On-line Monitoring Development in Support of the Nuclear Fuel Cycle

Dr. Amanda Lines and Dr. Samuel Bryan
Pacific Northwest National Laboratory, USA

31 July 2024

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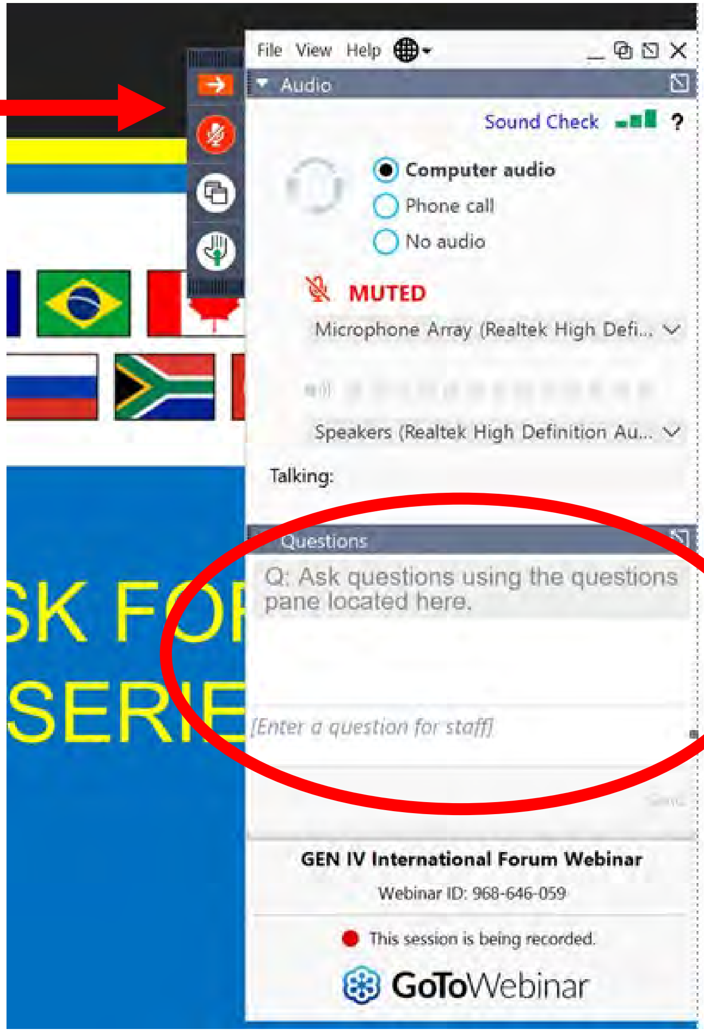

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PNNL-SA-201278

Meet the Presenters

Dr. Amanda Lines is a Chief Scientist at Pacific Northwest National Laboratory with experience in the design and deployment of on-line monitoring and sensor technology. Dr. Lines graduated from Washington State University with her Ph.D. in analytical chemistry after earning her undergraduate degrees in chemistry and chemical engineering from Purdue University. Her work primarily focusses on the development of optical sensors for highly harsh environments, such as those common to nuclear materials processing, as well as the application of chemical data science tools to enable advanced, automated data output.

Dr. Samuel A. Bryan is a Laboratory Fellow in Nuclear Chemistry and Engineering at the Pacific Northwest National Laboratory (PNNL). Dr. Bryan joined PNNL in 1990, and has over 35 years' experience in optical spectroscopy, electrochemistry, and separations science. Bryan's research interests involve the design and development of spectroscopic and spectroelectrochemical sensors for the measurement of actinides, lanthanides, fission products and transition metal complexes in aqueous and molten salt media. He also serves as an Adjoint Faculty member in the Department of Chemistry at Washington State University.

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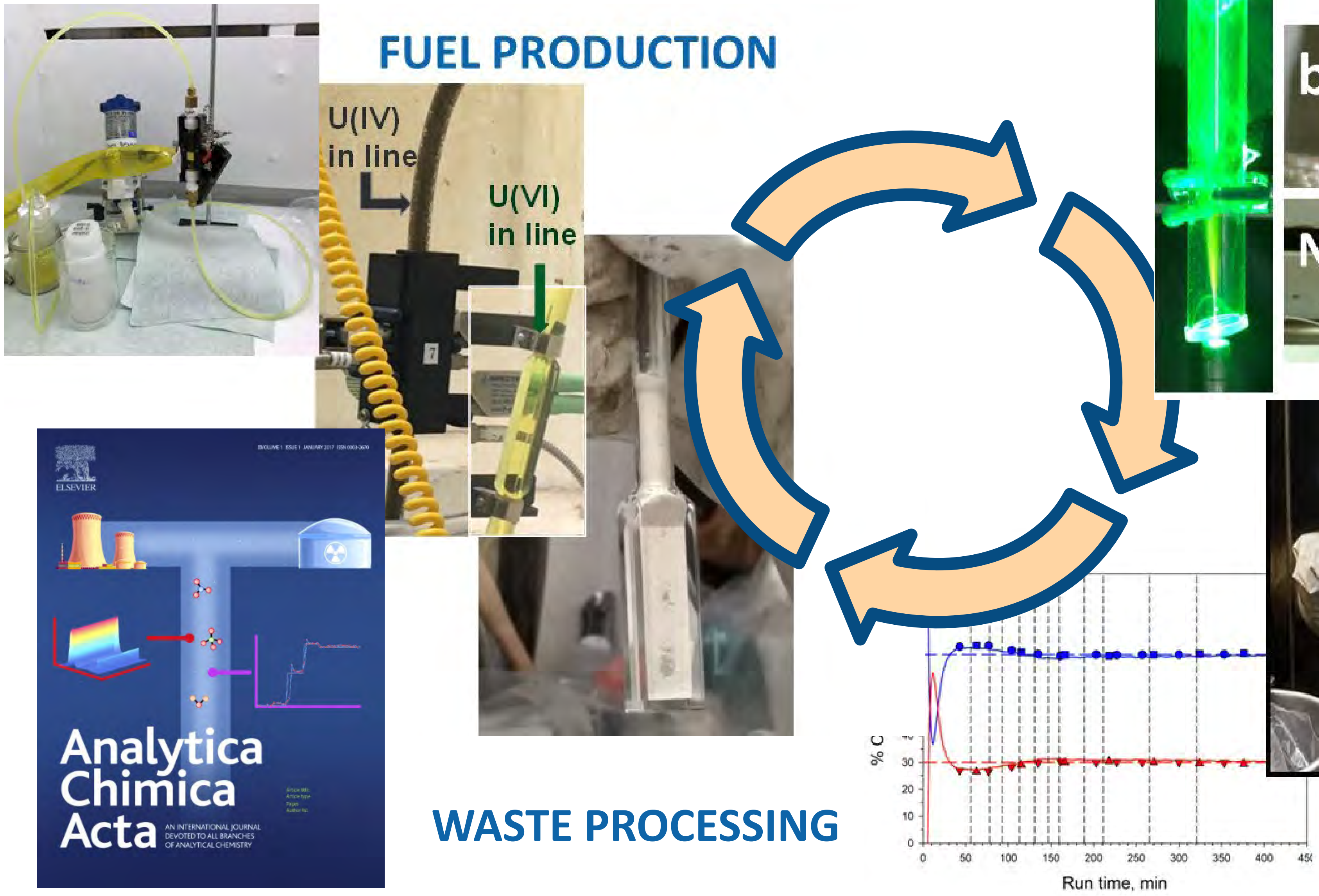
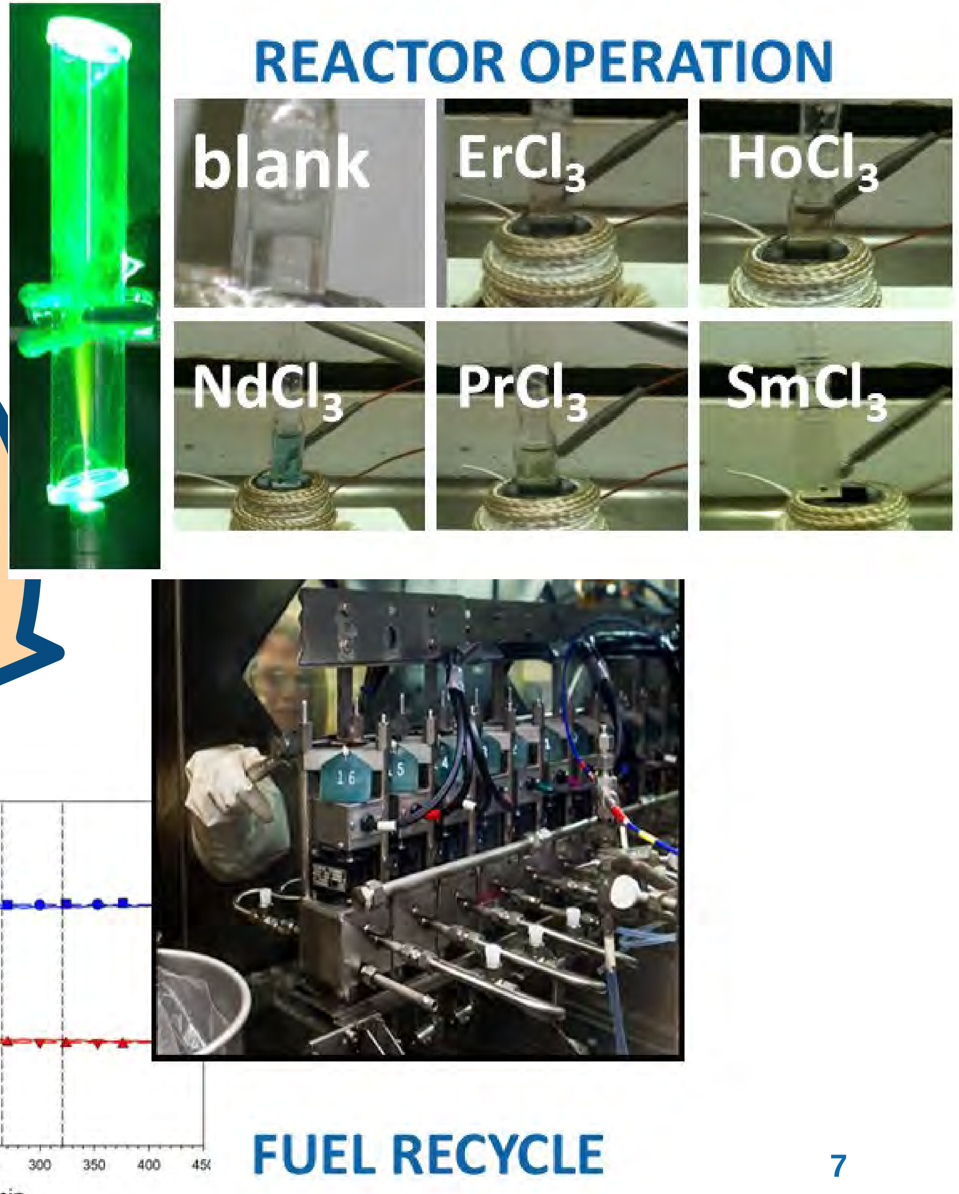
The Benefits of *In Situ*, Real-time Monitoring

- Gaining unapparelled insight into fundamentals
- Improving the route of designing and optimizing new processes
- Enabling informed scale up
- Supporting better, faster, safer, and more cost-effective deployment of nuclear material processing

How is the Fuel Cycle Benefited?

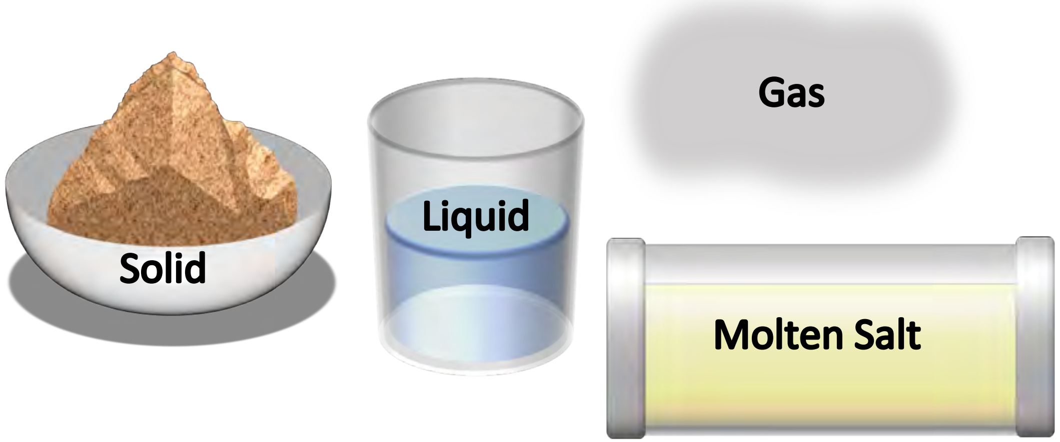




Many Tools and Sensors are Available: Focus on Optical Spectroscopy for Chemical Composition Analysis

- Provides chemical information
  - Identification and quantification
  - Oxidation state
    - Essential information for control of systems
  - Molecular and elemental species
    - Essential information to control system behavior
- Highly mature technology
- Simplistic integration
- Versatile

System matrix



System scale

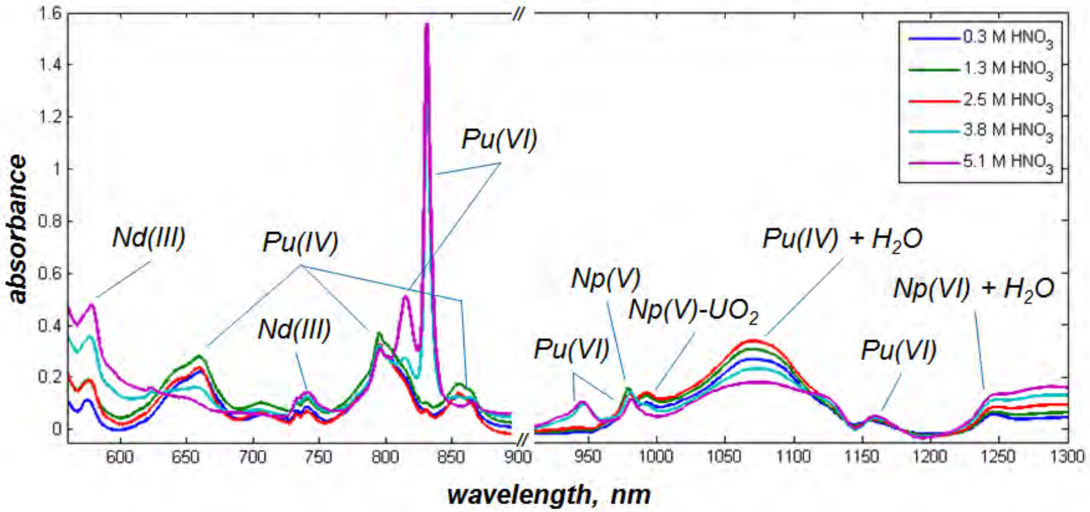
Optical spectroscopy comes in many forms, allowing for analysis of a huge range of chemical targets

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

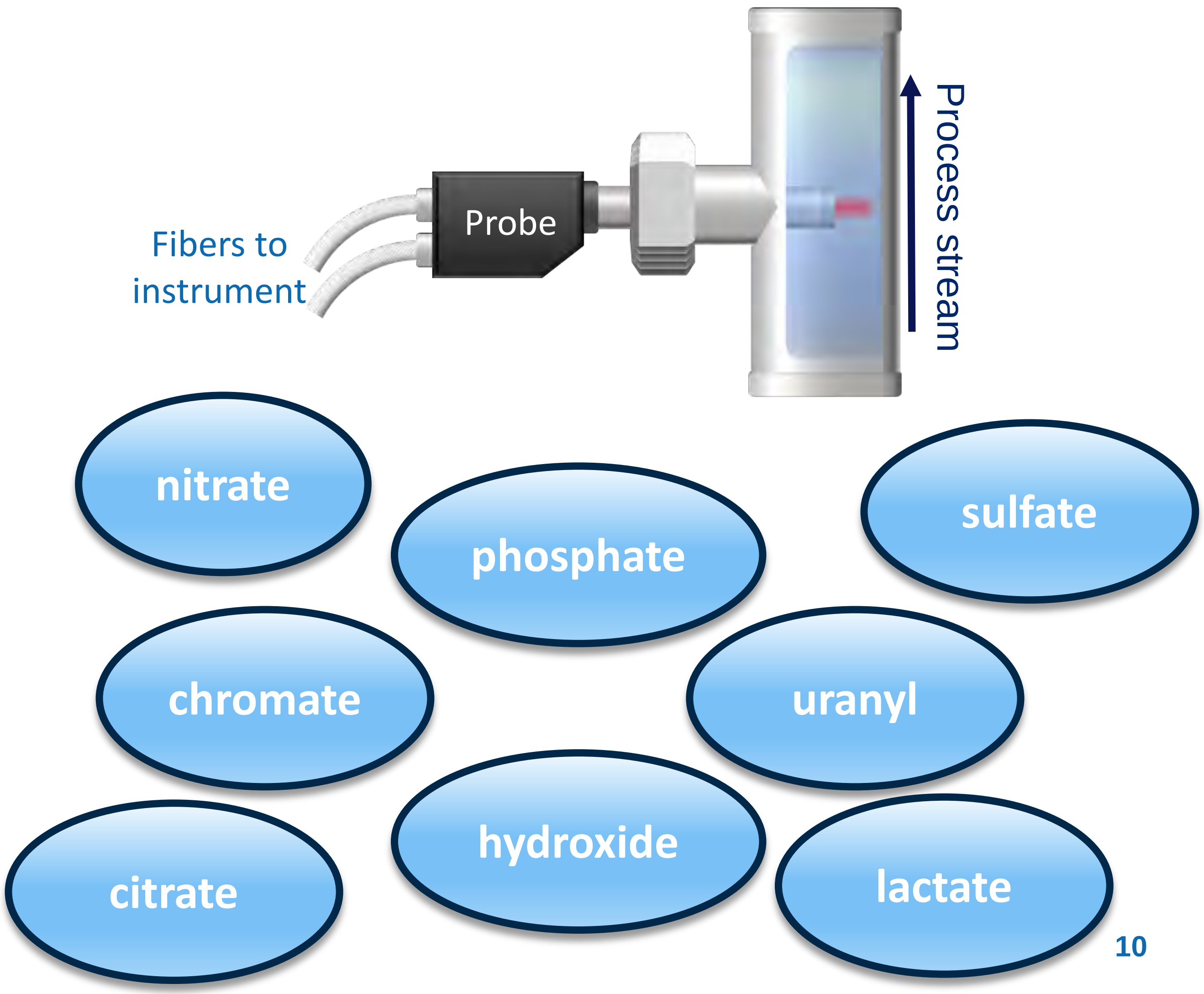
- **FTIR**
  - Organic complexants
- **Light scatter**
  - turbidity
- **Optical density**
  - Formation of complexes

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

The Greatest Strength of Optical Spectroscopy

- A wide range of optical tools are available, and can provide pathways to characterize almost any analytical target

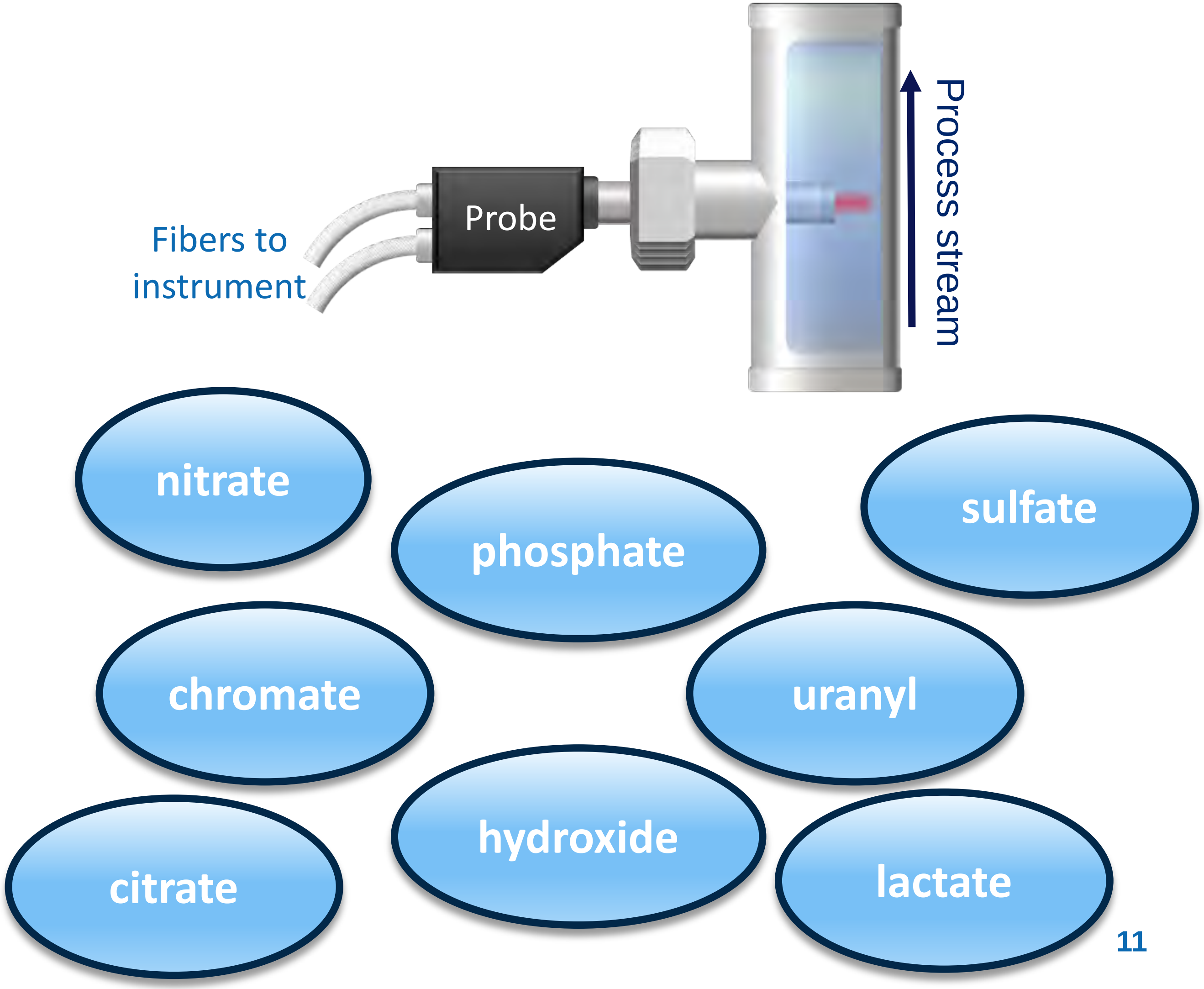
- For examples such as Raman and UV-vis absorbance, numerous metal, organic, etc. species can be characterized with a single in-process probe



The Greatest Weakness of Optical Spectroscopy?

- A wide range of optical tools are available, and can provide pathways to characterize almost any analytical target

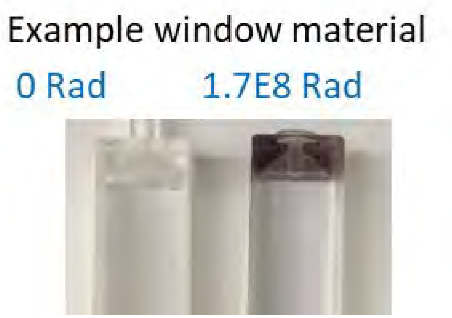
- For examples such as Raman and UV-vis absorbance, numerous metal, organic, etc. species can be characterized with a single in-process probe

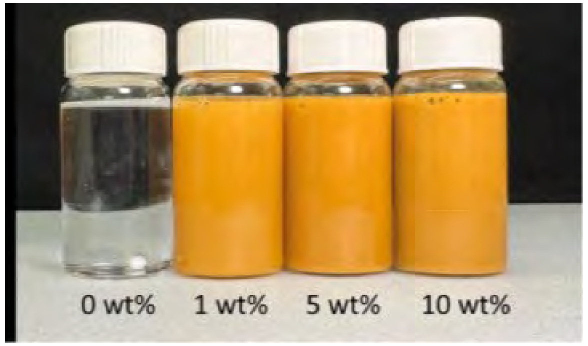


Is Chemical Complexity the Only Challenge We Face in Applications to the Nuclear Fuel Cycle?

Environments that damage sensors

- Highly corrosive or chemically destructive environments
- High temperatures (molten salts)
- High radiation



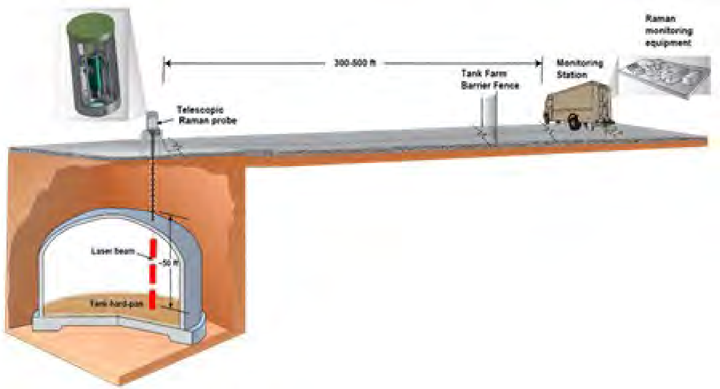


Chemistry or process conditions that complicate analysis

- Variable turbidity
- Highly sensitive matrix effects (e.g., speciation in variable pH processes)
- Confounded signals

Real processes where frequent calibrations or probe maintenance is not realistic

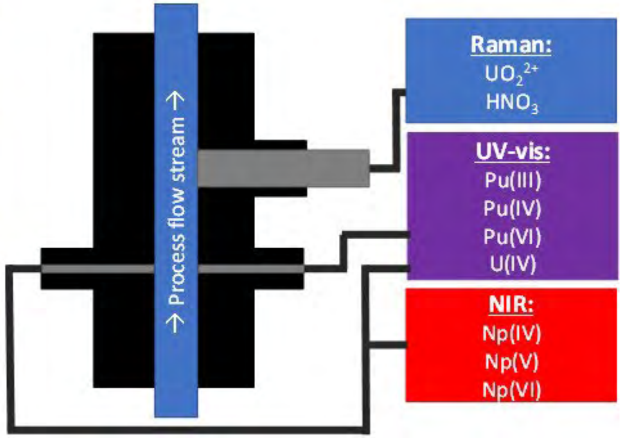
- Processes that cannot be accessed due to hazards



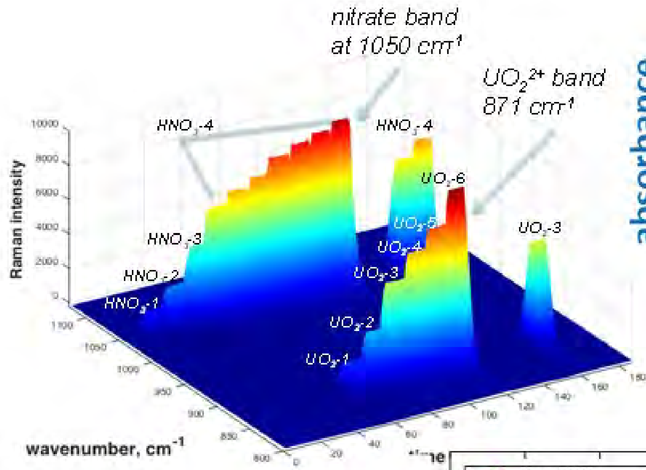
The Two Prongs of Focus

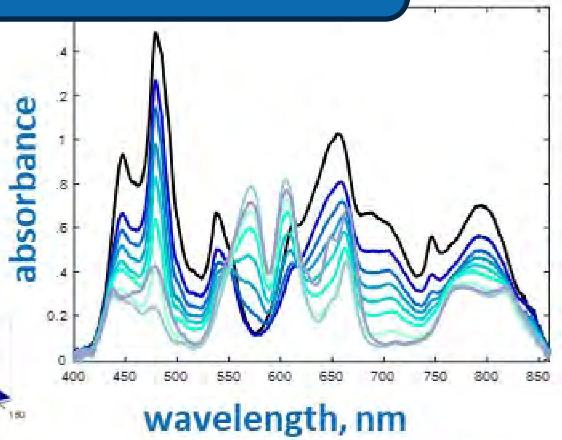
Sensor Hardening and Design

405 nm 532 nm 671 nm



Making Sensors Smart





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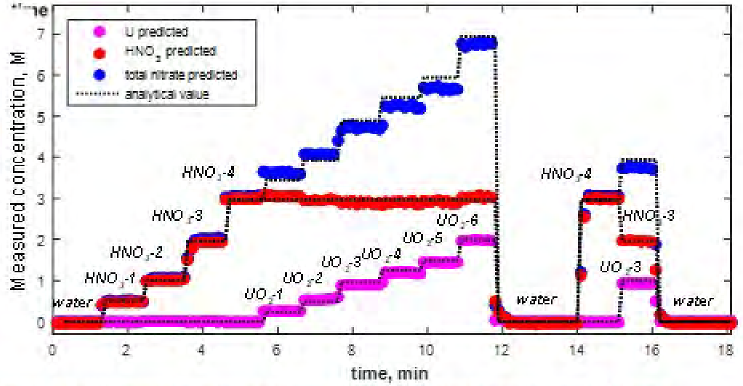

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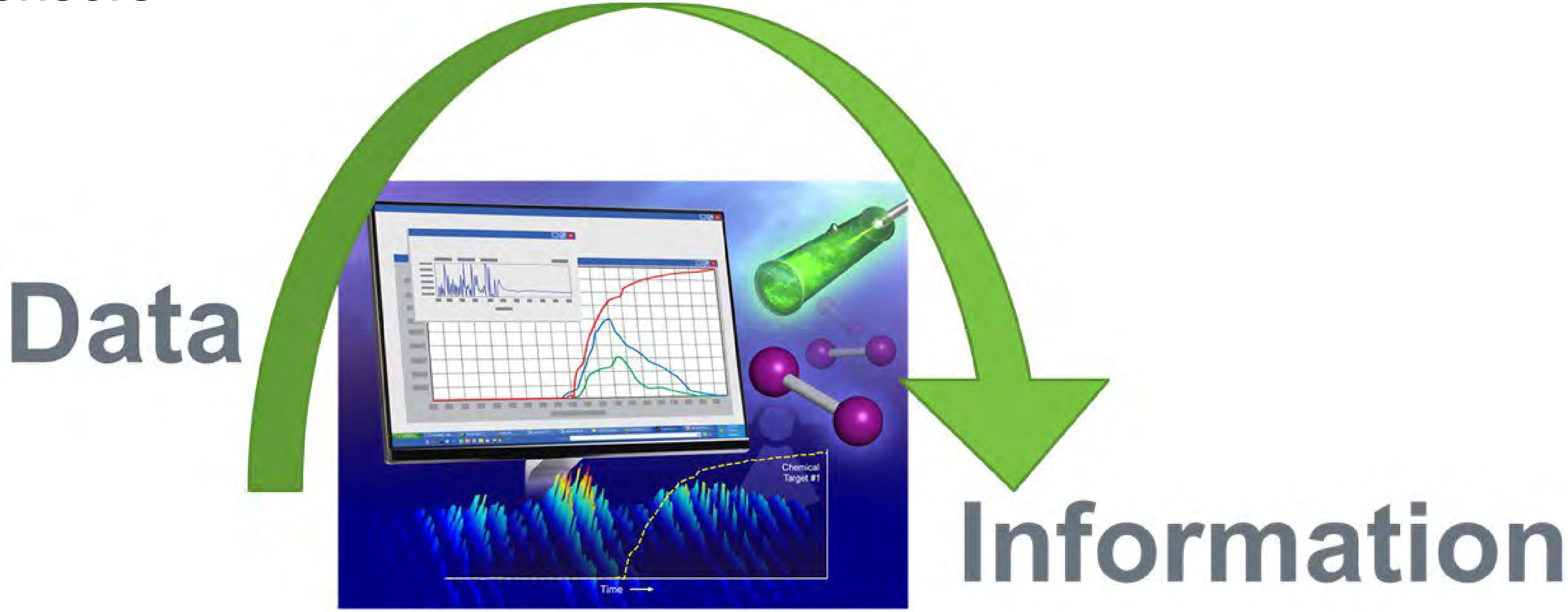
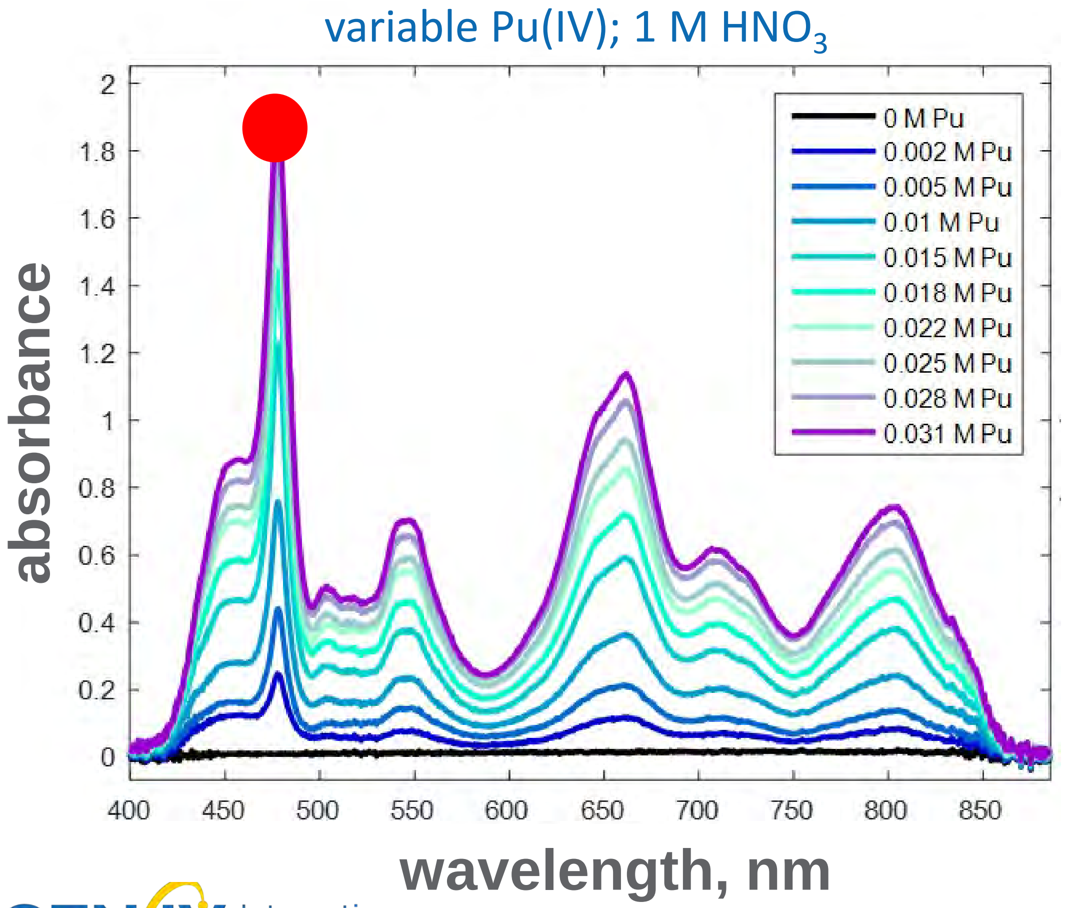
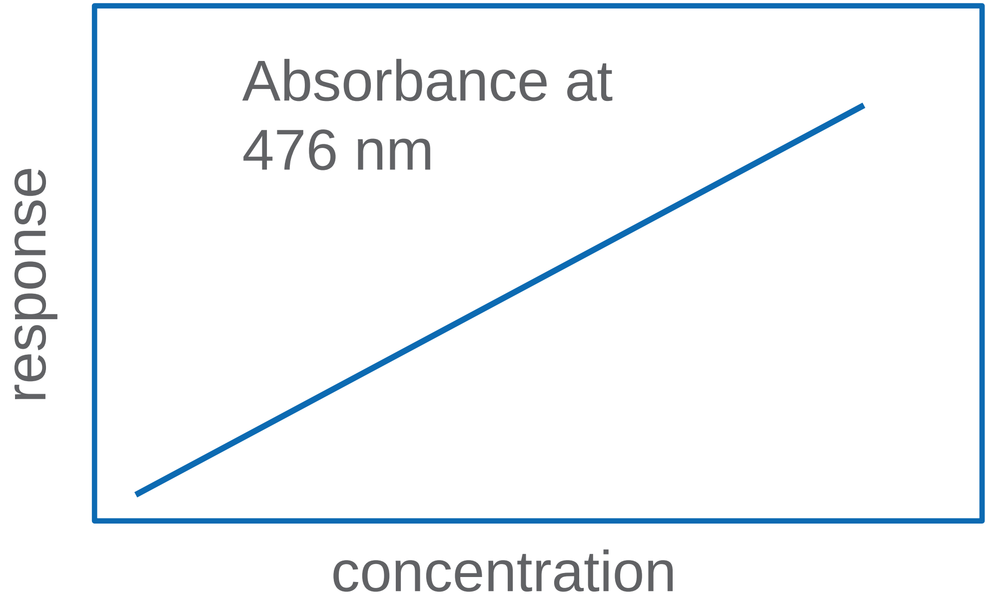
Why We Need Advanced Tools for Data Analysis

Integrating advanced tools for spectral analysis improves not only accuracy, but also speed of obtaining results, BUT most importantly expands the applicability of our sensors



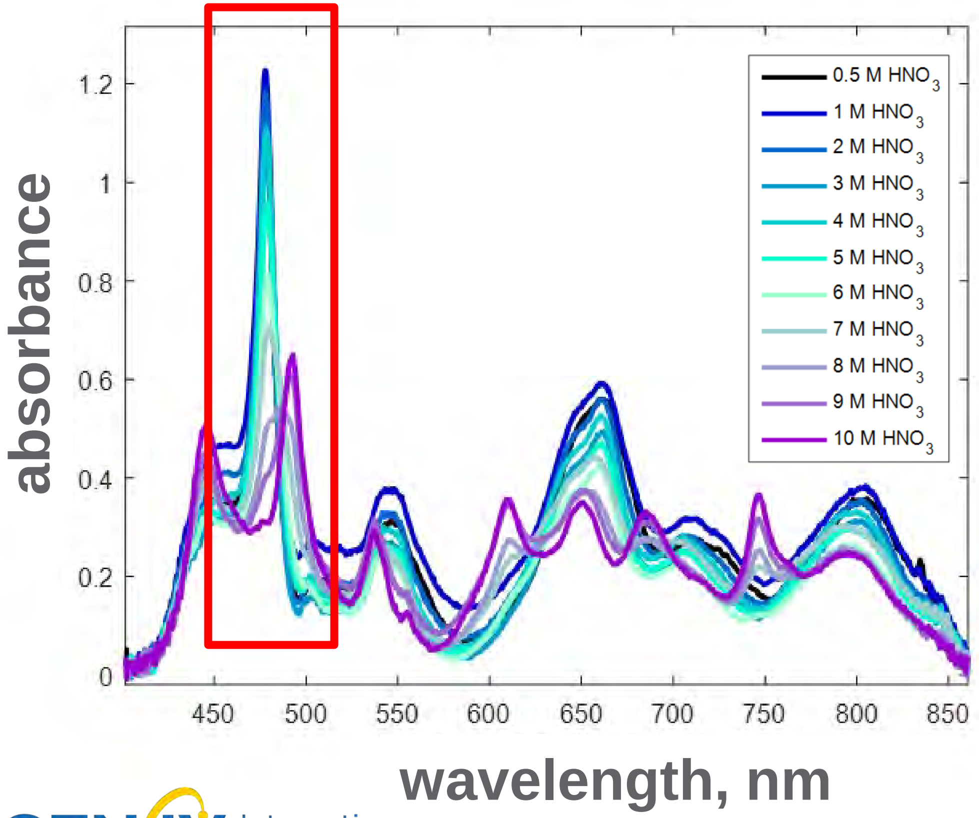
How Chemometric Modeling Works: Graphical Example of Chemical Data Science Application

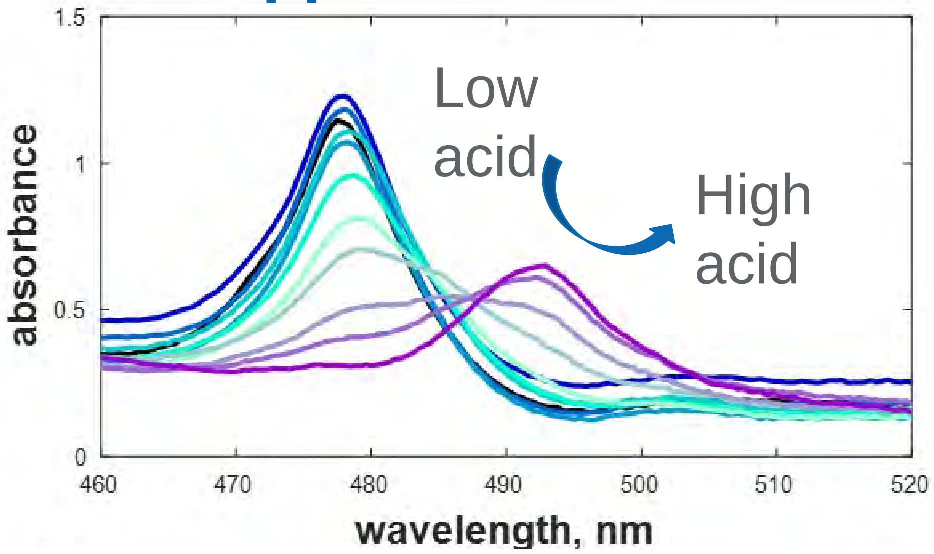




How Chemometric Modeling Works: Graphical Example of Chemical Data Science Application

15 mM Pu(IV); variable M HNO_3

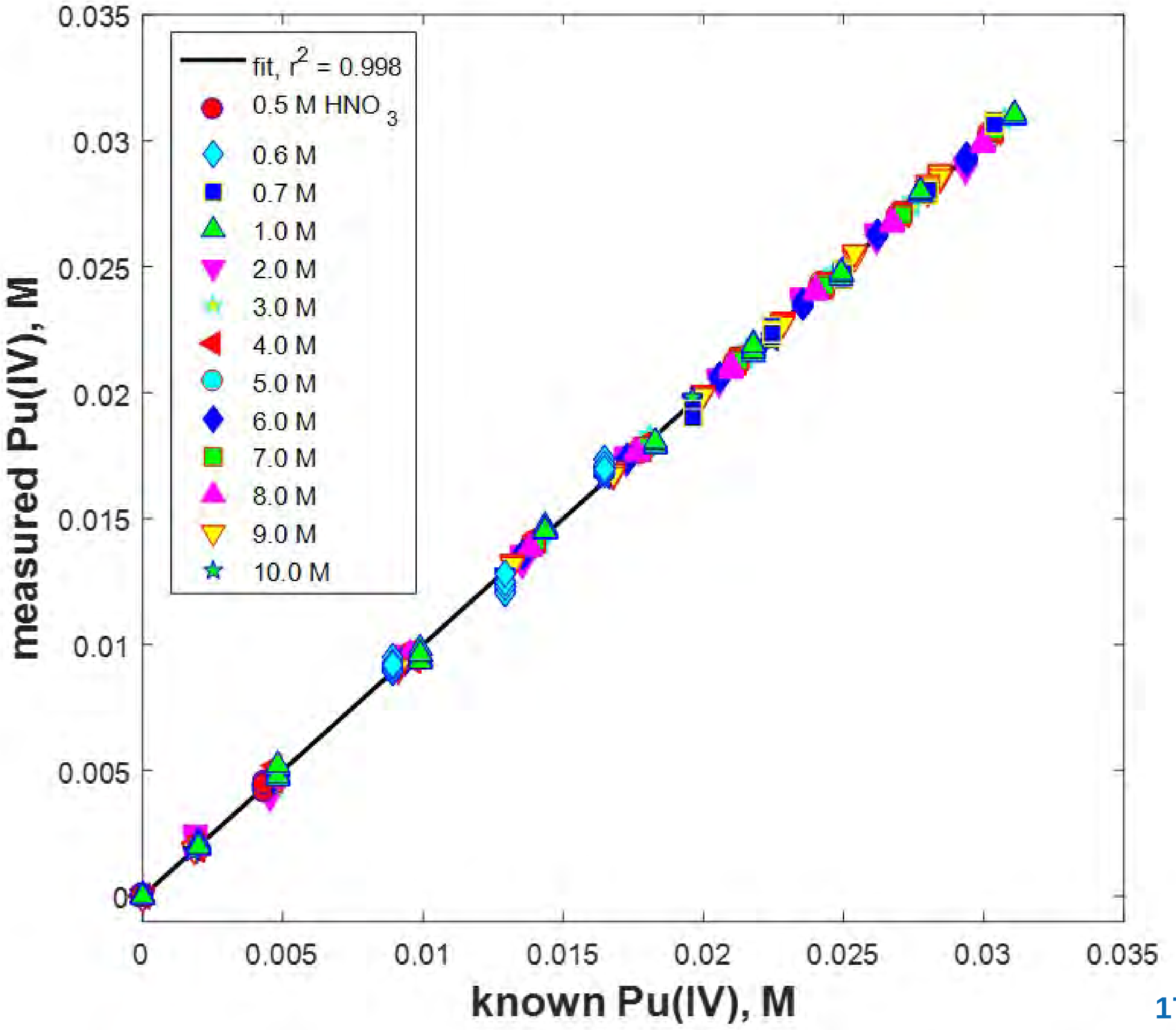




How Chemometric Modeling Works: Graphical Example of Chemical Data Science Application

- Highly accurate quantification despite wide range in Pu and HNO_3 concentrations

- Multiple applications beyond quantification as shown here



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Exploring Challenging Applications and Demonstrations: both in sensor design and analytical tool development

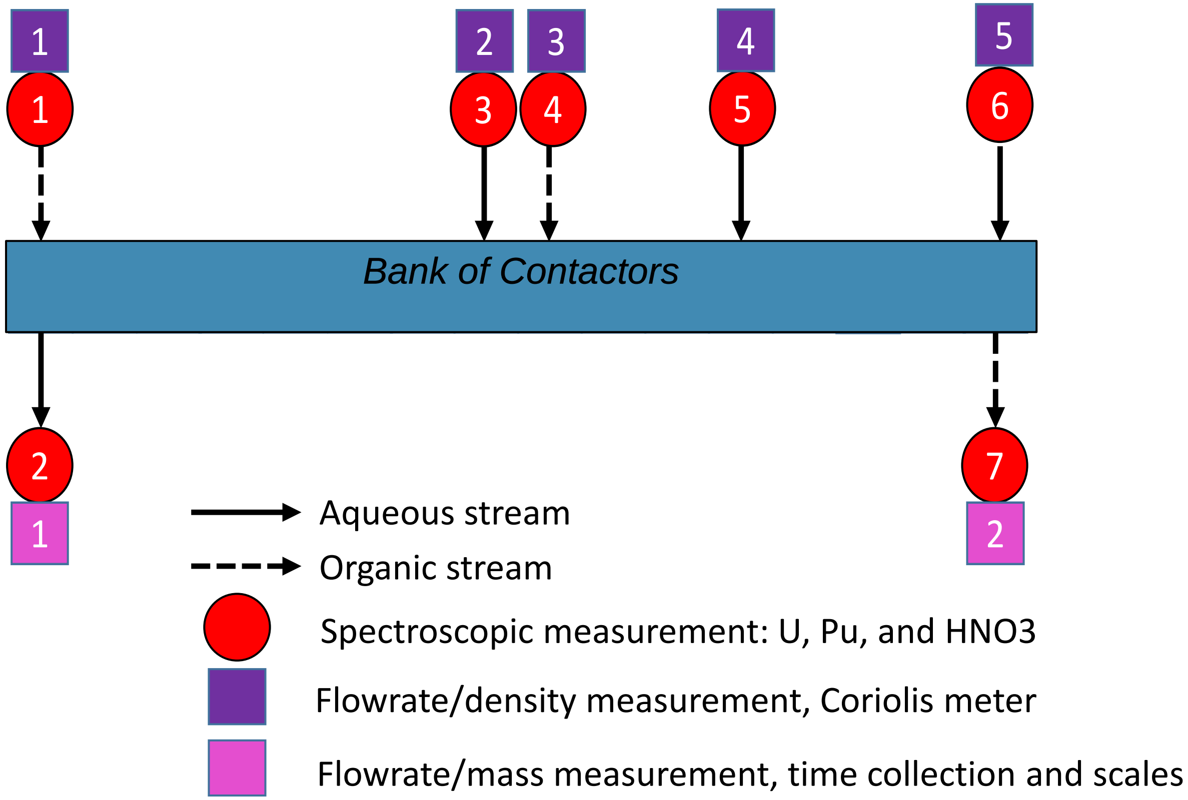
- Highly complex chemical compositions (many interferents to optical fingerprints or other matrix effects)

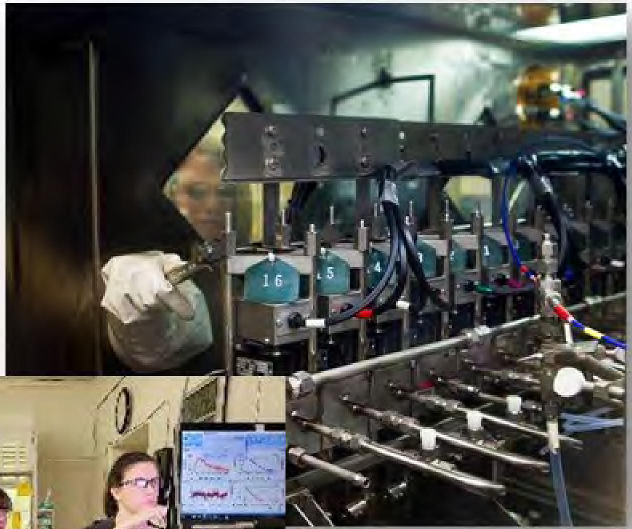
- Extremely harsh environments that impact sensors and therefore impact optical outputs

- Highly variable processes that require robust approaches to data analysis

- Demonstrations of real-time process control (manual and automated)

CoDCon Application: Used Nuclear Fuel Recycle

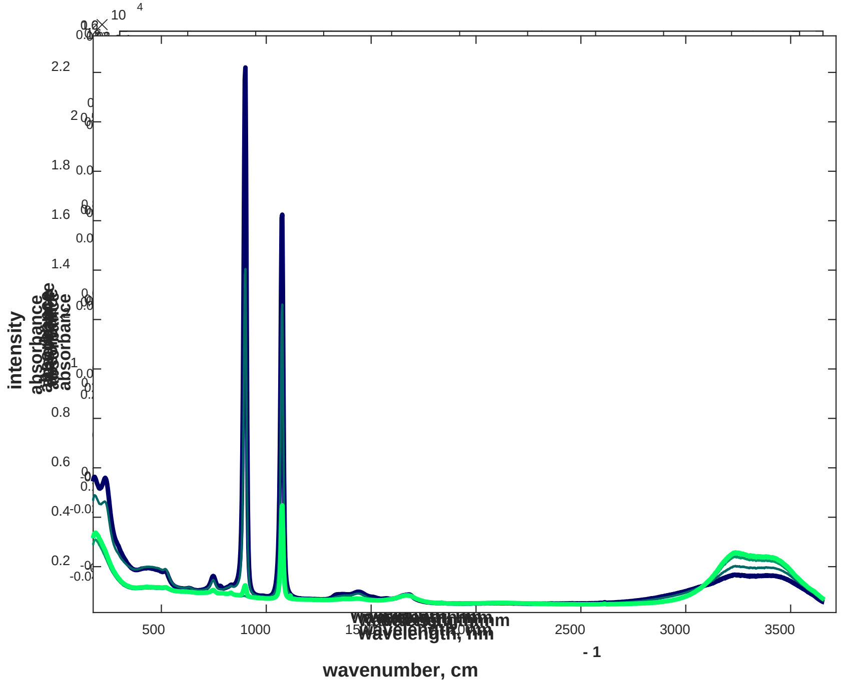




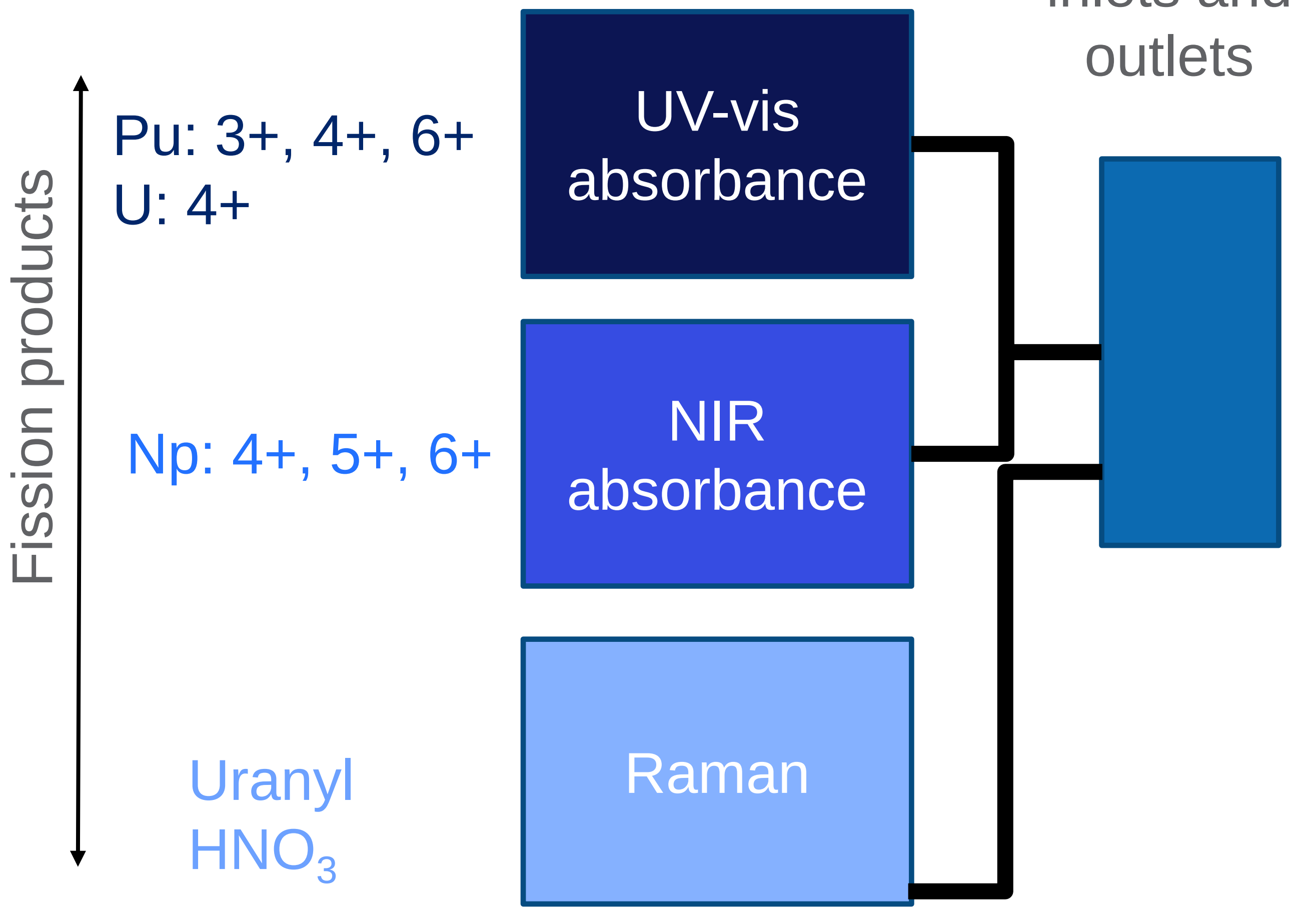
Lumetta, G. J.; Allred, J. R.; Bryan, S. A.; Hall, G. B.; Levitskaia, T. G.; Lines, A. M.; Sinkov, S. I., Simulant testing of a co-decontamination (CoDCon) flowsheet for a product with a controlled uranium-to-plutonium ratio. Separ Sci Technol 2019, 54 (12), 1977-1984

CoDCon Application: Used Nuclear Fuel Recycle

Raman



Flow cell installed on all inlets and outlets



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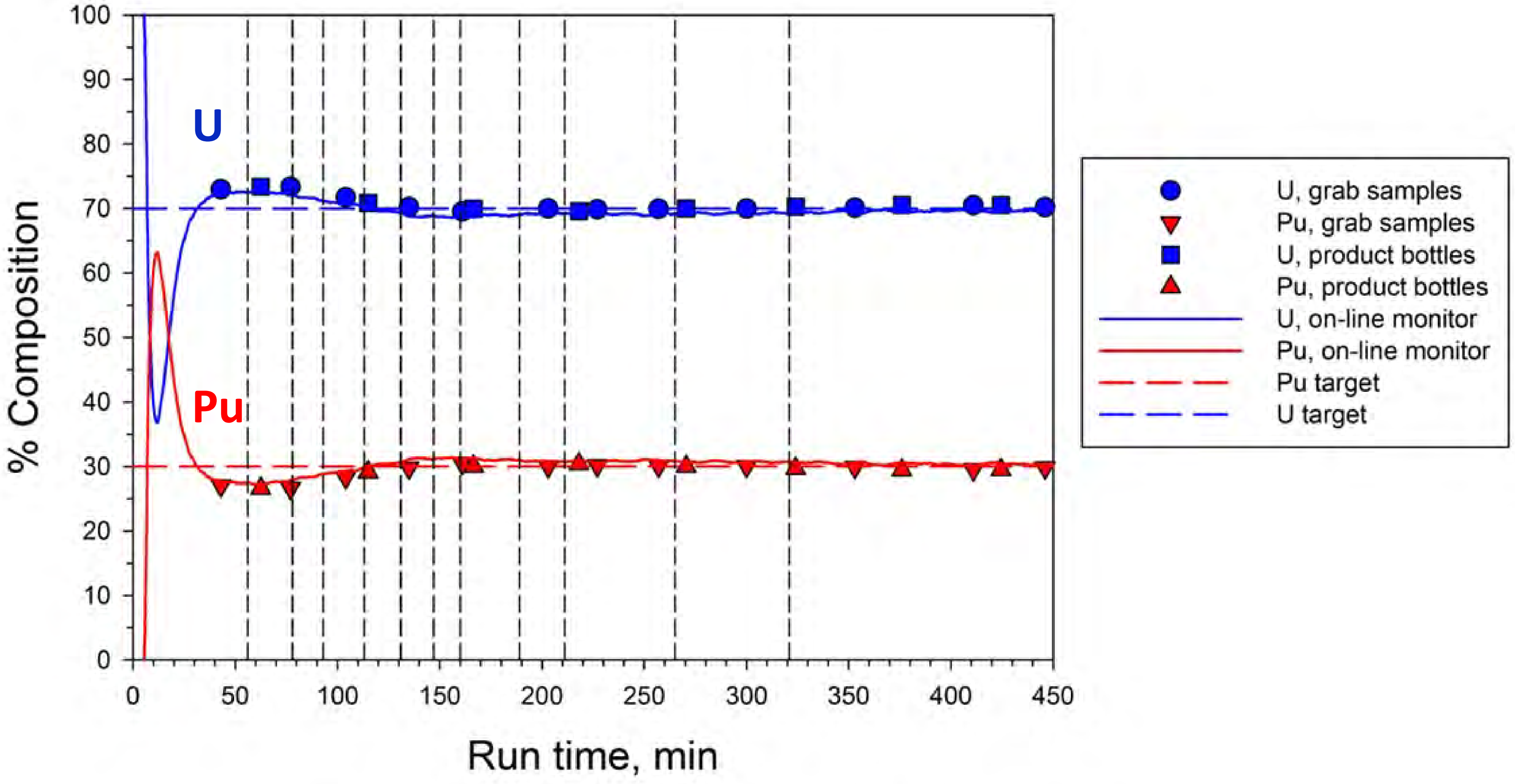
CoDCon Application:
Used Nuclear Fuel Recycle



Hanford waste applications

- Legacy waste clean-up efforts present some of the most challenging process conditions
  - Often not a great record of what is in the waste
  - Conditions can be very harsh

- For sites such as Hanford, this is particularly true
  - Millions of gallons of radioactive waste that was produced during plutonium production and recovery
  - Chemically complex
  - Highly turbid

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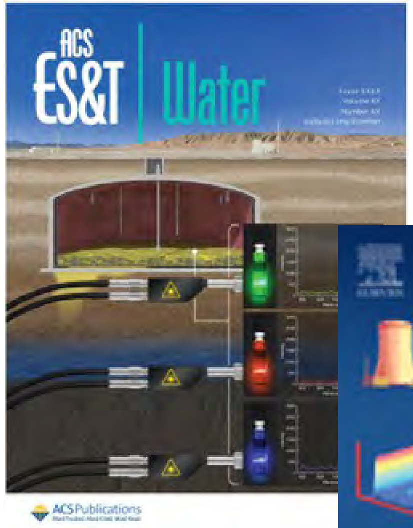
Hanford waste applications: past demonstrations

- Hanford tank salt cake retrieval (2002-2005)
  - Flow measurements, up to 40 gal/min
  - 8 analytes by Raman: NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}, AlO_2^-, CO_3^{2-}, CrO_4^{2-}, OH^-
- Pretreatment Engineering Platform (PEP-WTP) Project (2008-2009)
  - Discrete sample analysis (9 analytes by Raman, $C_2O_4^{2-}$ added)
  - Full QA/QC HASQARD compliant procedure
- Near-Tank Treatment System: Pilot Scale CSL Testing (2011)
  - Real-time monitoring during continuous sludge leaching (CSL) campaign February - April (~2.5 months)
  - Measured Al and OH^- in real-time during 2.5 mo. processing



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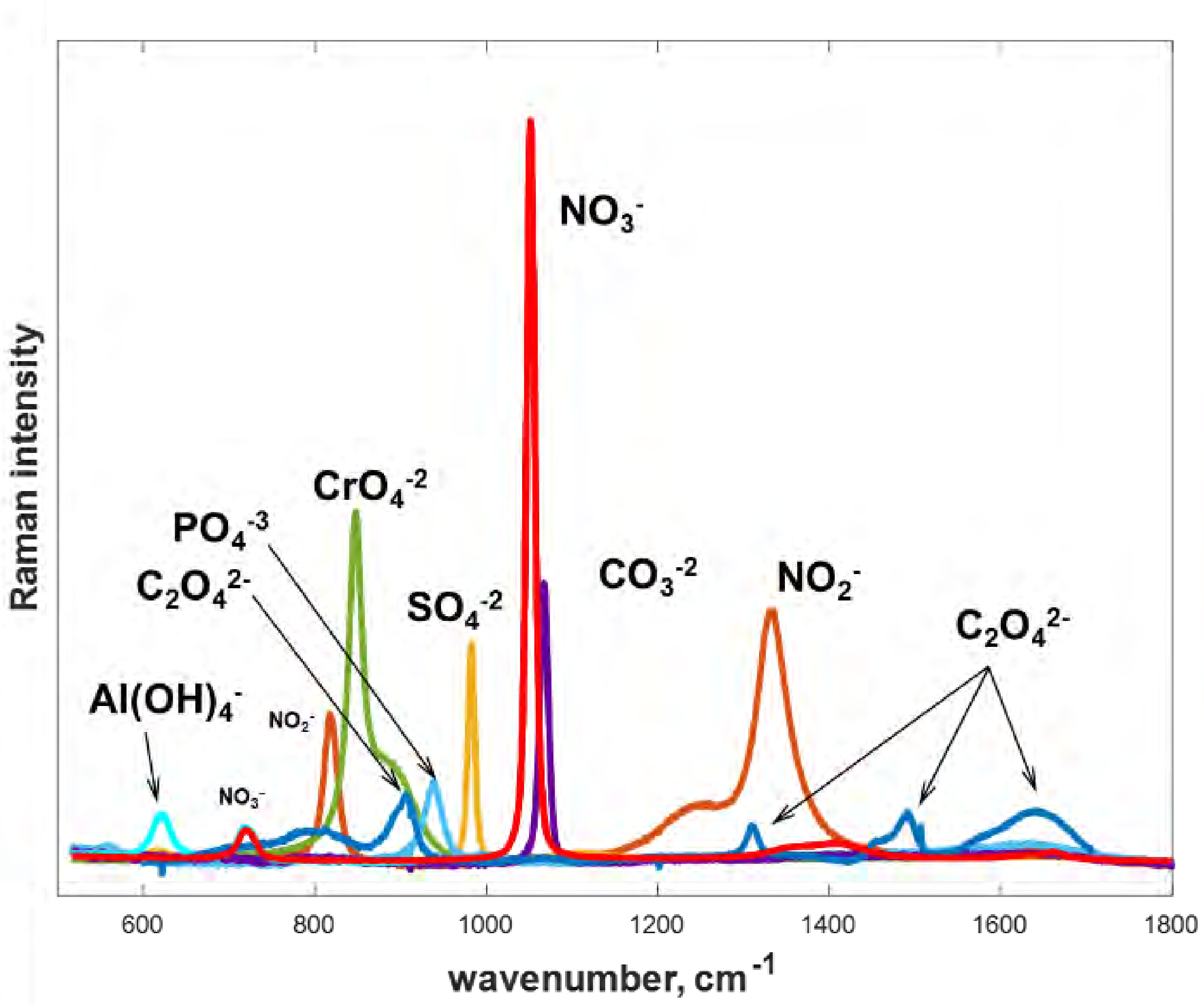
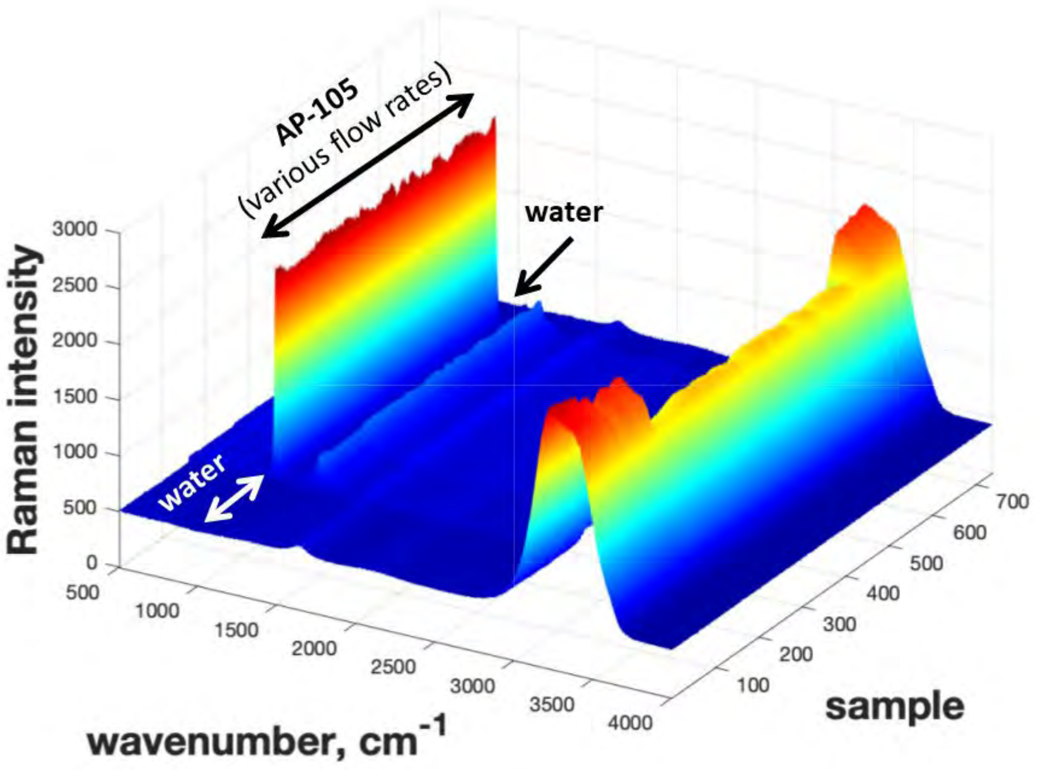
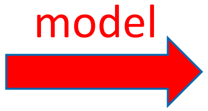
Hanford waste applications: Raman spectroscopy

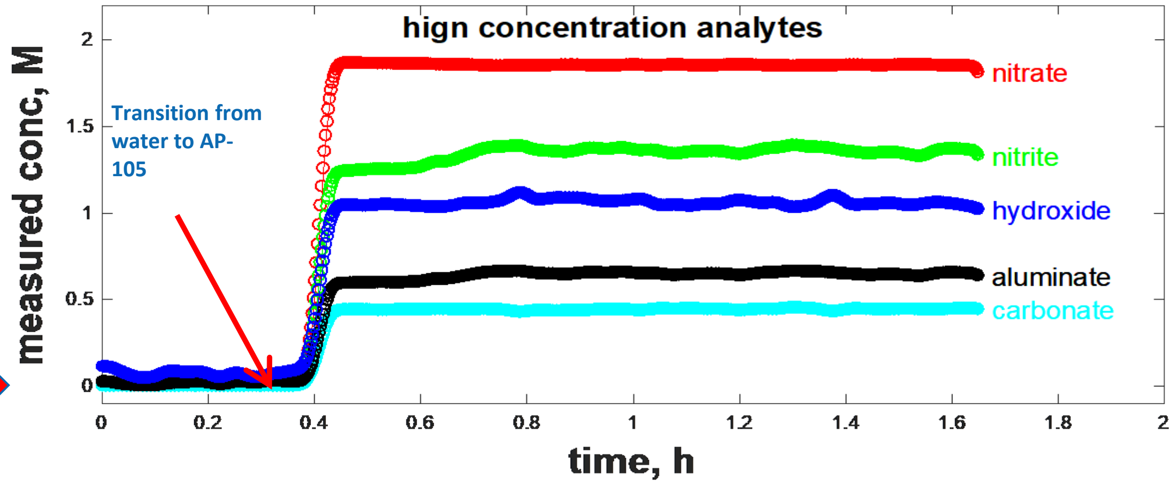
- Significant sampling burden on clean up sites, can on-line process monitoring help reduce this?
- Raman spectroscopy is an ideal tool for characterizing many of the polyatomic species within tank wastes
- This includes targets that represent process upset concerns, e.g., phosphate as well as a variety of species that are valuable to know when optimizing glass formulation

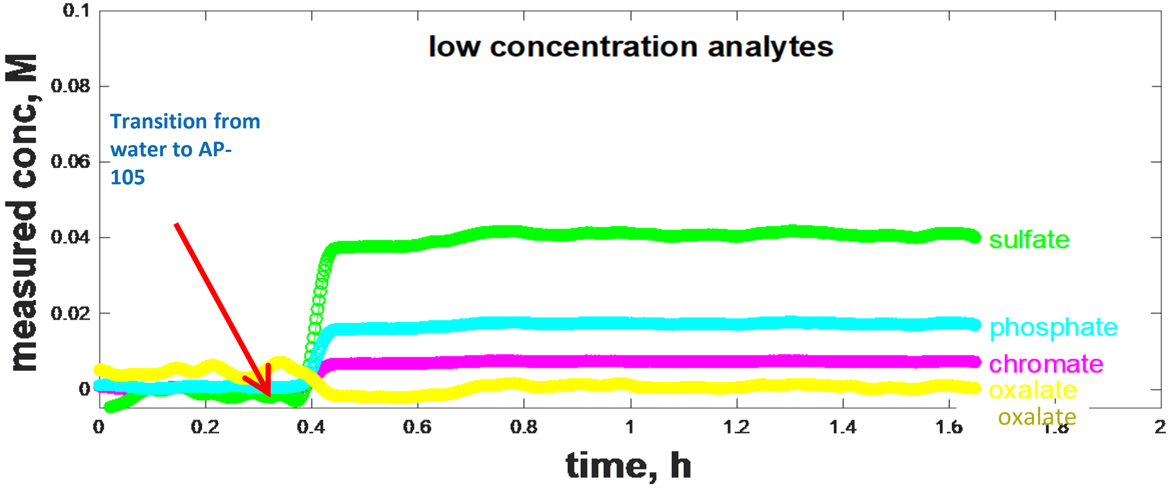


Hanford waste applications: actual waste demo





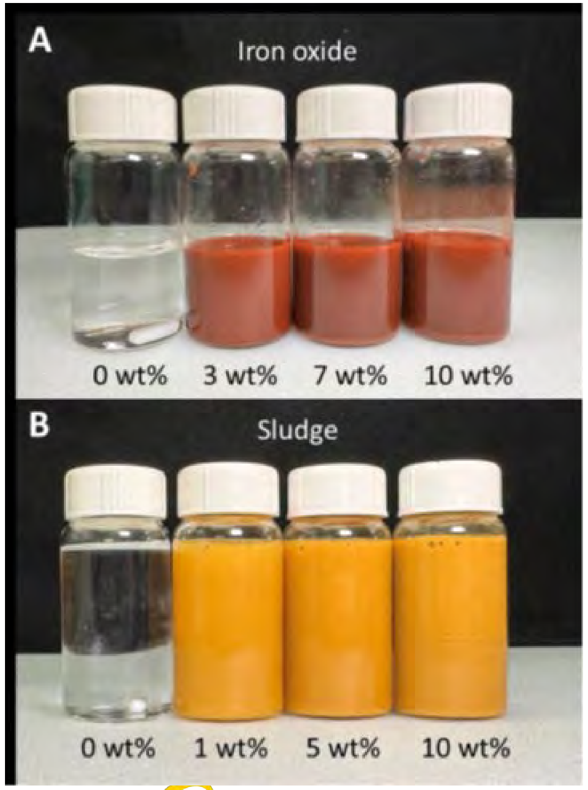


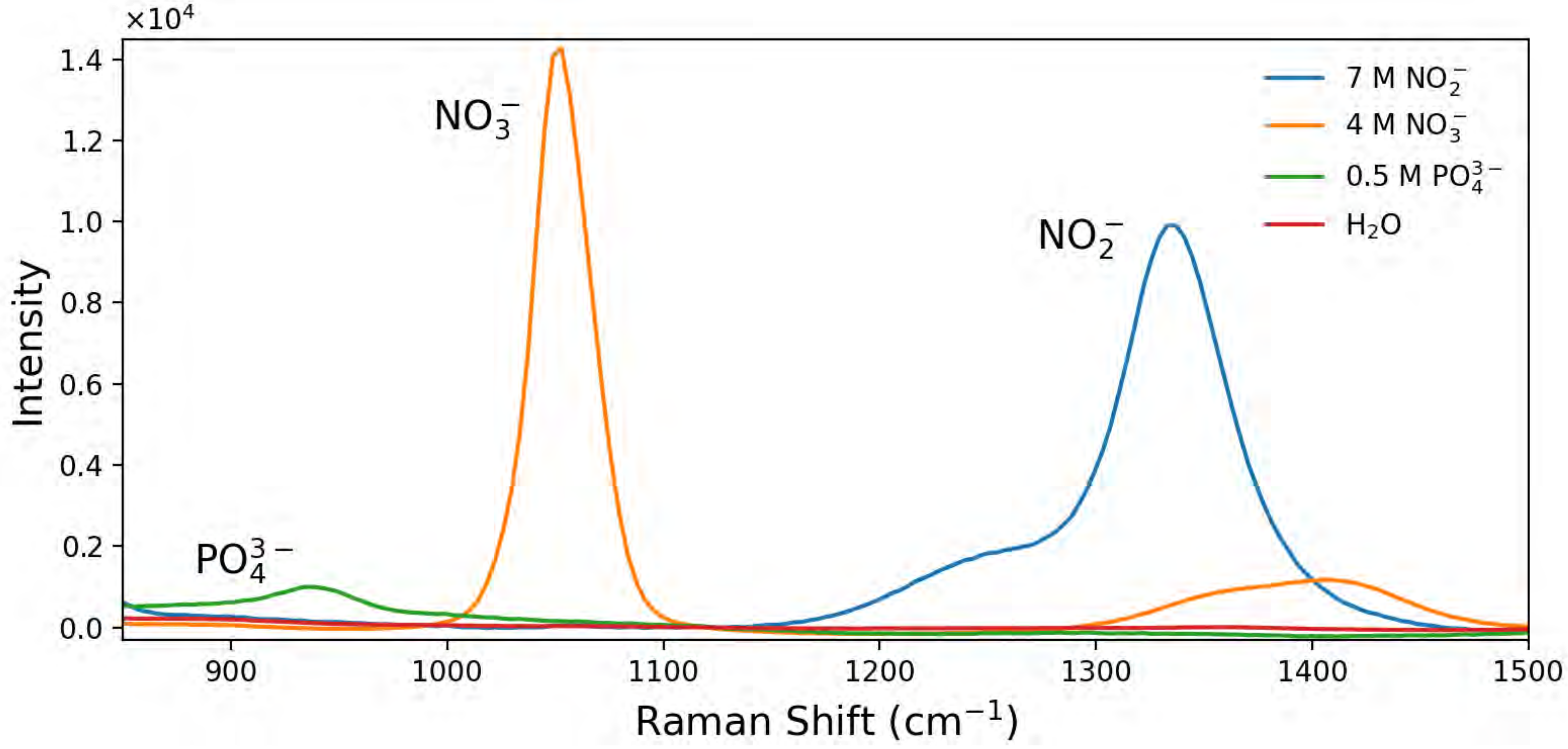


Ind. Eng. Chem. Res., 2019, 58, 47, 21194-21200

Hanford waste applications: high turbidity / solids

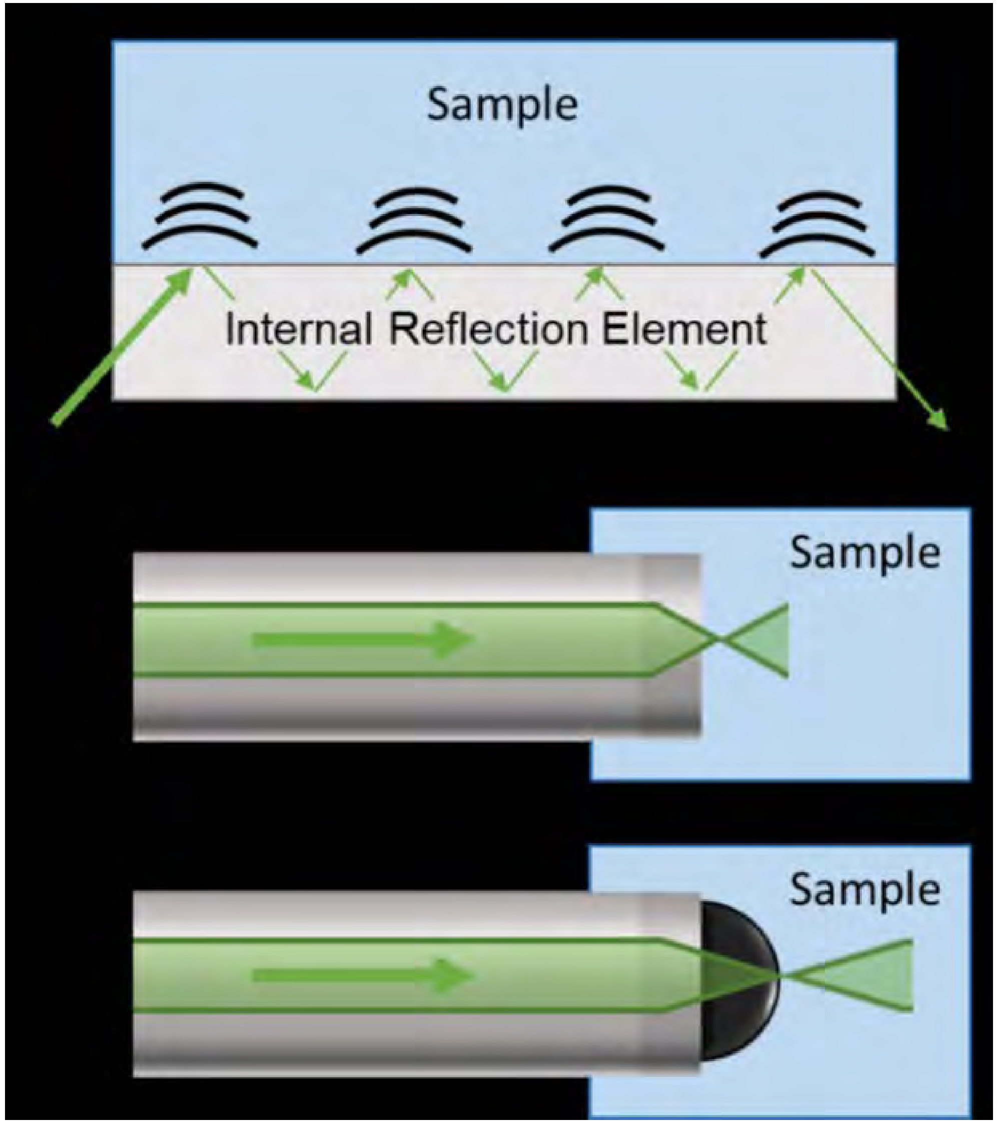
- Explore applications to three chemical targets of interest for process control purposes
- Vary turbidity of system using both iron oxide solids and a tank sludge simulant





Hanford waste applications

- Re-think probe design to better interrogate systems of high and variable turbidity
- Exploring very close focus probes that are available commercial off the shelf
- Ultimately tie data from optimized probes into chemical data science analysis to build highly robust tools for quantifying tank waste components

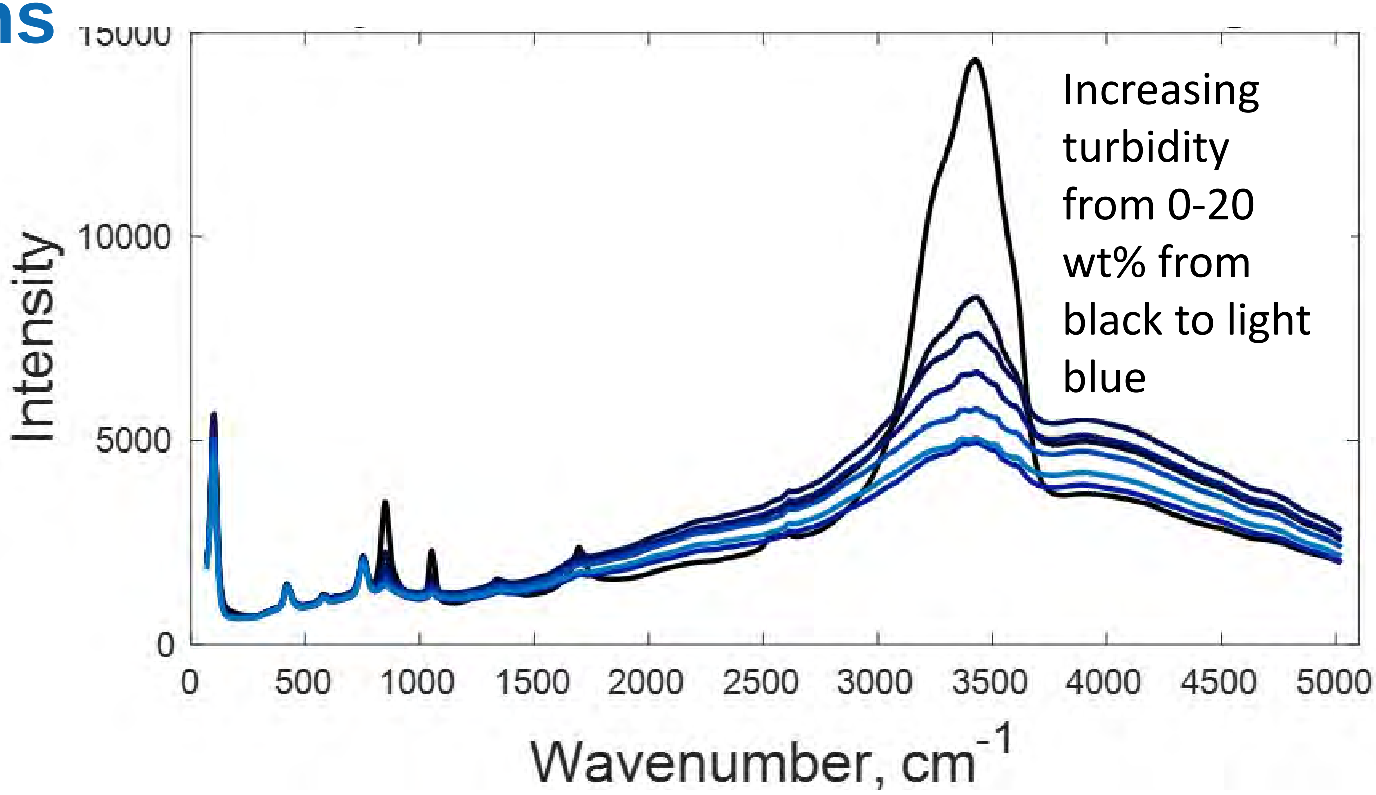


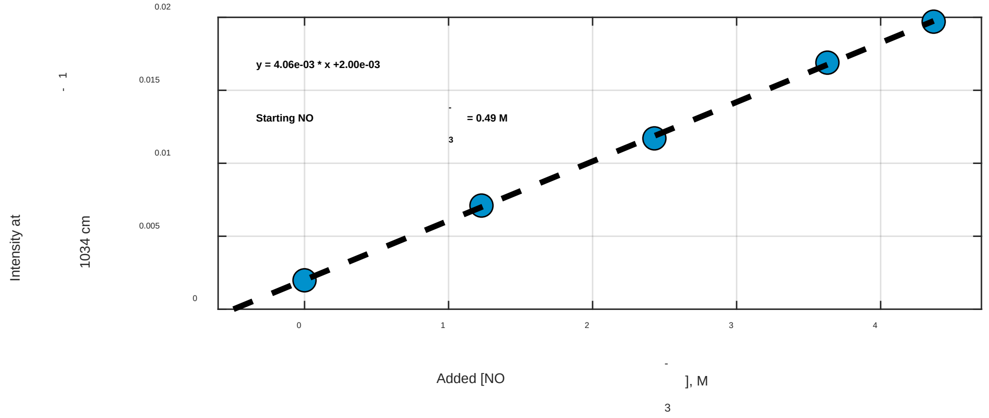
Hanford waste applications

- Explore application to high level waste simulant provided by SRNL

- Expanded range of study from 0-20wt% solids loading

- With data pre-processing, qualitative analysis of results suggests highly accurate models could be built





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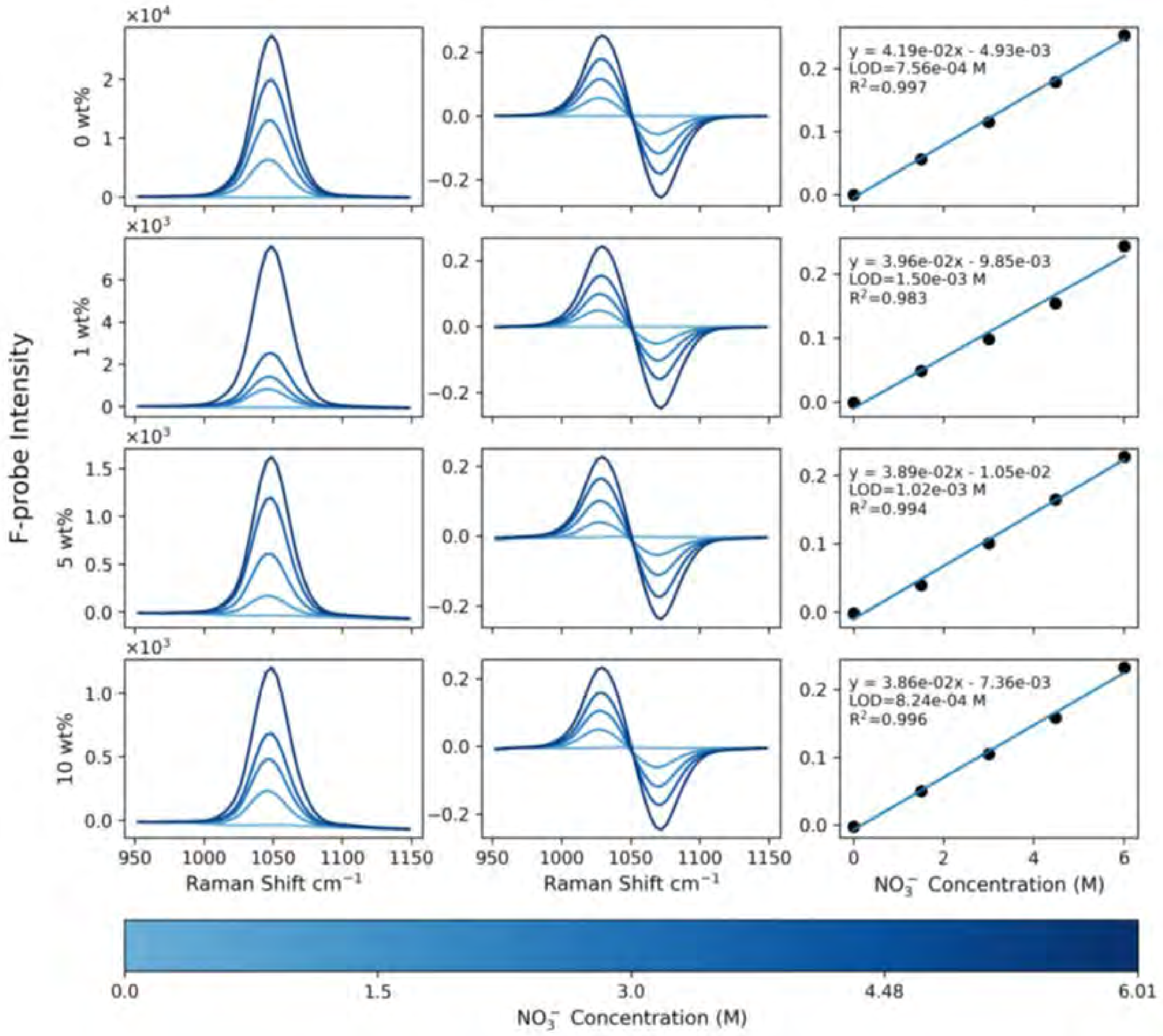
Hanford waste applications

- Utilizing data pre-processing, many impacts of turbidity can be mitigated
  - If using the correct probe/detector combo
- Here, even single variate results begin to look better after simple steps like normalization



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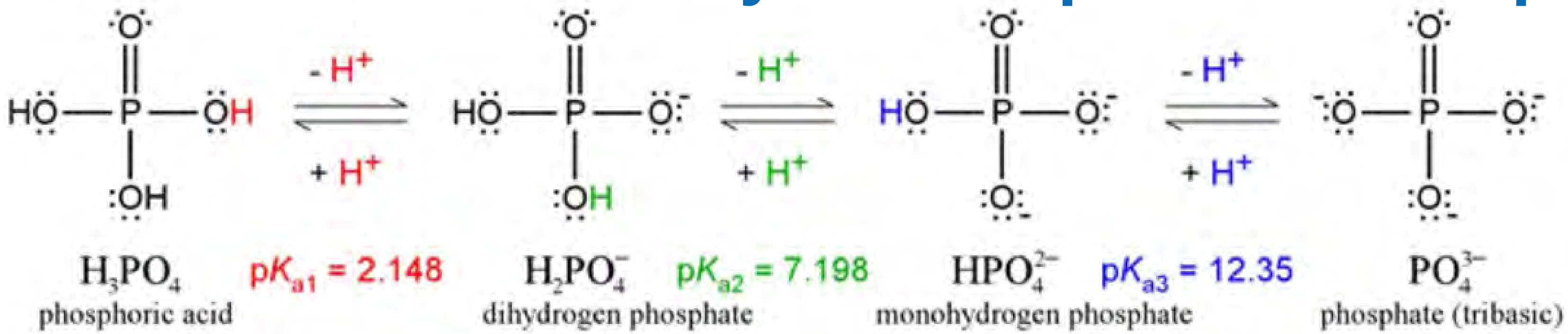
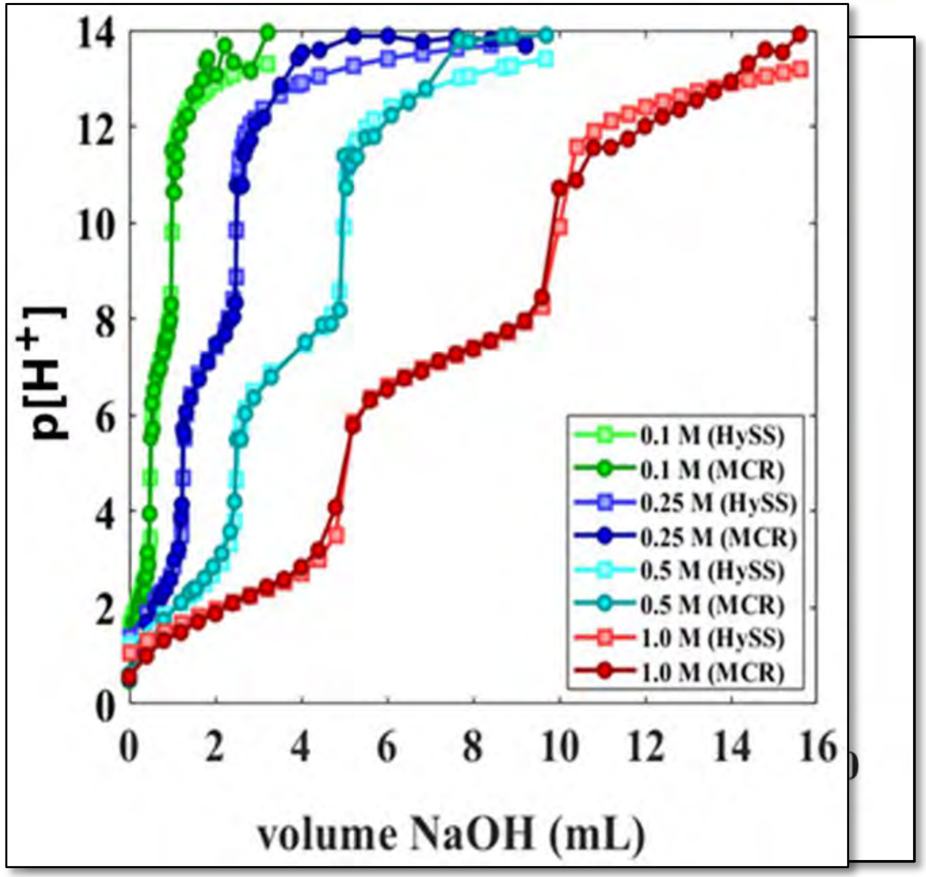
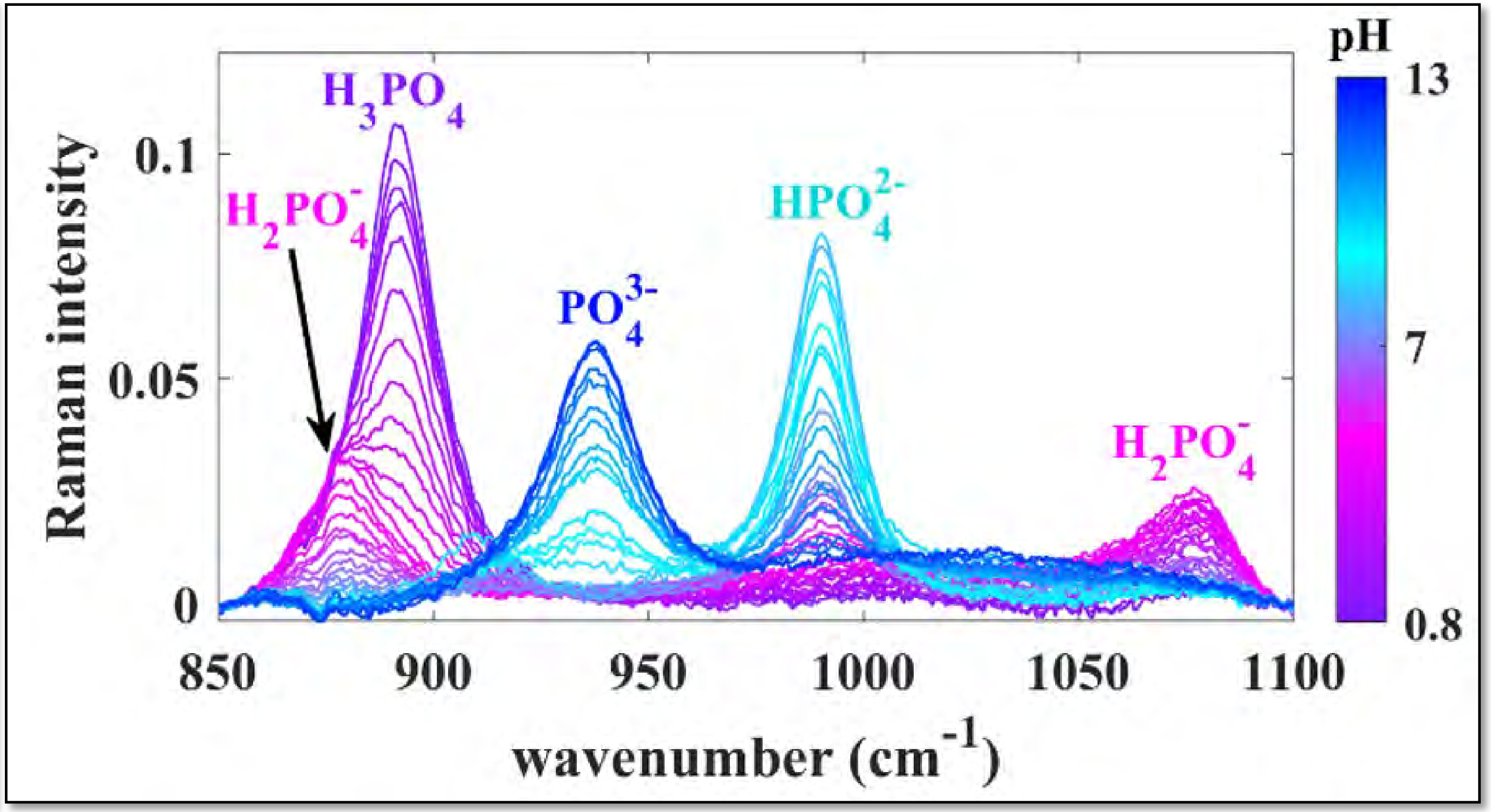
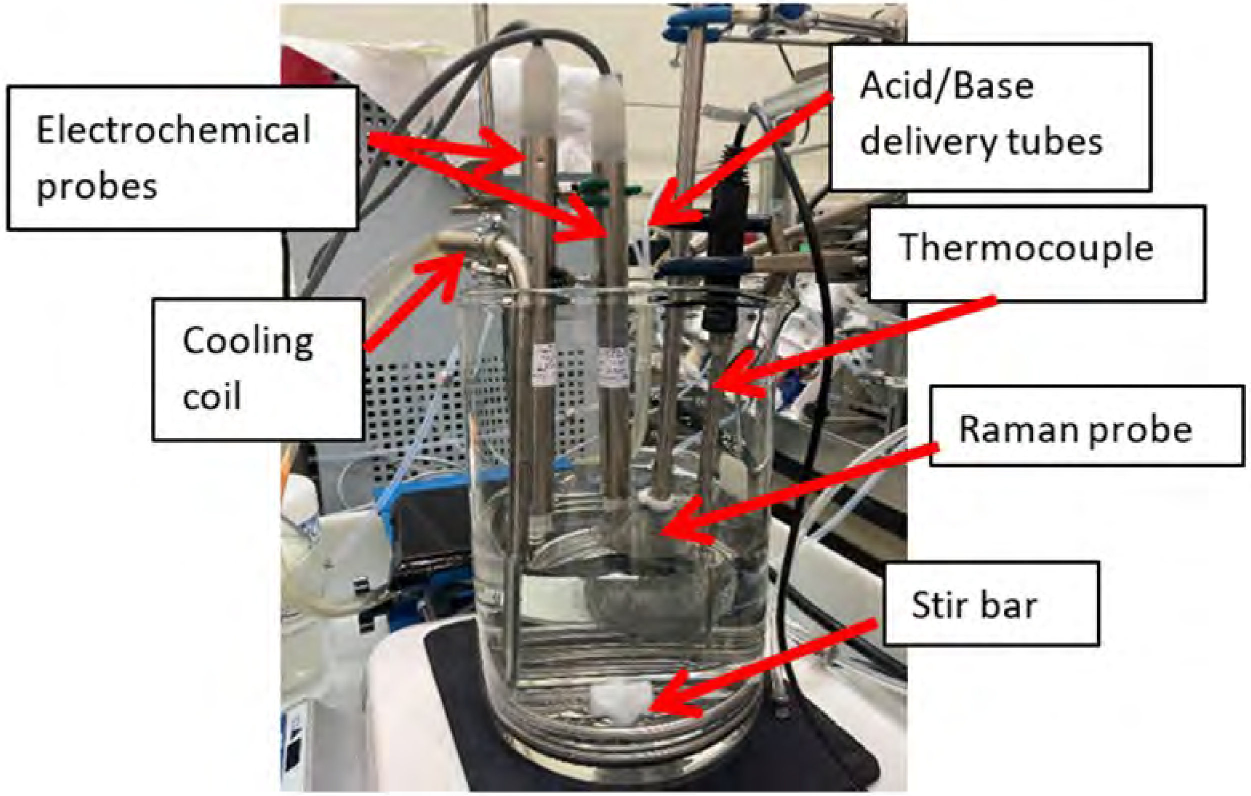
pH measurement: Raman Activity of Phosphoric Acid Species

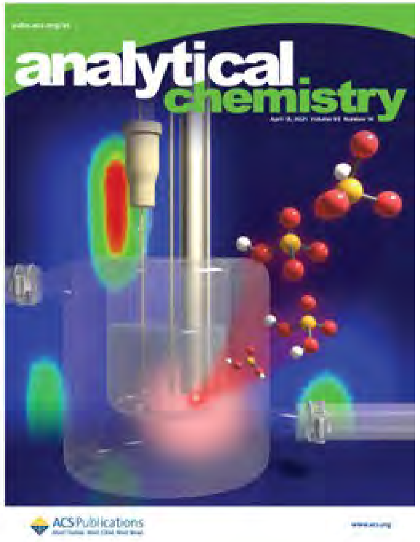






Automated Process Control:
pH Dependent Processing Schemes





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Clifford, A. J.; Lackey, H. E.; Nelson, G. L.; Bryan, S. A.; Lines, A. M., Raman Spectroscopy Coupled with Chemometric Analysis for Speciation and Quantitative Analysis of Aqueous Phosphoric Acid Systems. ***Anal Chem*** 2021**,** *93* (14), 5890-5896.

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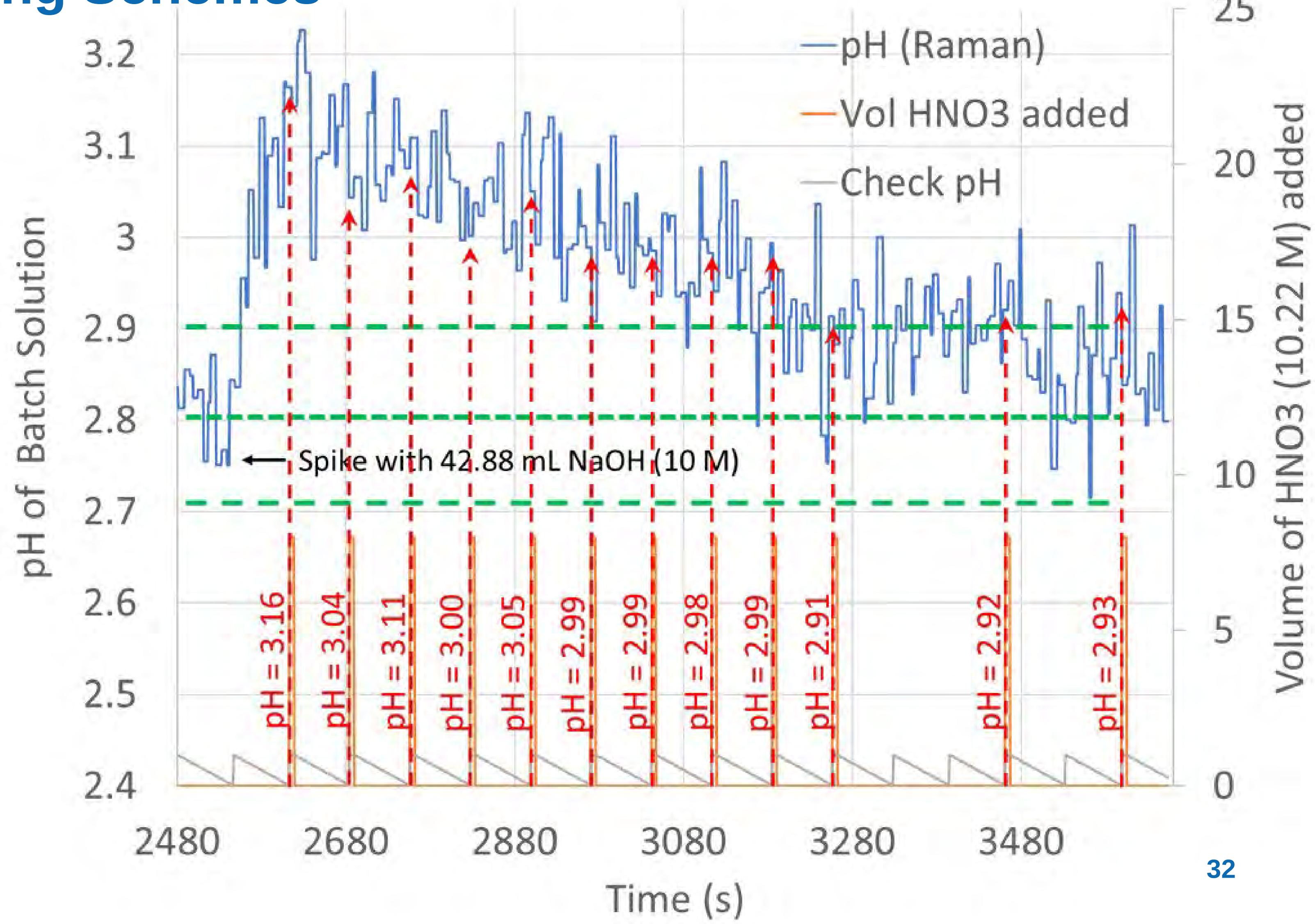
Automated Process Control:
pH Dependent Processing Schemes

- PLC injects volume preset by operator (here constant 8 mL) of acid or base to compensate for ΔpH incrementally

- PLC calculates injection time required based on pump strength to set the constant volume additions



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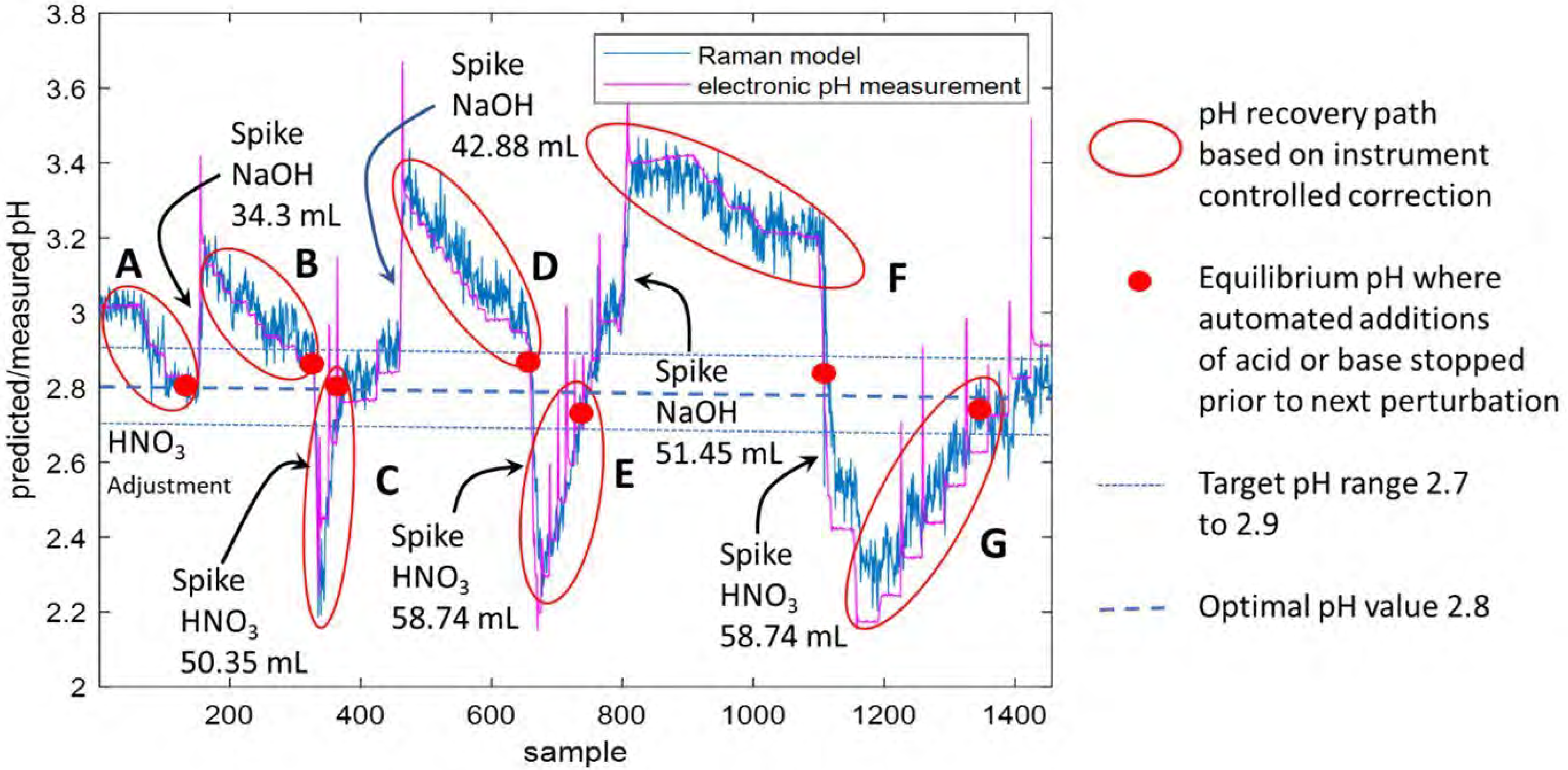
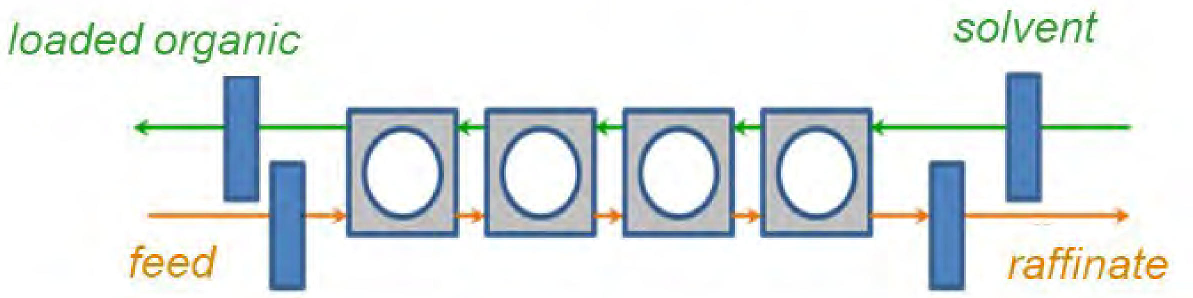
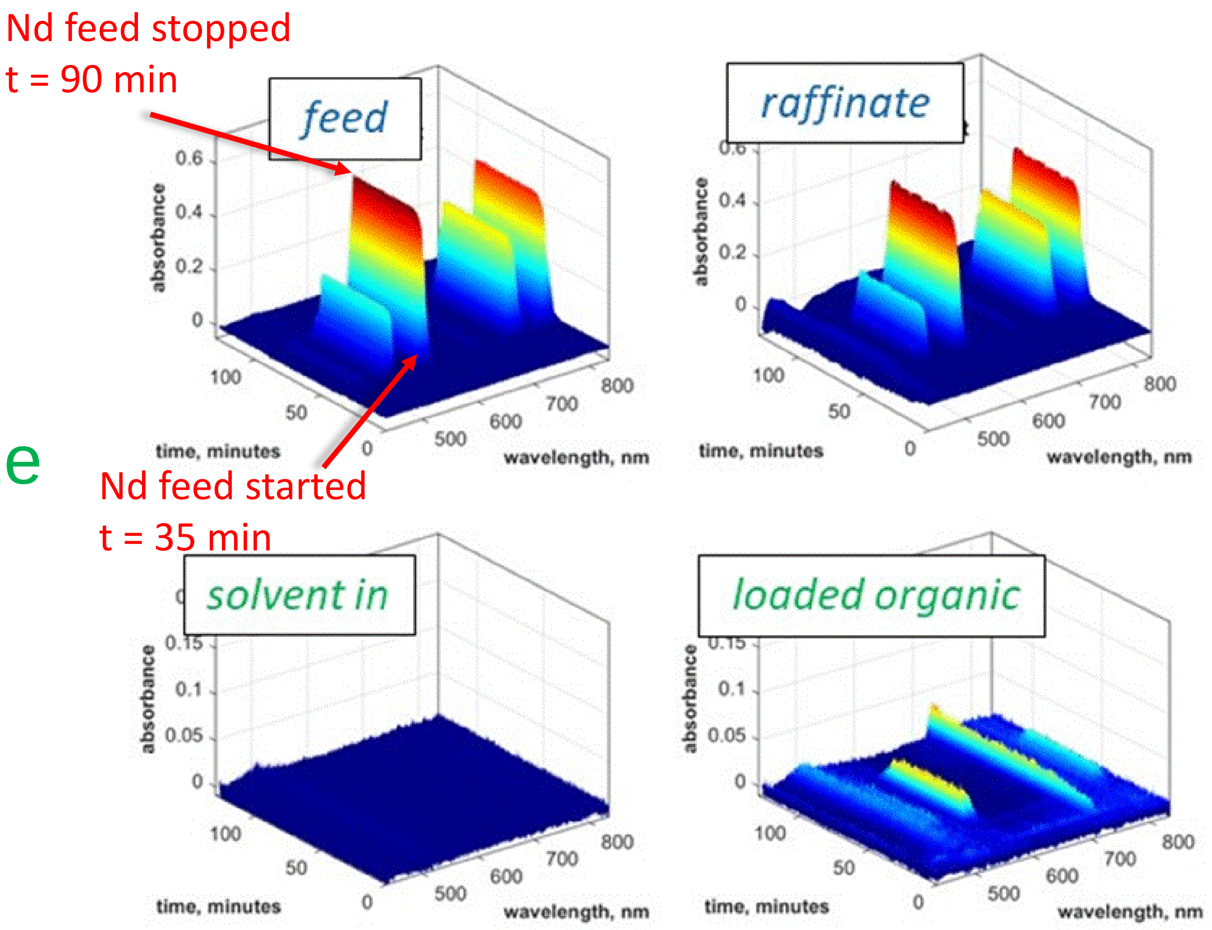
Automated Process Control: pH Dependent Processing Schemes



Automated Process Control: Mass Balance During Extraction

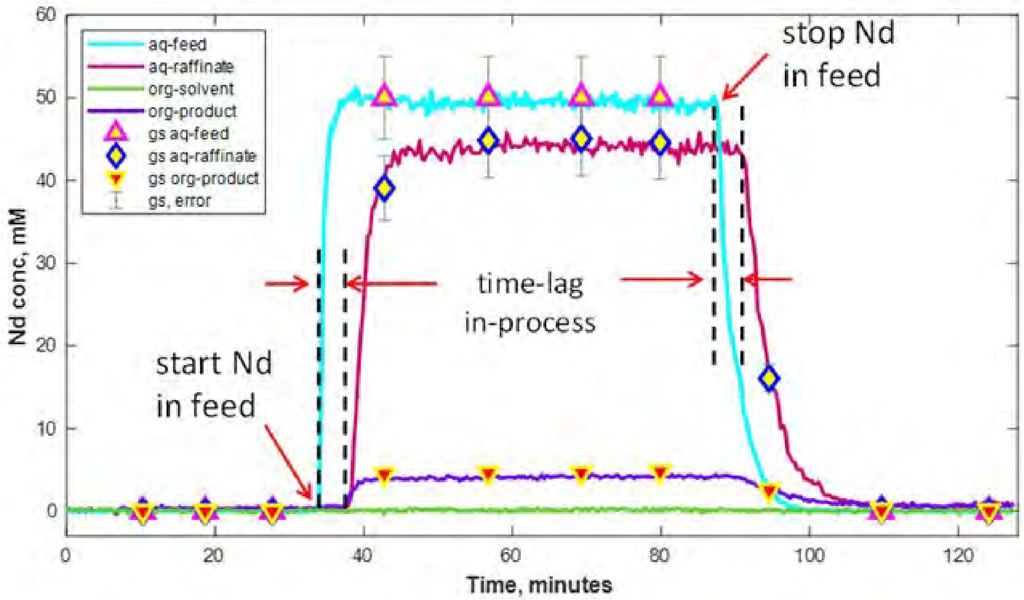


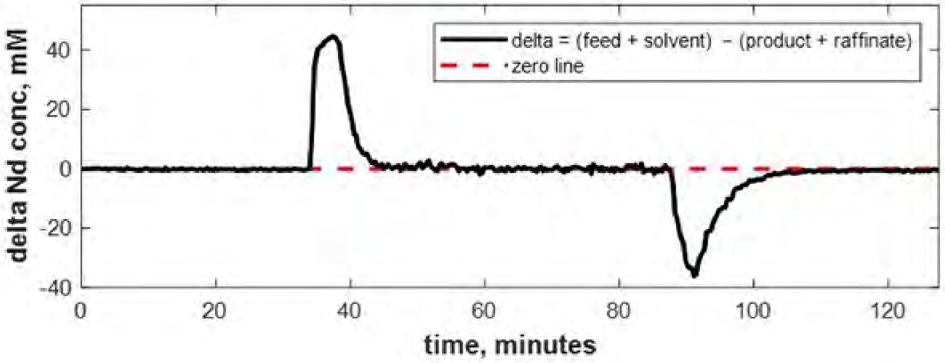
- Transition to characterizing counter current separation process on a bank of centrifugal contactors
- Outfit all inlets and outlets with optical sensors
- In addition to Raman for pH, utilize UV-vis for metal quantification
- gaining comprehensive insight into process chemistry



Automated Process Control:
pH Dependent Processing Schemes

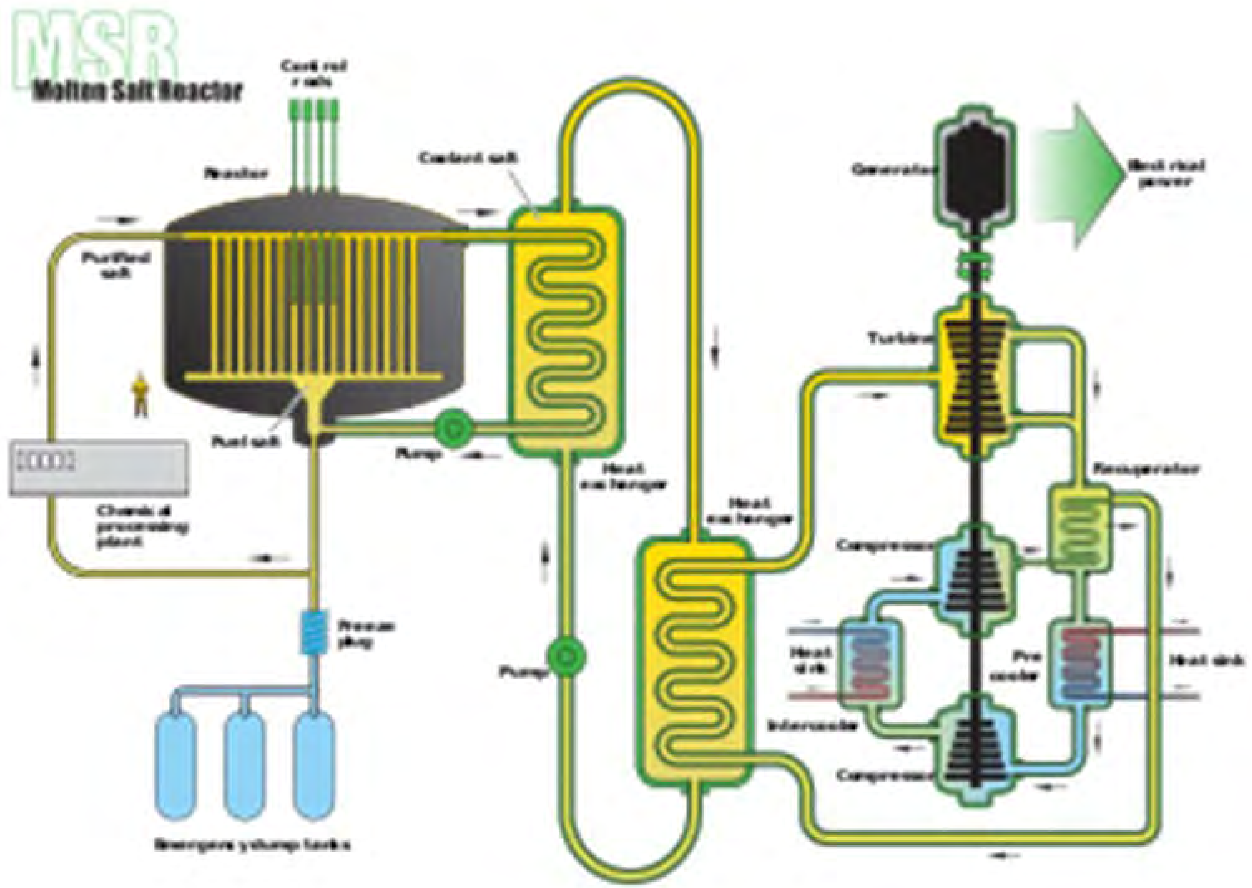
- Run flow tests to first demonstrate chemometric models for metal concentration are functional
- Models utilized LWR PLS algorithms to overcome nonlinear response in variable pH environment
- Note, this data can be paired with flow/density measurements to allow for mass balance





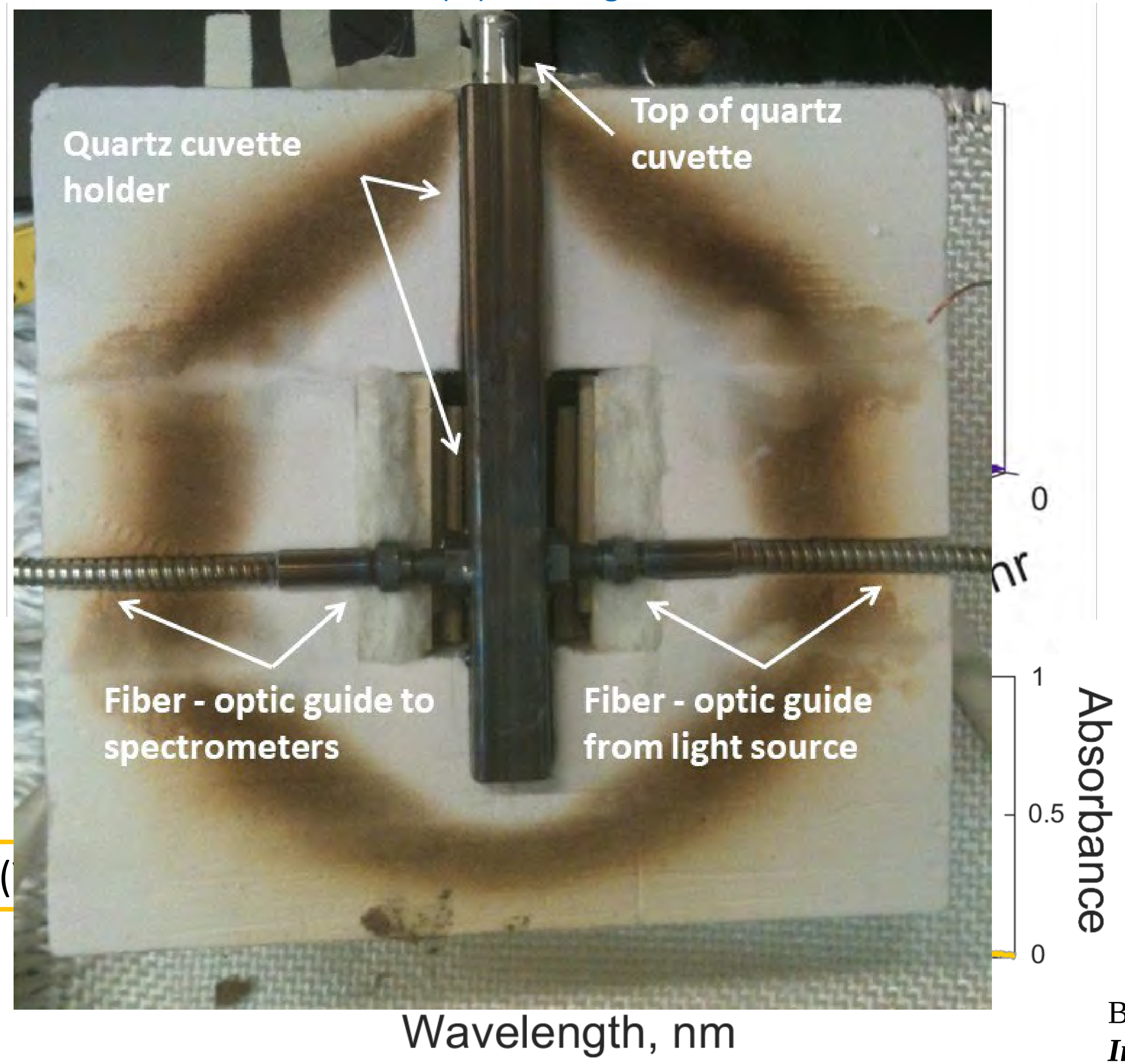
Application to MSR Salts

- Build and demonstrate applications throughout the treatment process
- Sensors operating in extremely harsh environments
  - Temperatures > 500°C
  - Highly corrosive solutions/gases
  - Radiation environments
- Applications for material accountancy, process control, and fundamental characterization



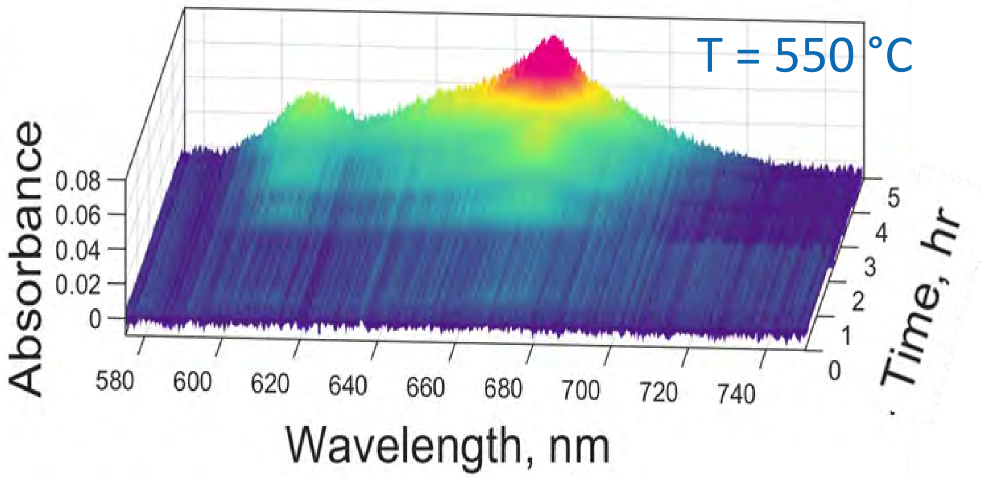
Building library for chemometric modeling

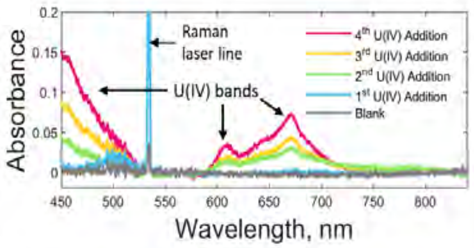
U(III) in NaMg-Cl

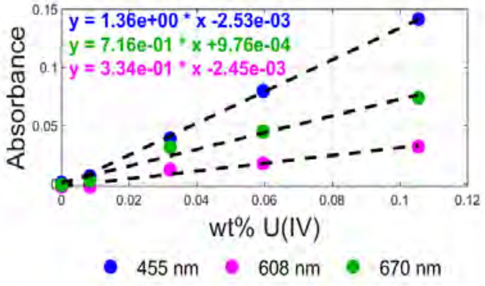


U(

U(IV) in NaKMg-Cl



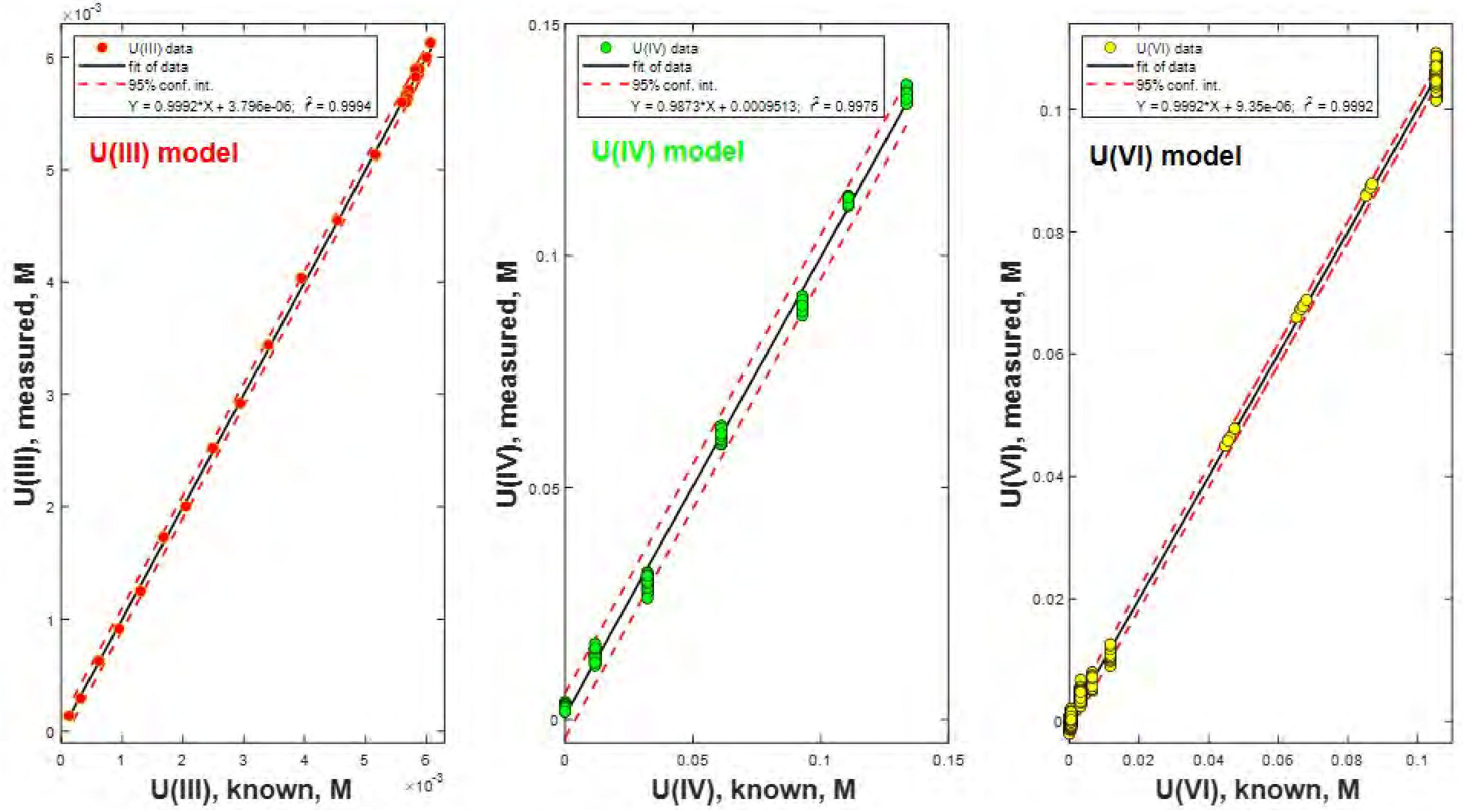




Branch, Felmy, Schafer Medina, Bryan, Lines
Industrial & Engineering Chemistry Research, 2023, 62, 37, 14901–14909.

Chemometric model building

Initial chemometric models showing accurate analysis of U in (III), (IV), and (VI) oxidation states within molten salt environment

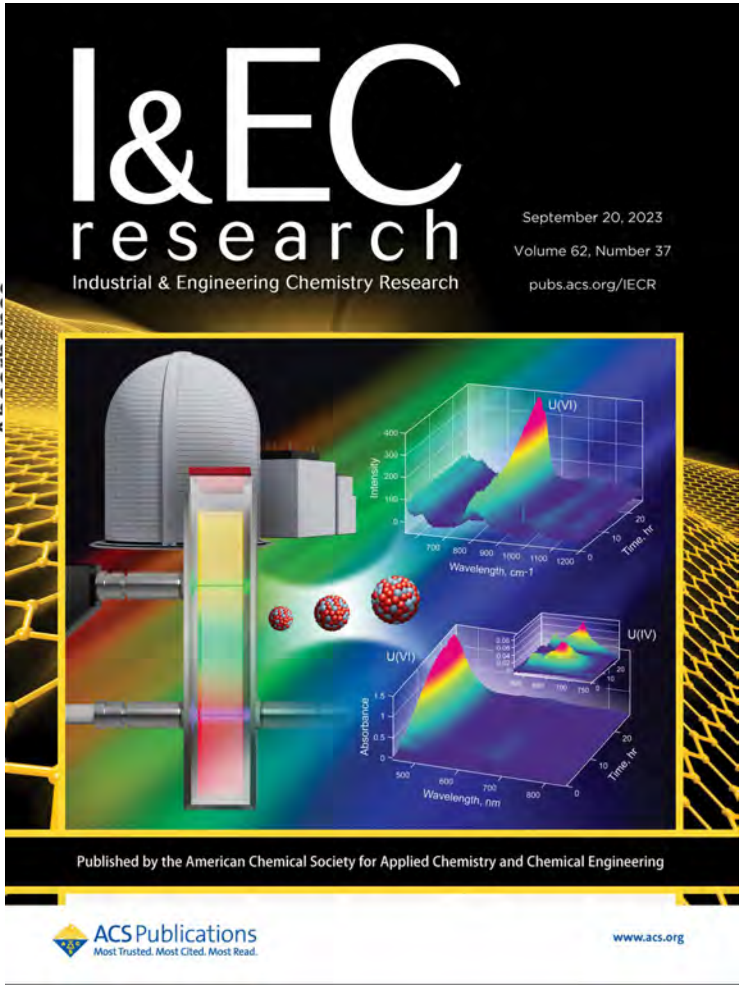


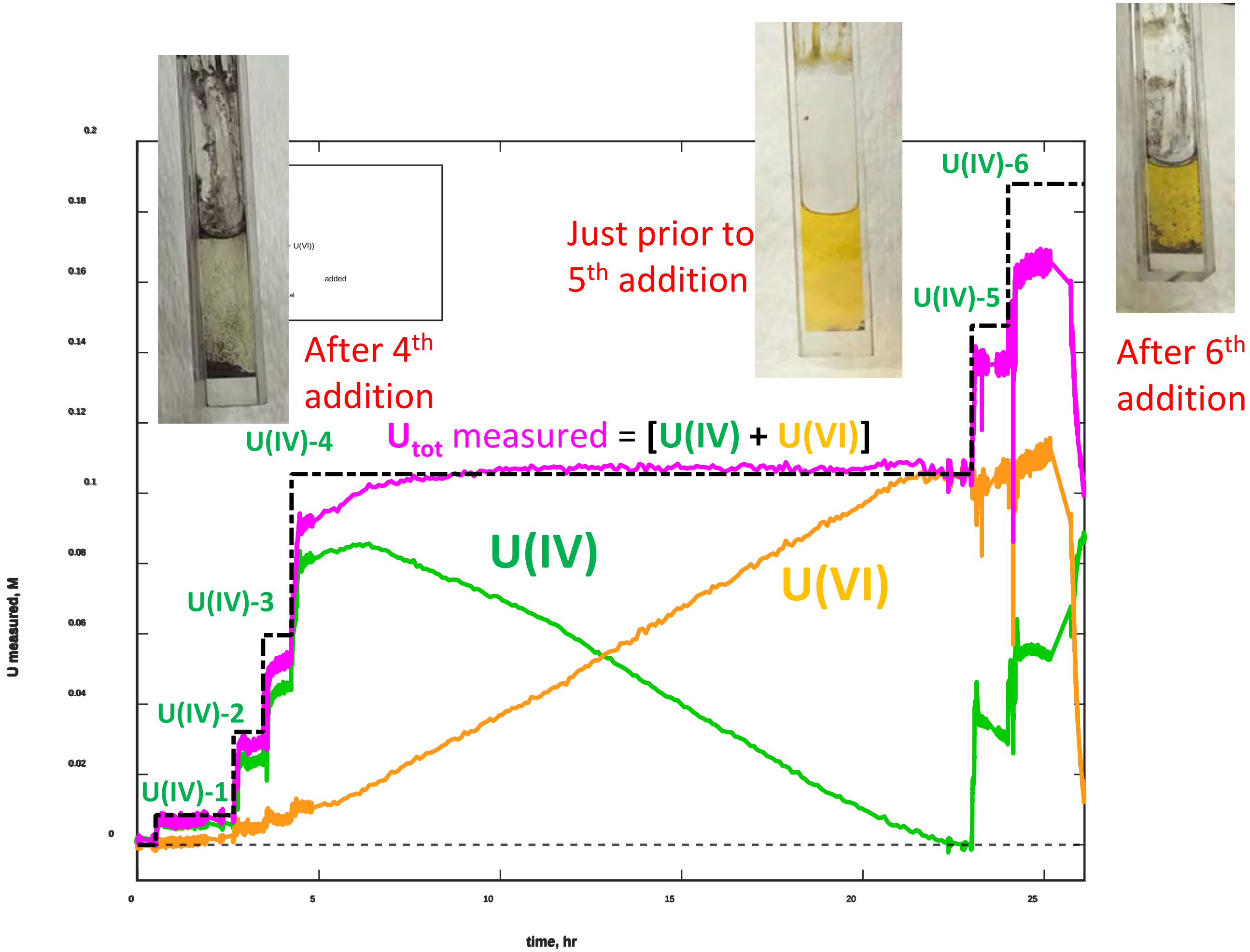
RMSECV (uncertainty)	
U(III)	0.00005 M
U(IV)	0.00416 M
U(VI)	0.00137 M

Branch, Felmy, Schafer Medina, Bryan, Lines
Industrial & Engineering Chemistry Research,
2023, 62, 37, 14901–14909.

U(IV)/U(VI) conversion in NaCl-KCl-$MgCl_2$ eutectic

U(VI)

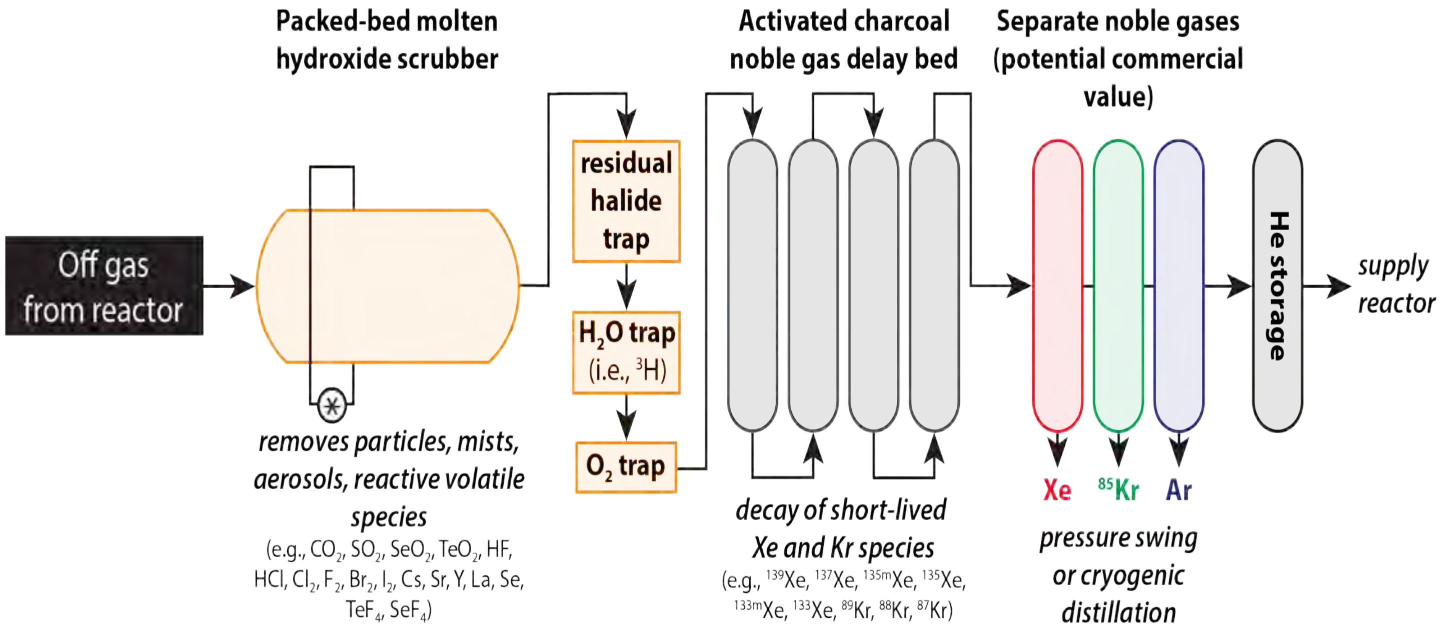




Branch, Felmy, Schafer Medina, Bryan, Lines
Industrial & Engineering Chemistry Research, 2023, 62, 37, 14901–14909.

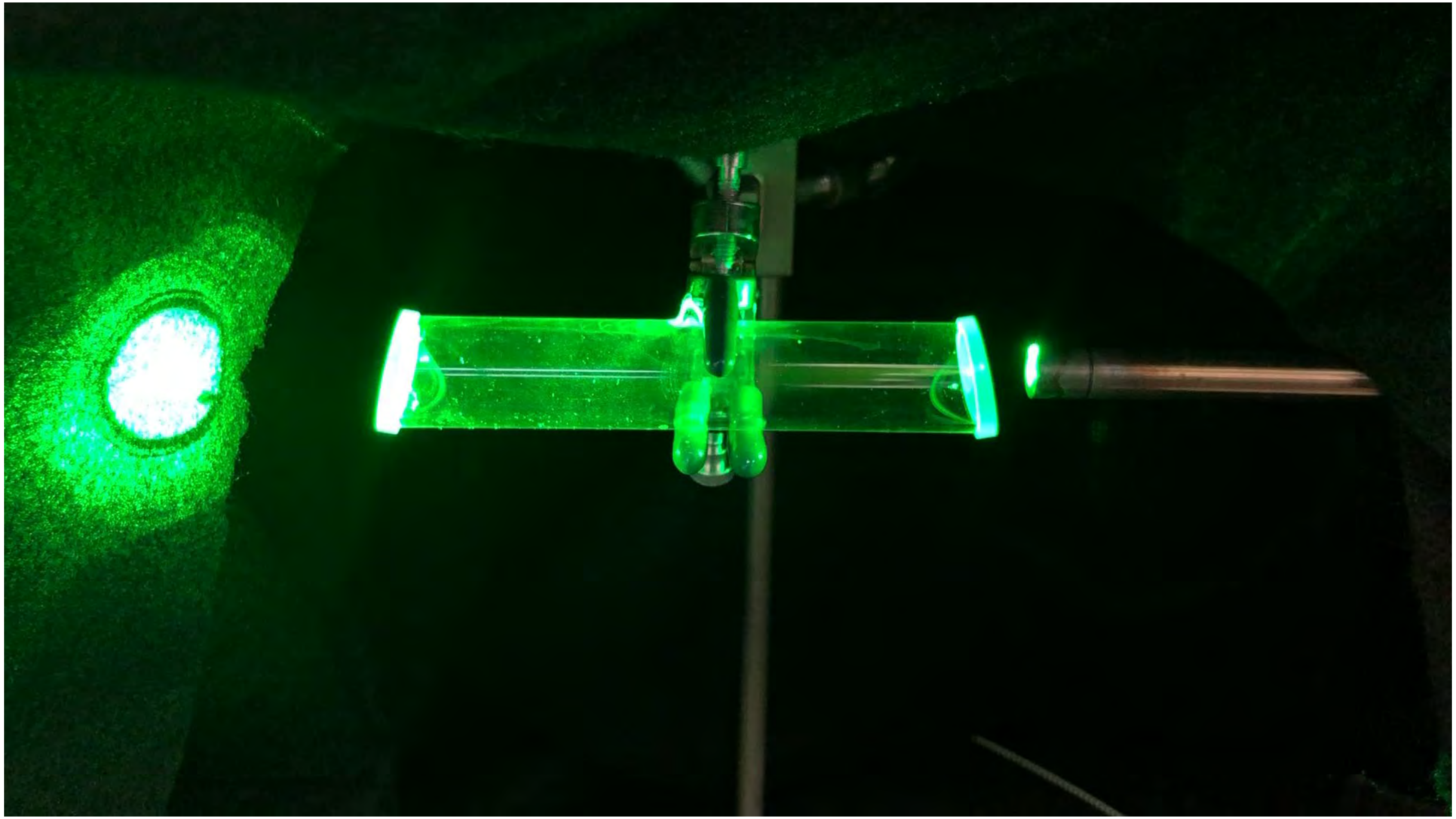
Application to MSR off-gas streams

- PNNL developing OLM capabilities for chemical characterization of off-gas components
  - Demonstration on I_2, ICl, and hydrogen isotopes
- Focus on Raman and FTIR
  - Ideal for deployment
- PNNL collaboration with ORNL

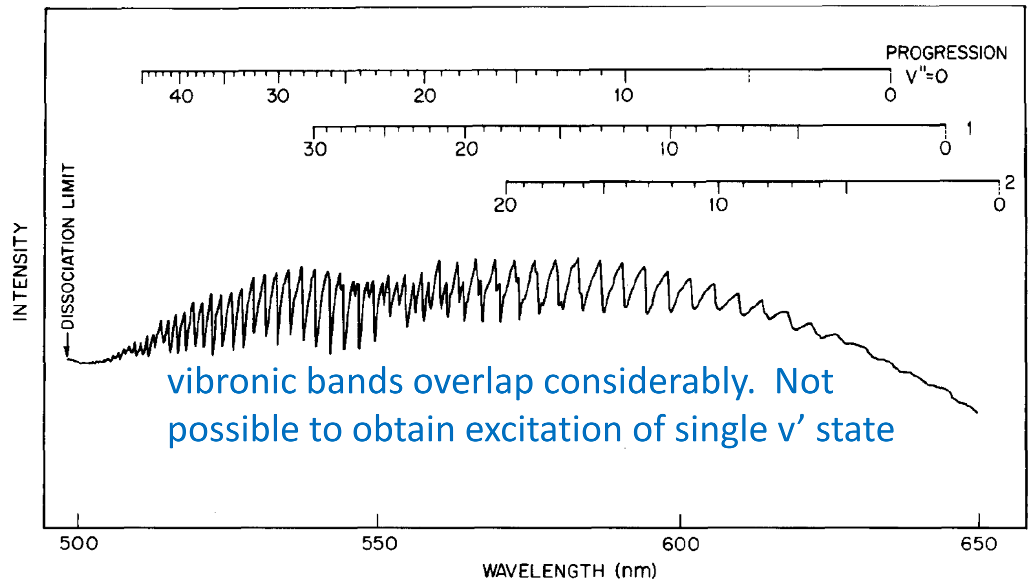


Mcfarlane, J.; Ezell, N.; Del Cul, G.; Holcomb, D. E.; Myhre, K.; Chapel, A.; Lines, A.; Bryan, S.; Felmy, H. M.; Riley, B. *Fission Product Volatility and Off-Gas Systems for Molten Salt Reactors*; Oak Ridge National Lab.(ORNL), Oak Ridge, TN (United States): 2019.

Raman/fluorescence of I_2 gas



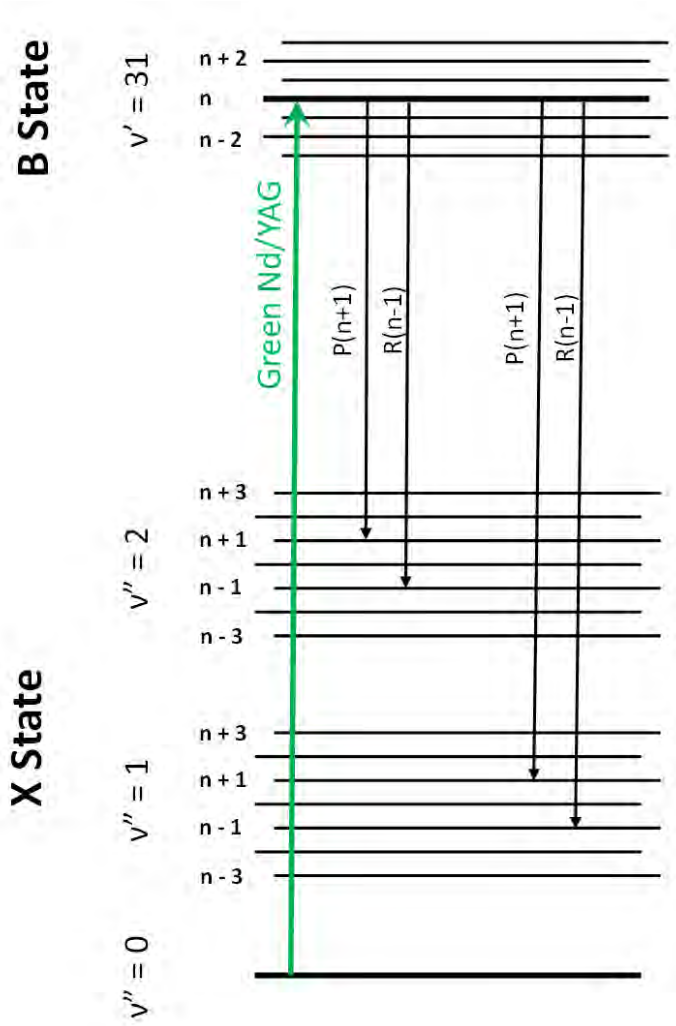
Off-gas measurements: I_2



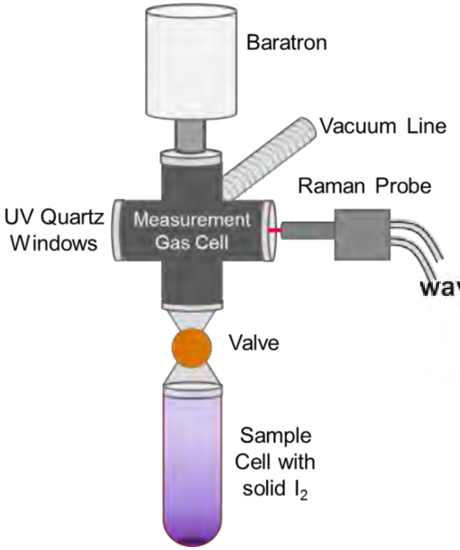
vibronic bands overlap considerably. Not possible to obtain excitation of single v' state

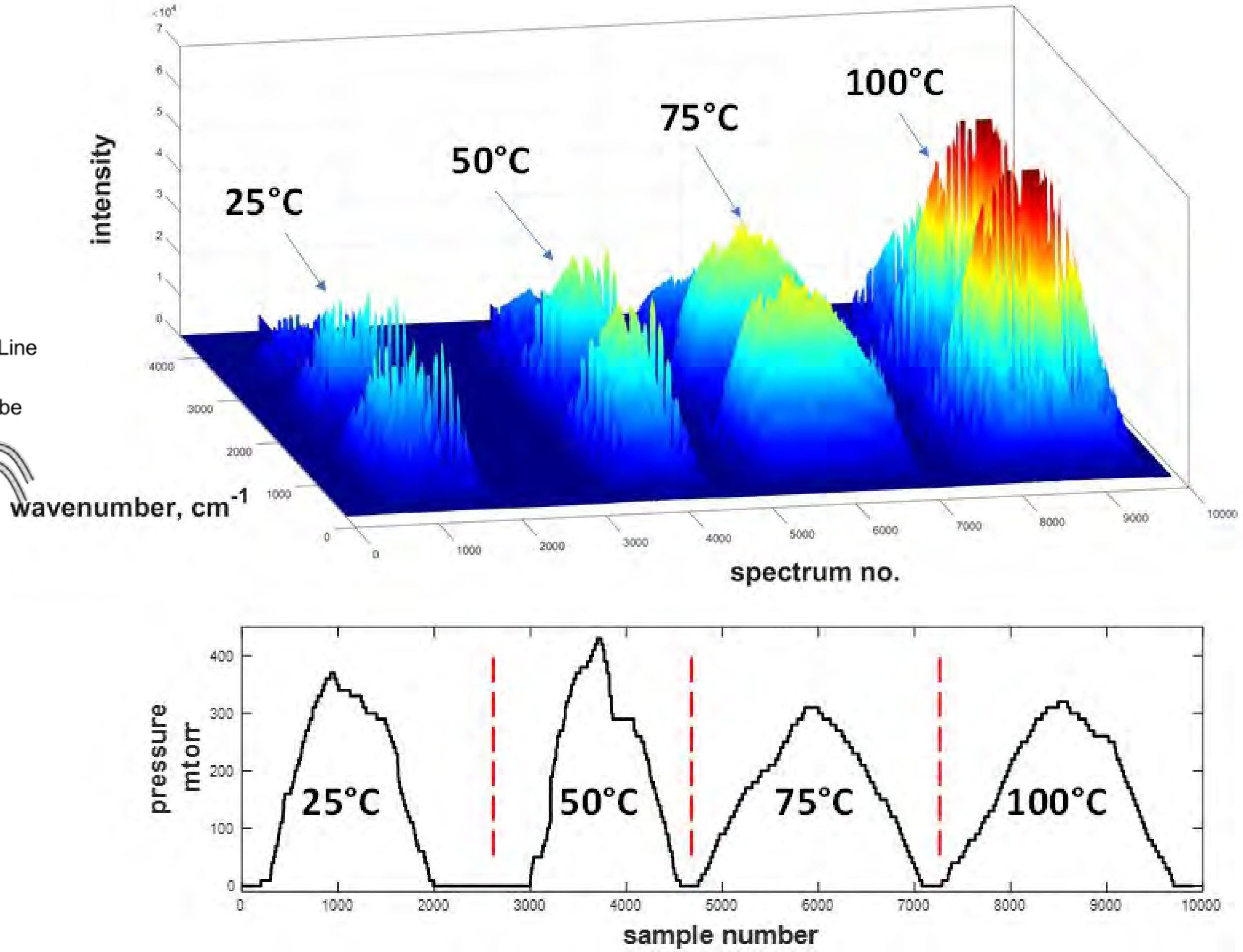
FIG. 2. Vibrational absorption spectrum of I_2 from 650 nm to the dissociation limit. Progressions to the lowest vibrational levels, $v''=0$, 1, and 2, from various electronically excited vibrational levels v' are indicated.

Capelle and Broida, **J. Chem. Phys**. 58, 4212–4222 (1973)



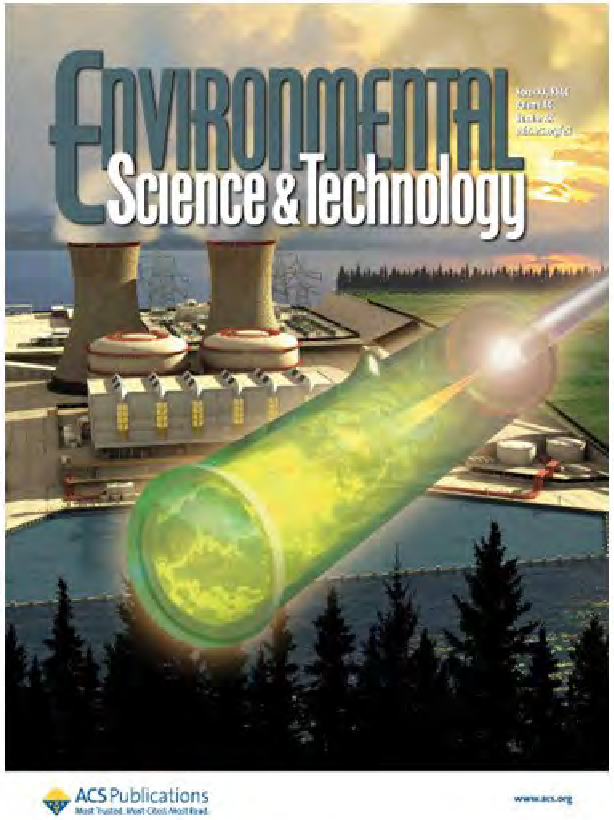
Off-gas measurements: I_2

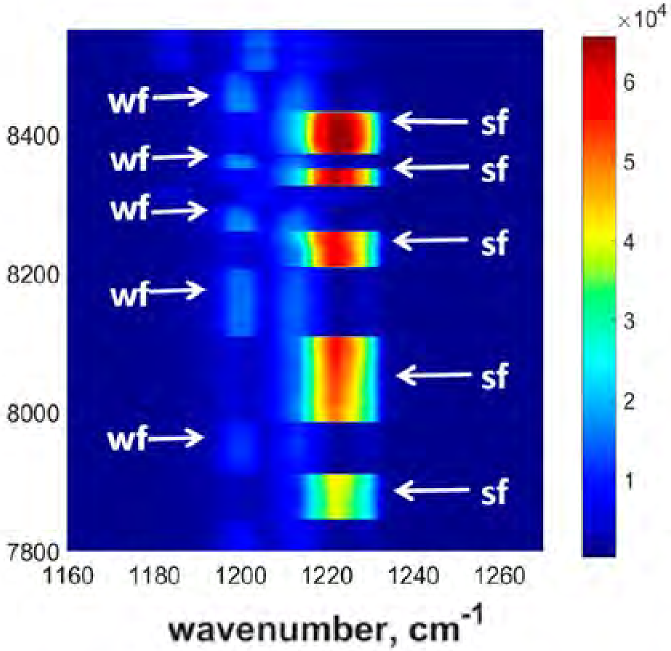


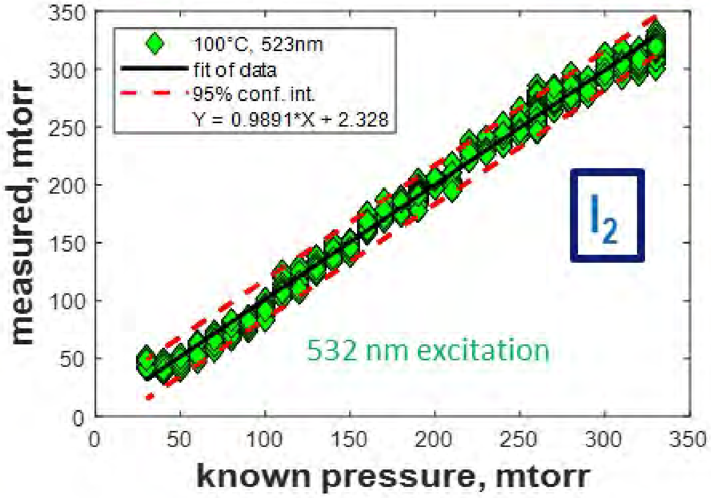


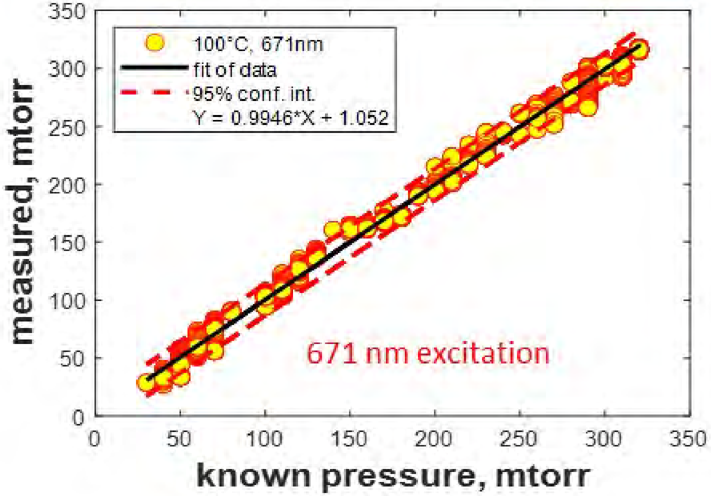
Felmy, Clifford, Medina, Cox, Wilson, Lines, Bryan
Environ Sci Technol *2021, 55, 6, 3898–3908.*

Off-gas measurements: I_2



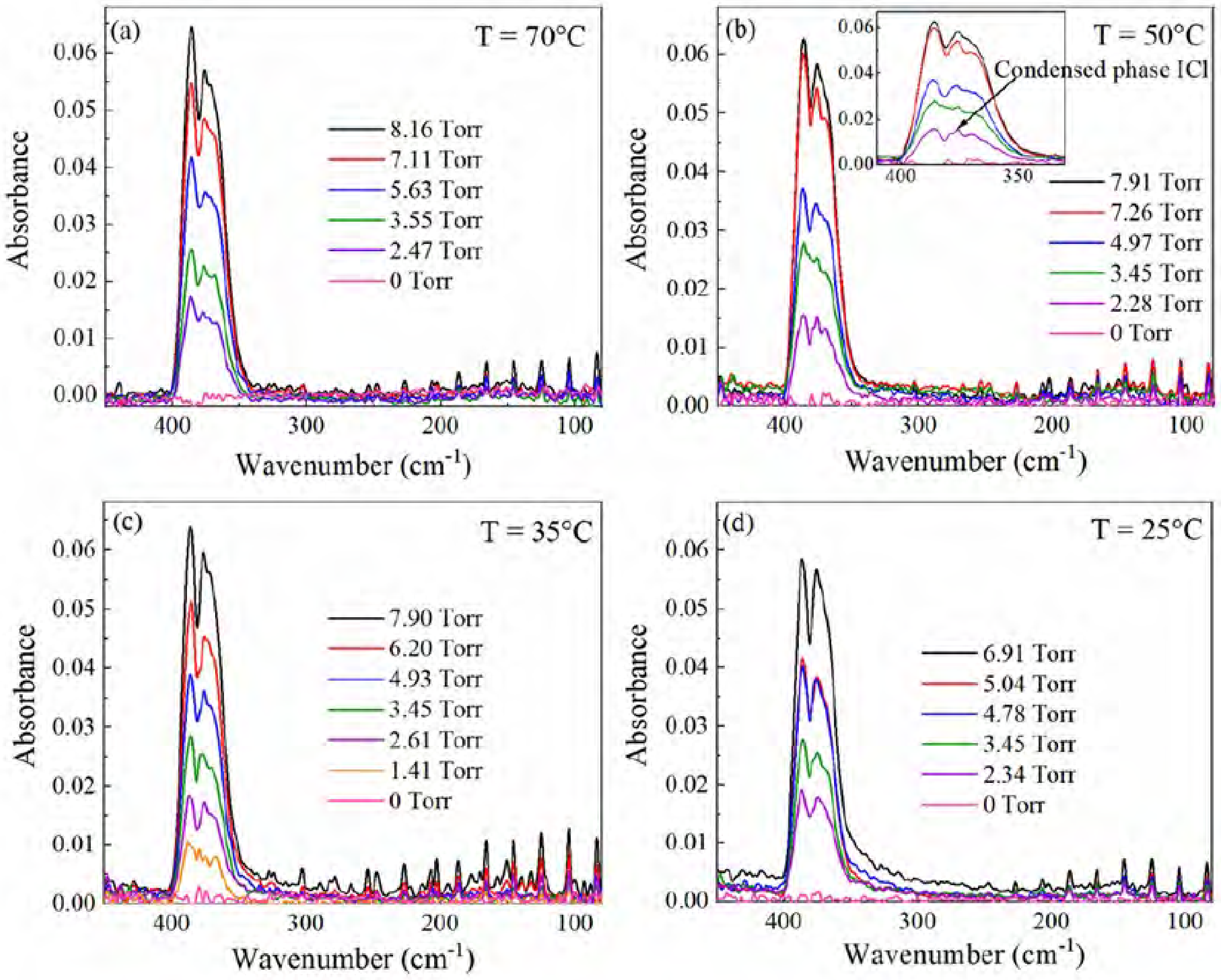


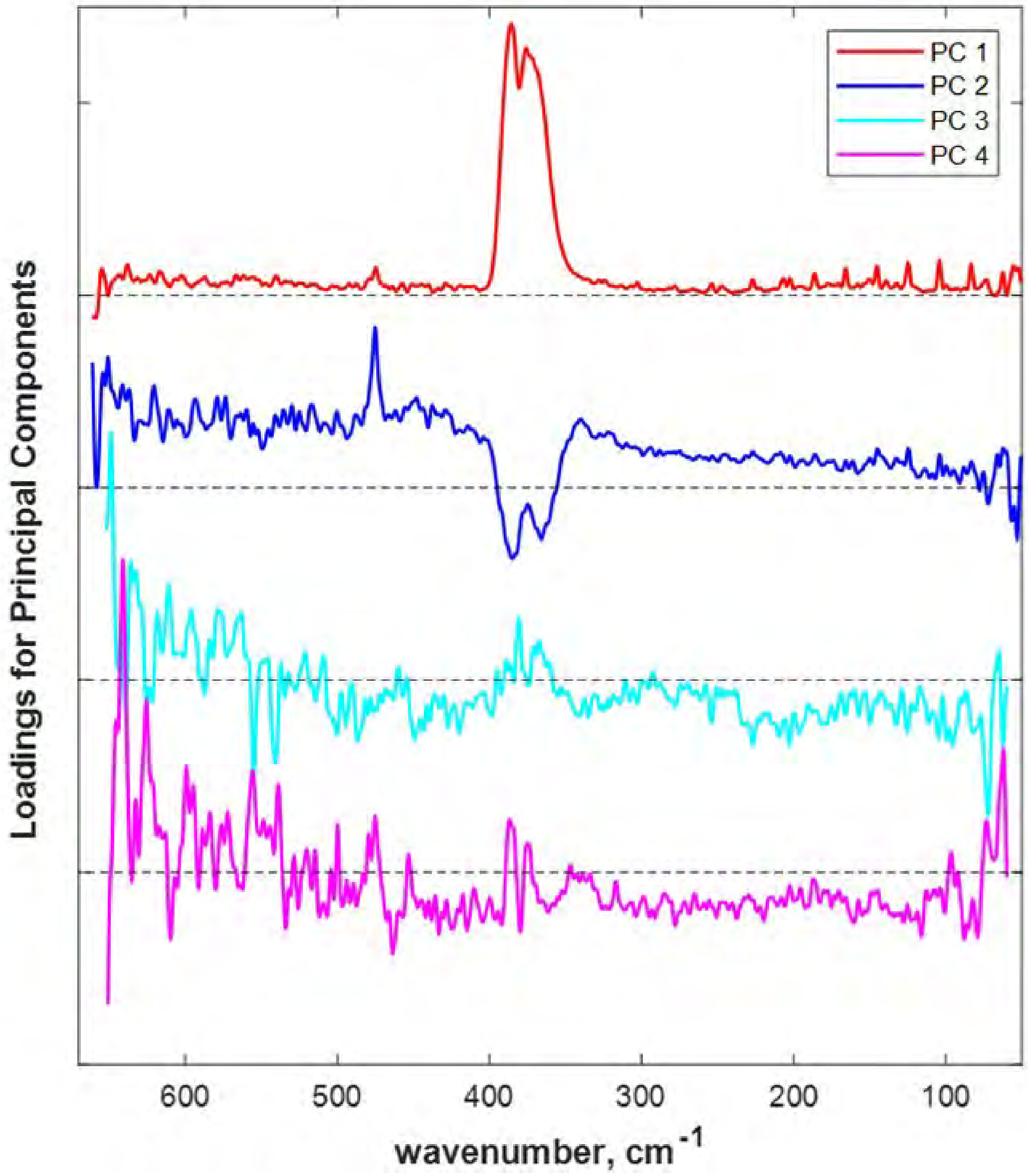




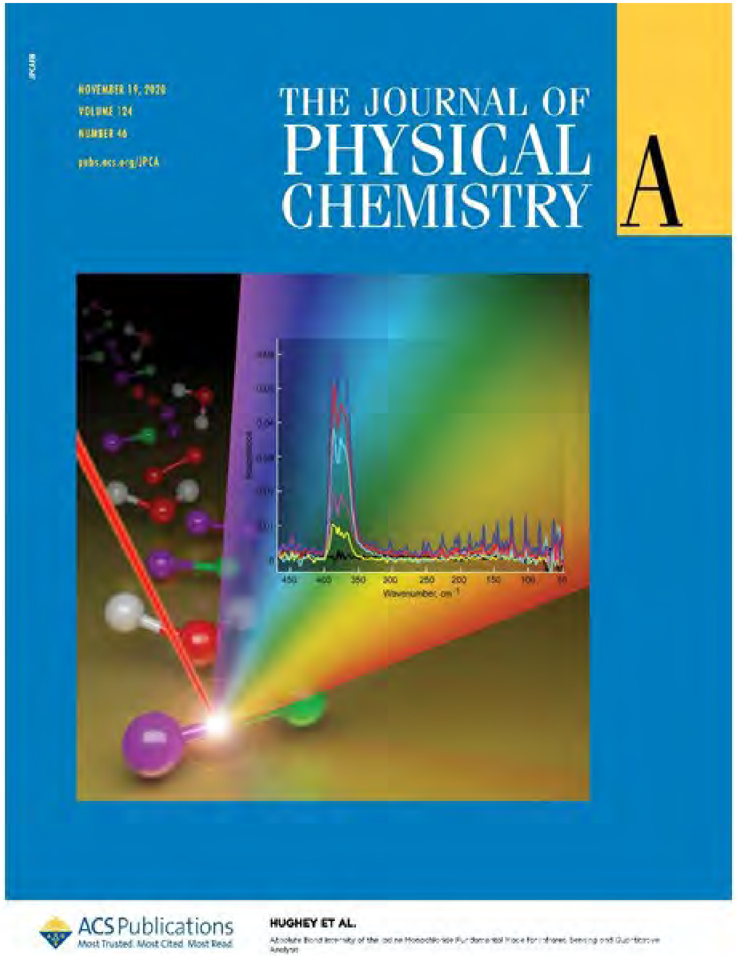
Felmy, Clifford, Medina, Cox, Wilson, Lines, Bryan
Environ Sci Technol *2021, 55, 6, 3898–3908.*

FTIR/Off-gas measurements: ICl





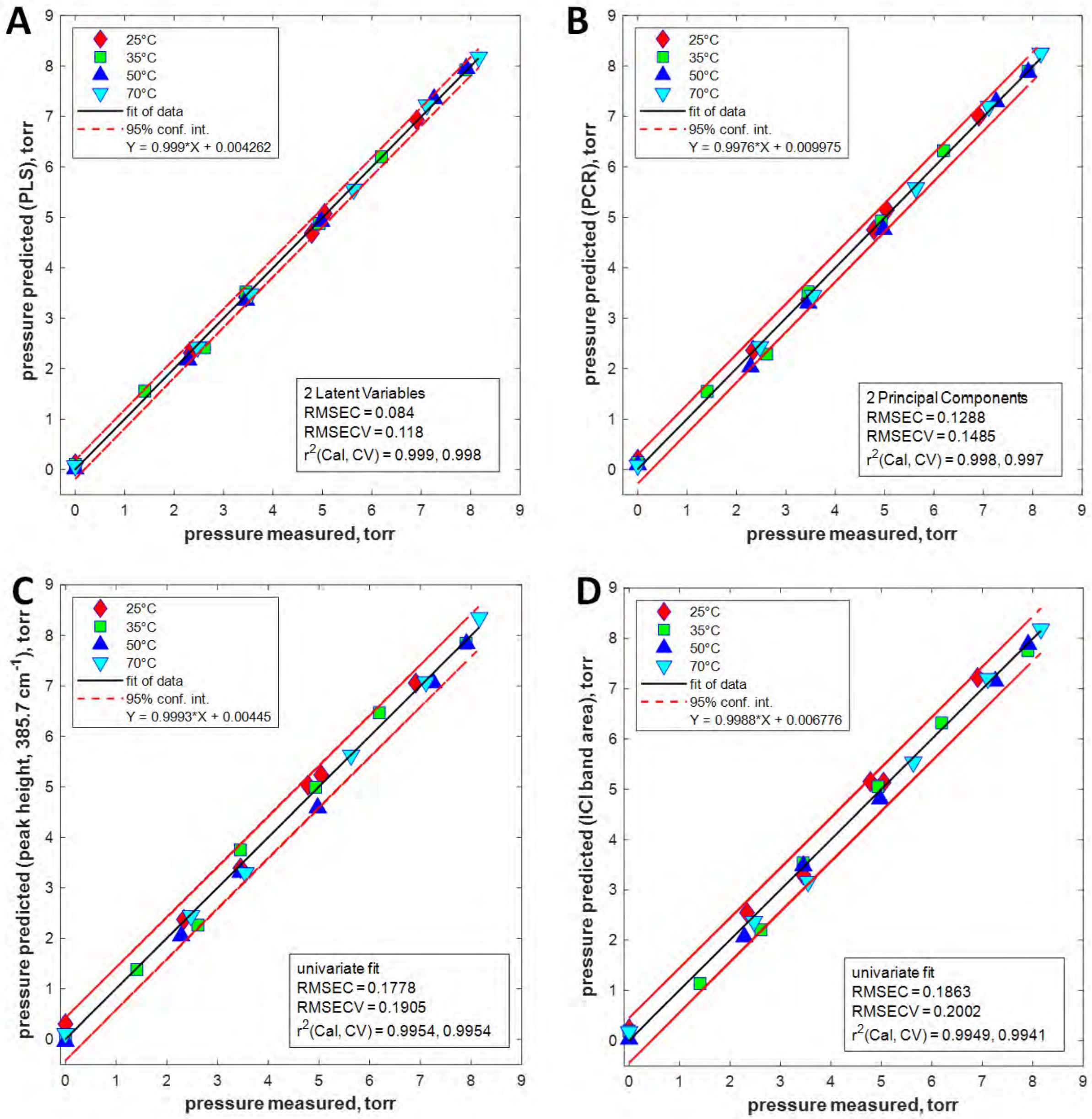
Off-gas measurements: ICl



Hughey, Bradley, Tonkyn, Felmy, Blake, Bryan, Johnson, Lines,
J Phys Chem A 2020, *124* (46), 9578-9588.

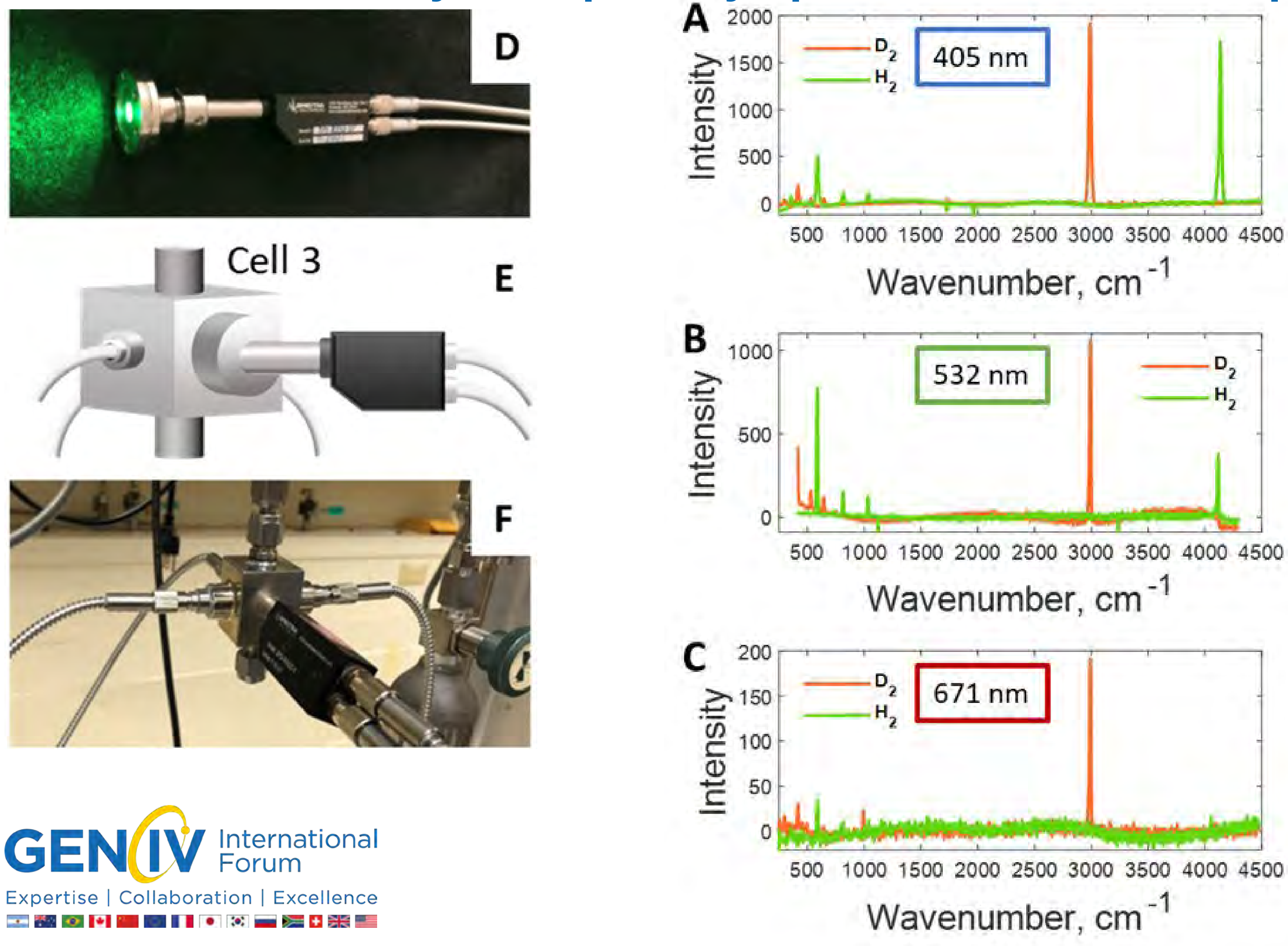
Multivariate methods

Univariate methods (Beers law)



Building a better gas cell for hydrogen isotopes

Raman can identify and quantify speciation and H isotopics



405 nm 532 nm 671 nm

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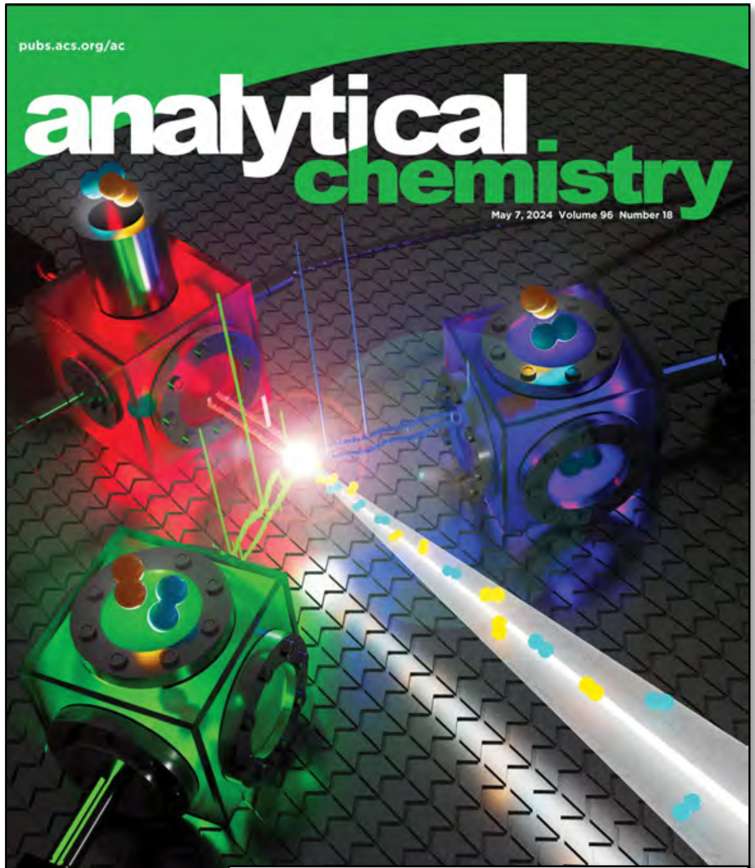
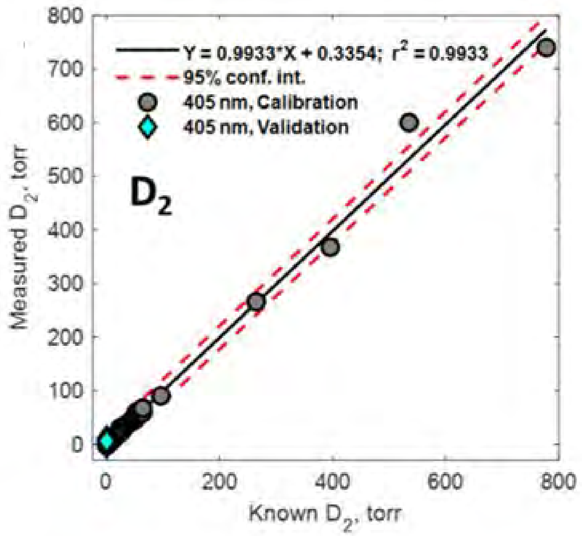
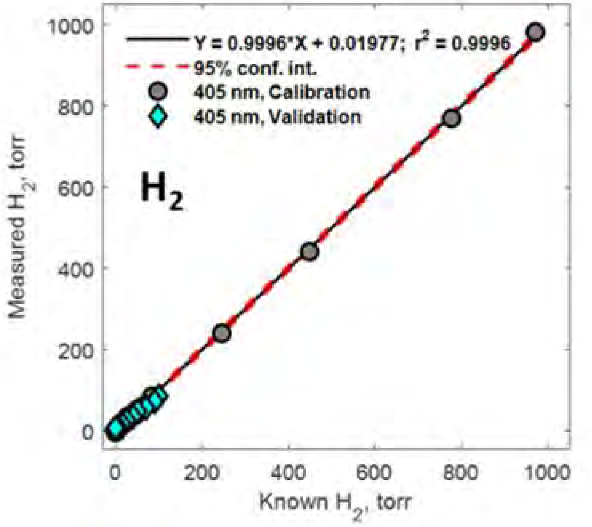
Demonstration of Hydrogen isotopes

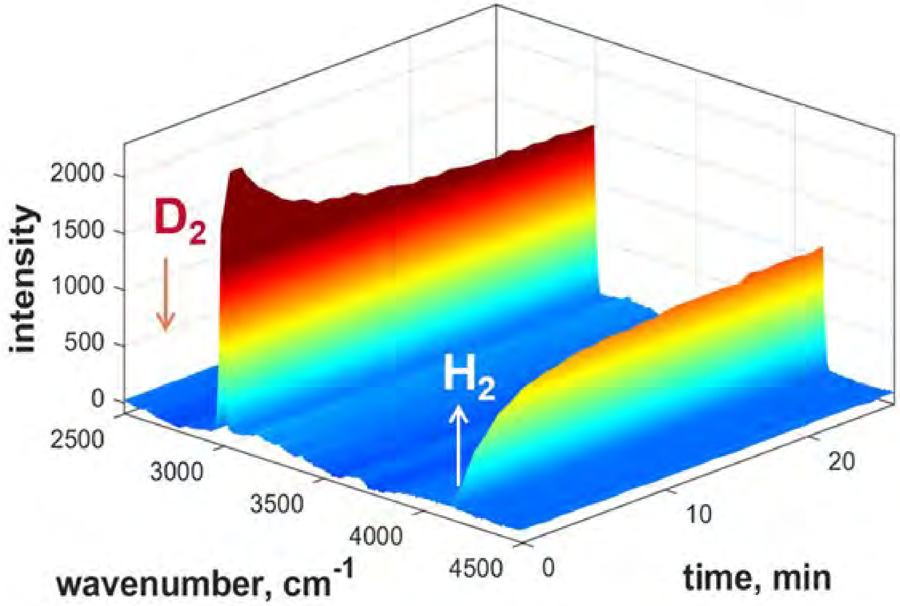


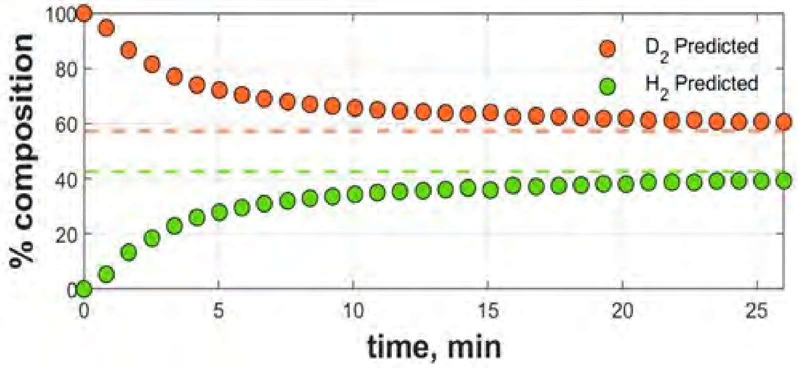
Felmy, Cox, Espley, Campbell, Kersten, Lackey, Branch, Bryan, Lines
Anal Chem., 2024, 96, 18, 7220–7230

D_2 Pressure, torr









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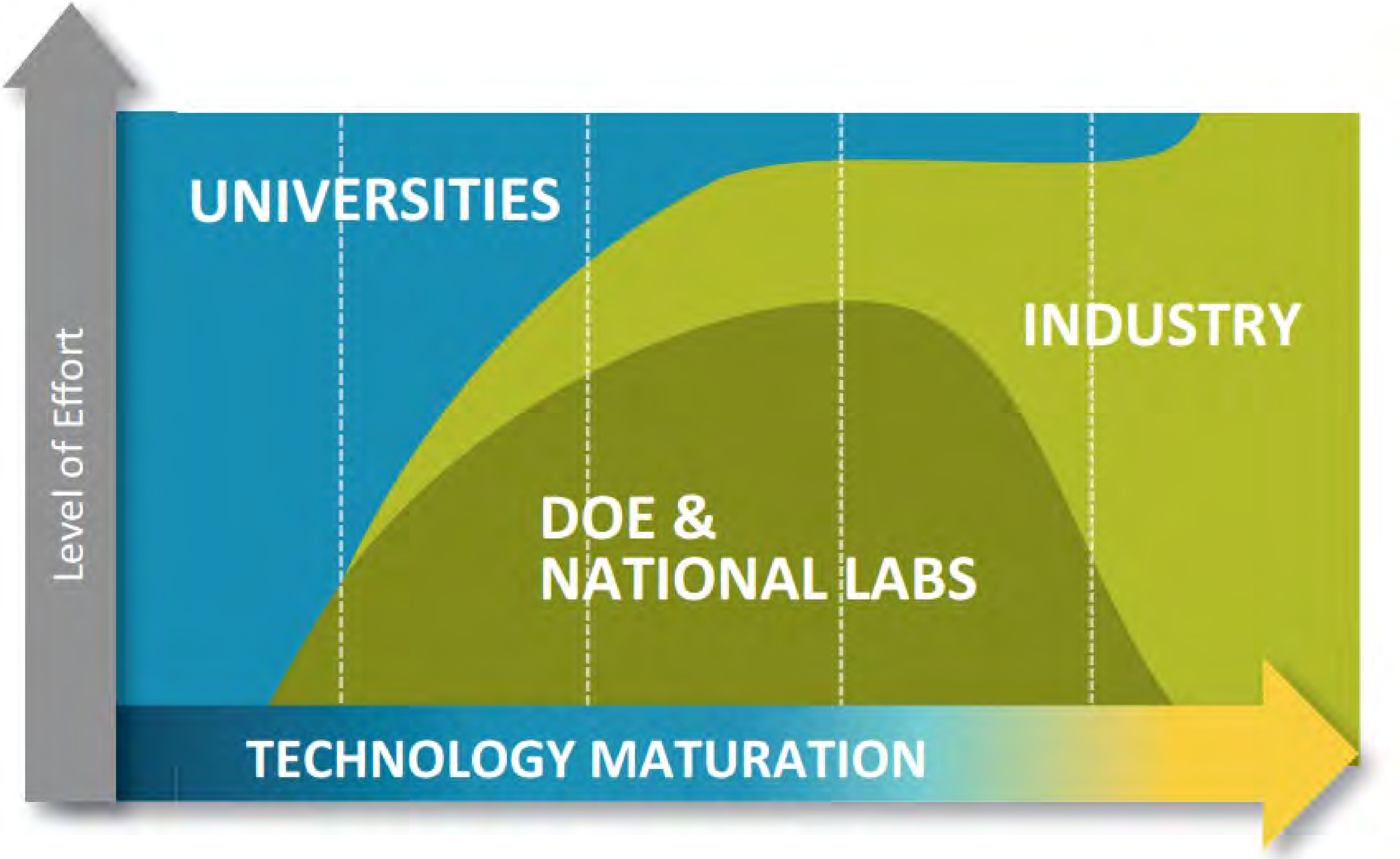
Enabling Transfers of Technology



Key Take-Aways

- Real-time process monitoring has diverse and wide-ranging applications
- Optical spectroscopy tools can provide powerful pathways to characterizing chemical composition of a given process (batch or flow)
  - But in any moderately complex process, advanced analytical tools are required for fast and accurate translation of data into information
- This approach can be leveraged in even some of the most challenging applications: nuclear materials processing
- Utilizing these tools can enable better, faster, safer, and more cost-effective processing in highly harsh environments

This work was supported by
DOE EM, NE, NNSA

Acknowledgements

PNNL Team:

Amanda Lines
Sam Bryan
Heather Felmy
Shirmir Branch
Brian Riley

Adan Schafer Medina
Poki Tse
Nathan Bessen
Gabe Hall

Gregg Lumetta
Brienne Seiner
Thomas Serrano
Jarred Allred

Prof. Gilbert Nelson (C. Idaho)
Job Bello (Spectra Solutions Inc.)
Hope Lackey (WSU)

Alyssa Espley
Savannah Potter
Nikolas Boily

Upcoming Webinars

Date	Title	Presenter
28 August 2024	International Molten Salt Research in Support of MSR Development	Aslak Stubsgaard, Denmark Isabelle Morlaes, France Ed Pheil USA Markus Piro, Canada Jeremy Pearson, USA
September 2024	Overview and Update of Sodium Fast Reactor Activities within the Gen IV International Forum	Yoshitaka Chikazawa, JAEA, Japan
October 2024	Overview and Update of Gas-cooled Fast Reactor Activities within the Gen IV International Forum	Petr Vacha, UJV, Czech Republic