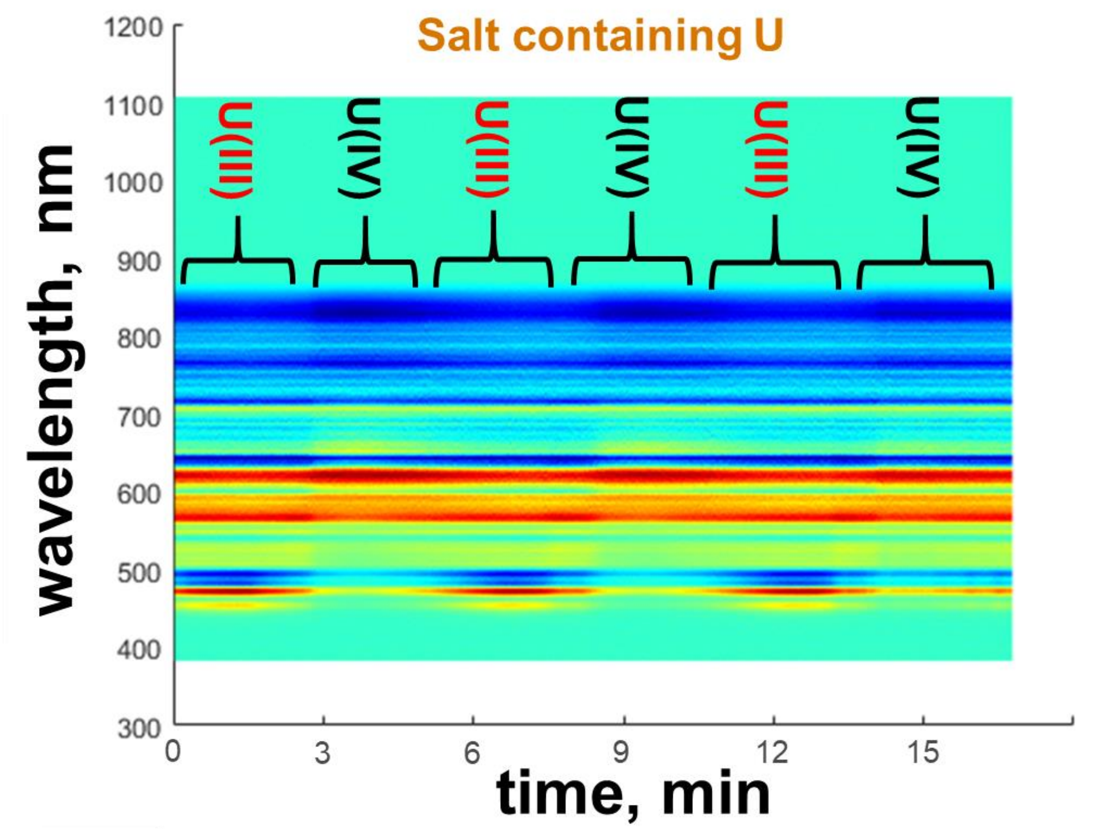
*Band assignment: ***J. Chem. Phys.*** 52, 399 (1970).

Additional Opportunity Space

- On-line monitoring as well as fundamental analysis of salt melts
- Applied to Cl salts, with plans to test NaOH and F salts







Application Within Harsh Environments

- High temperatures (>600°C)
- Highly corrosive liquids and gases
- High radiation dose

Probe face

0 Rad 1.7E8 Rad

Example window material

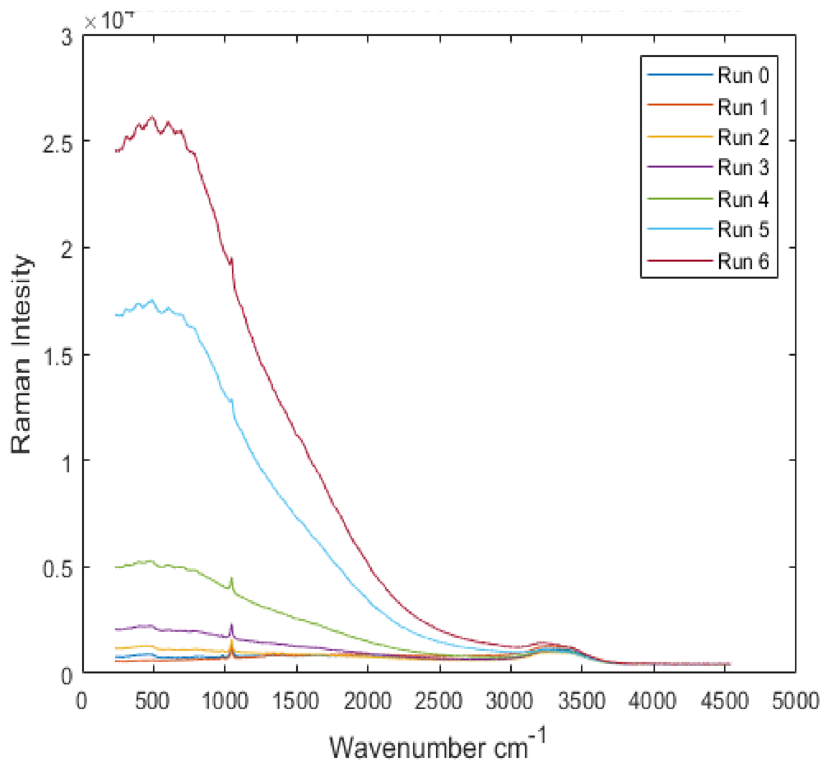
0 Rad 1.7E8 Rad

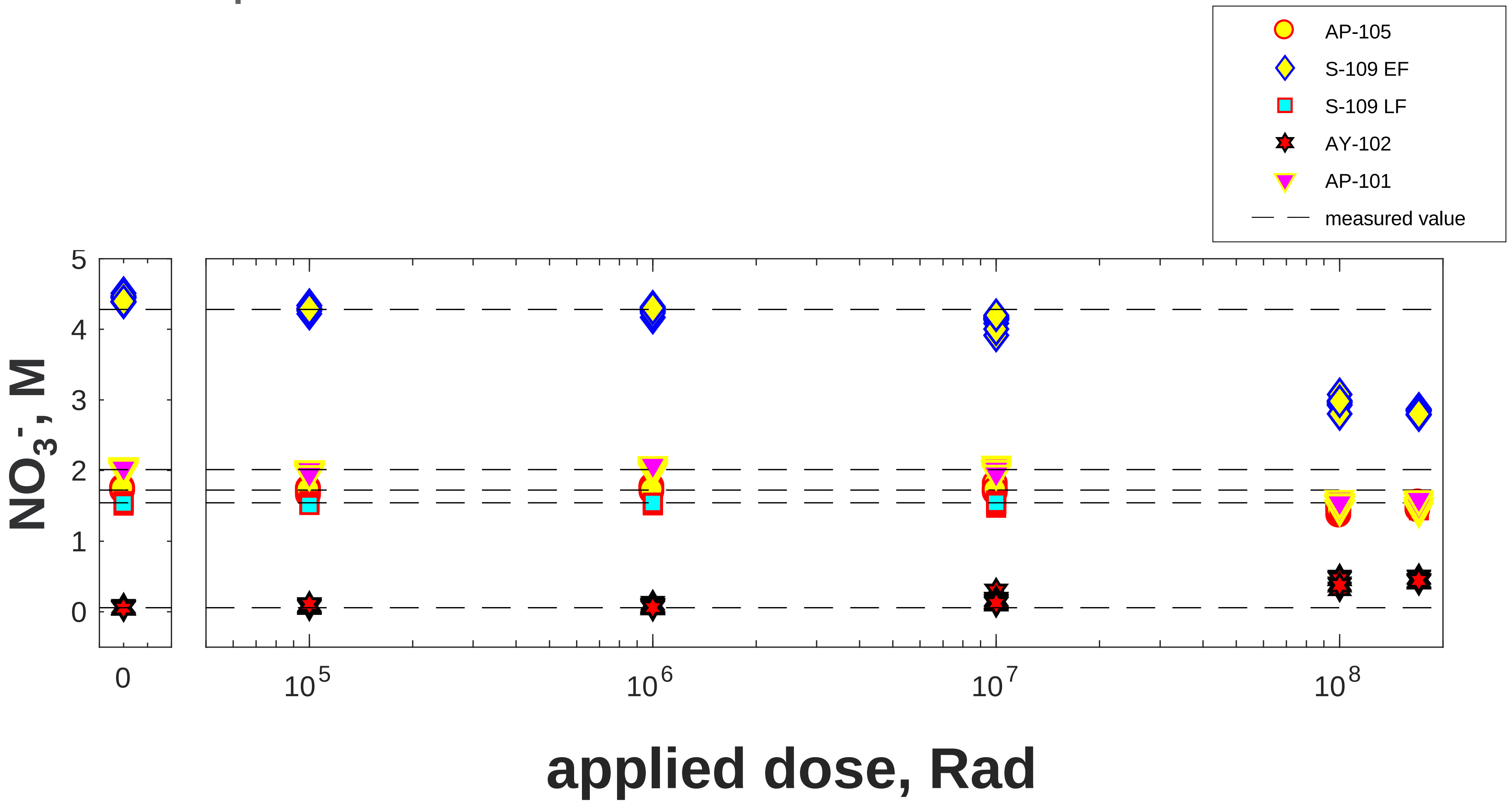
Instrument computer operator

Significant distance

Modeling of data during irradiation dose tests

- Spectral background changes with radiation dose
- Chemometric analysis can compensate for this and enable accurate quantification





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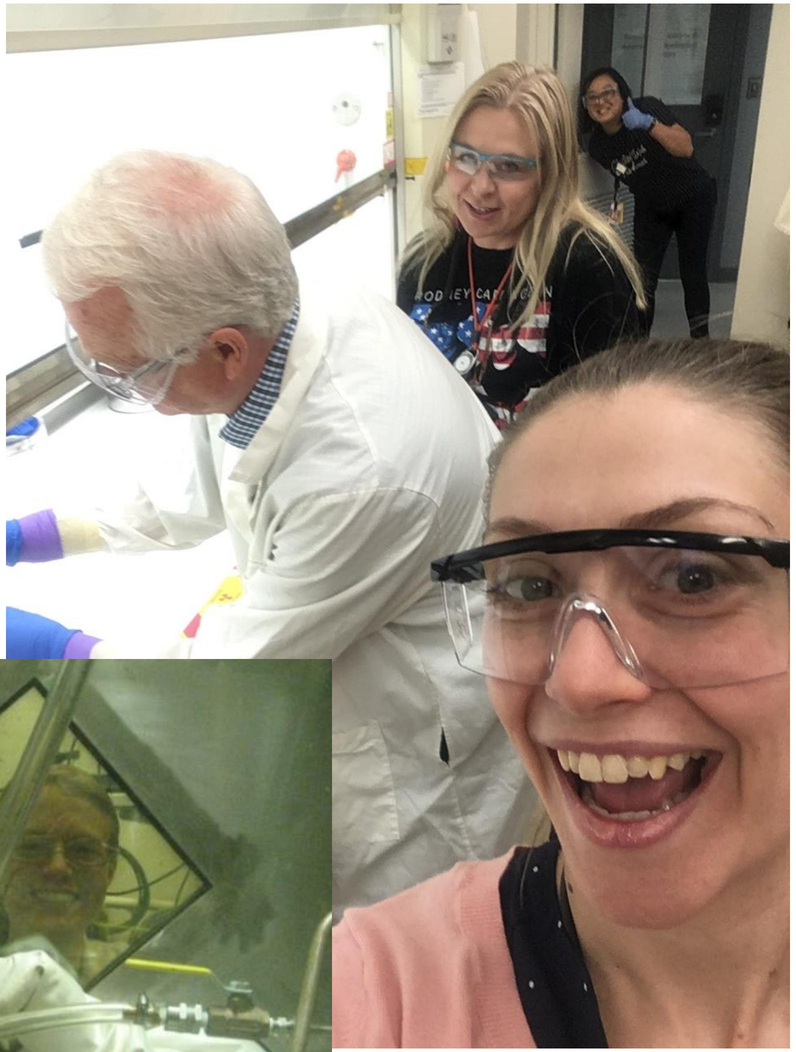
Conclusions

- On-line monitoring can offer significant advantages
  - Identification and quantification of target analytes
  - Fast, versatile application
- Real-time characterization
  - Safeguards
  - Process control/optimization



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Team:

Sam Bryan
Amanda Lines
Gregg Lumetta
Shirmir Branch
Gabe Hall
Jarrod Allred
Job Bello
Amanda Casella
Forrest Heller
Susan Adami
Brian Riley
Susan Asmussen

Students/visiting faculty:

Gilbert Nelson
Hope Lackey
Jen Wilson
PoKi Tse

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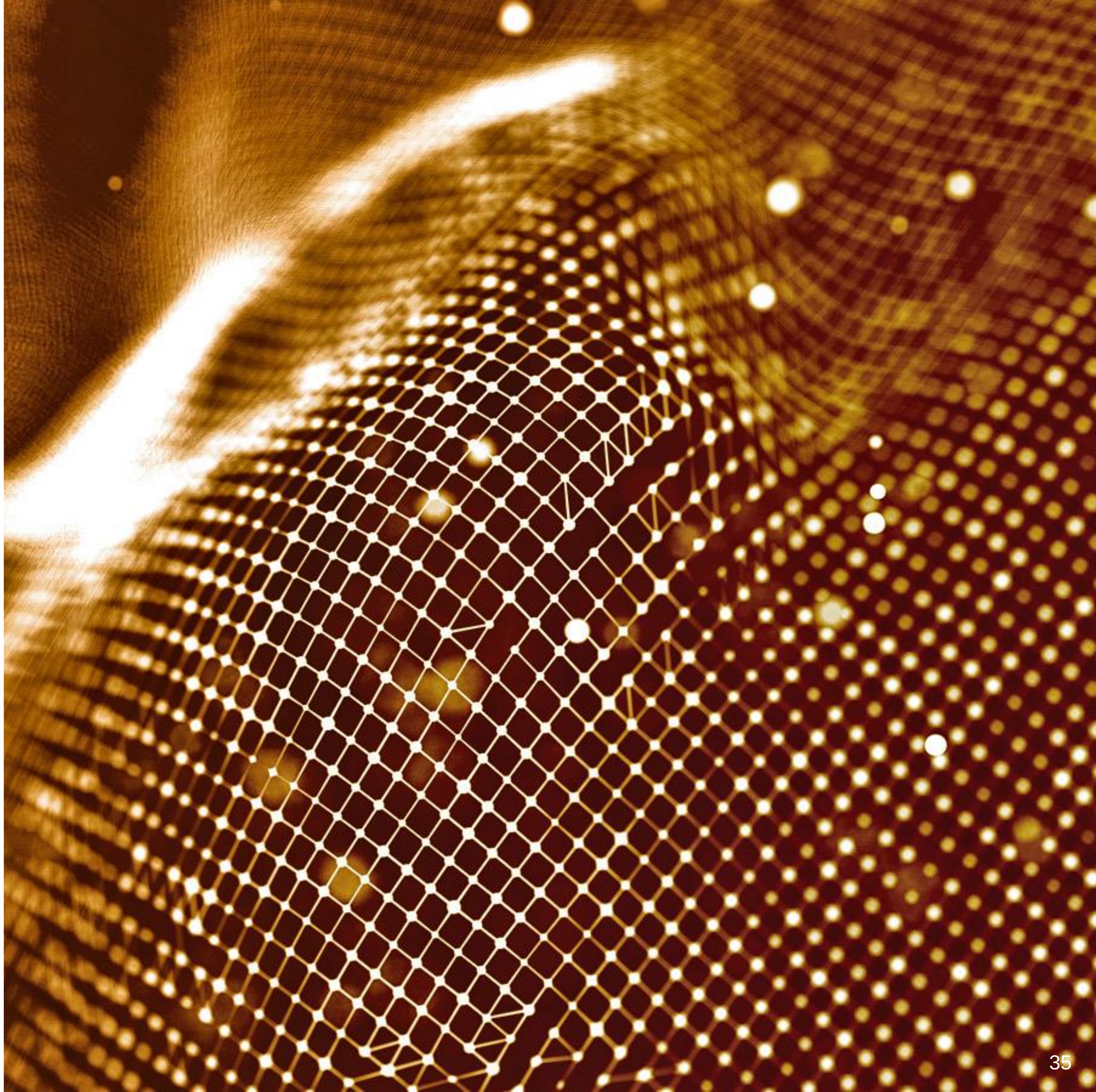
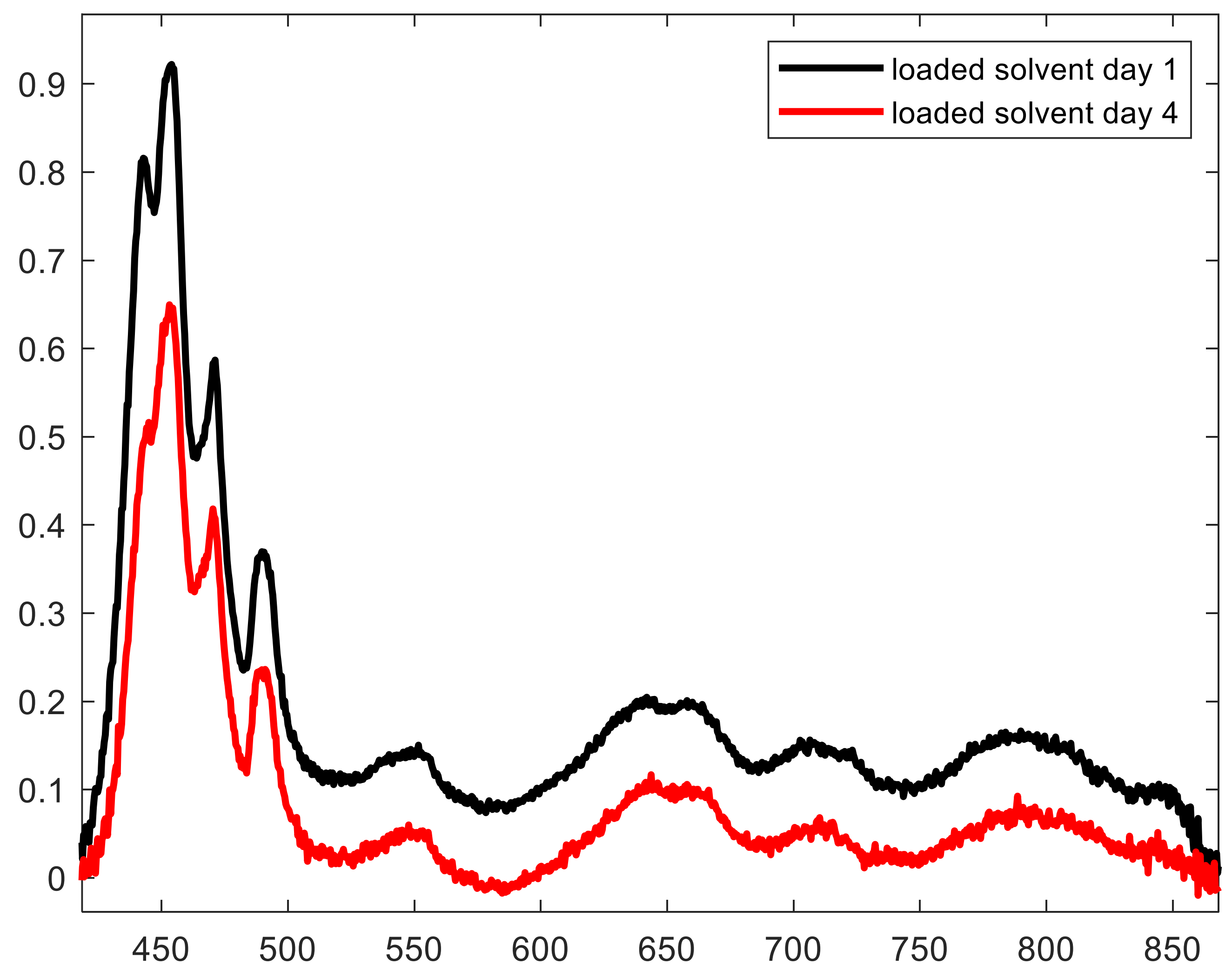
Thank you

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loaded solvent day 4
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
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500
550
600
650
700
750
800
850