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ENERGY

Nuclear Energy

SPECTROSCOPIC ON-LINE MONITORING OF RADIOCHEMICAL STREAMS

**NEET Review
September 17, 2014**

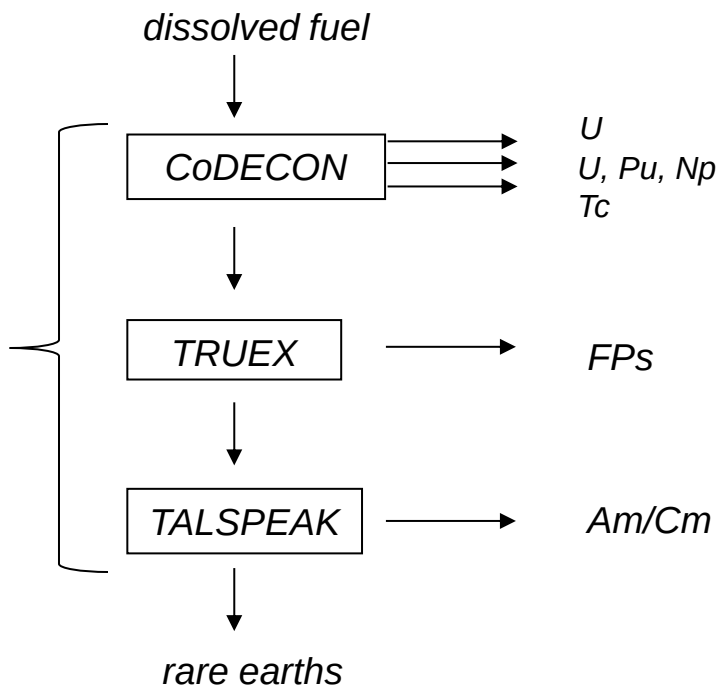
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Process Monitoring Can Be Achieved Throughout the Flowsheet

*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*

*Coriolis and conductivity
instruments can be used on
all process streams*

Monitoring Is Not Flowsheet Specific



Approach: Online 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, strong acid (H^+), strong base (OH^-)
- pH – weak acid/base buffer systems

■ 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

■ Future – Cost share demonstration of performance in an actual processing plant and enable comparison to existing methods

- In discussions with SRS H Canyon

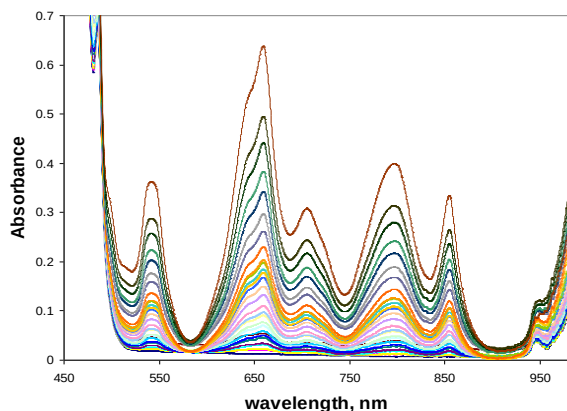


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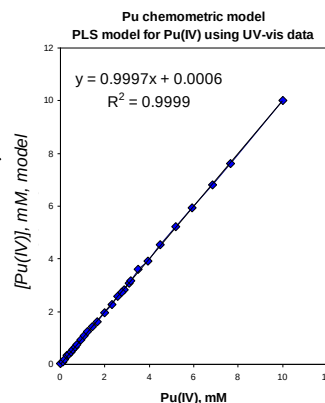
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Methodology for on-line process monitor development: from proof-of-concept to final output

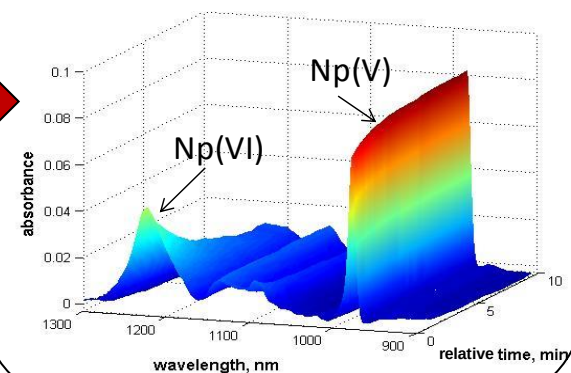
*Static measurements:
Model training database*



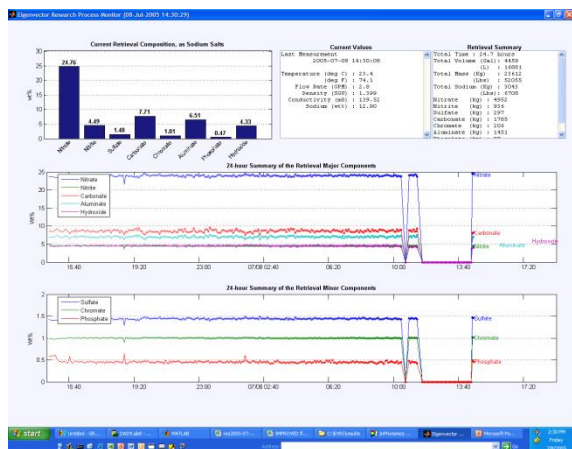
Chemometric model development



On-line model verification and translation



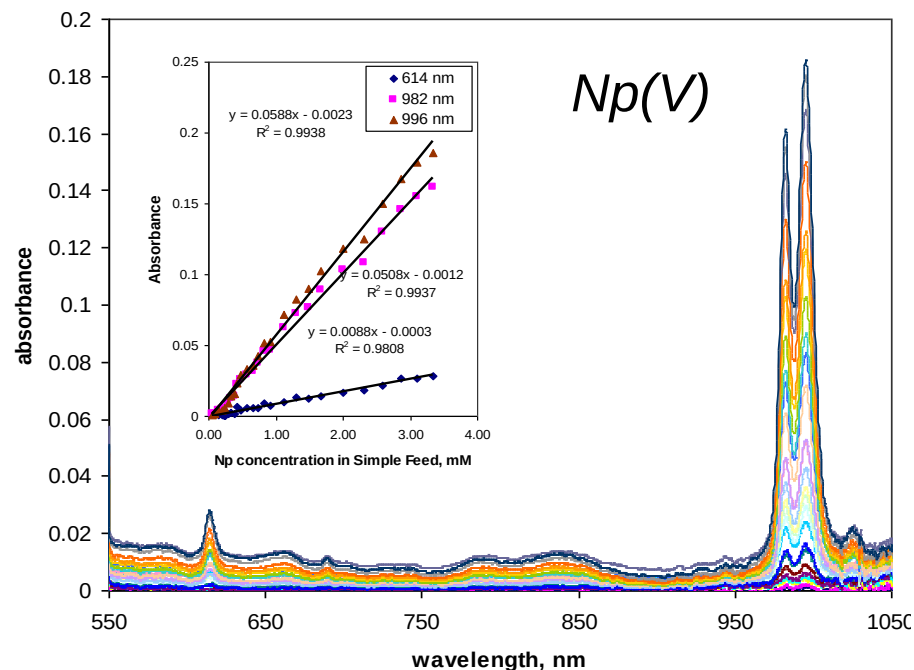
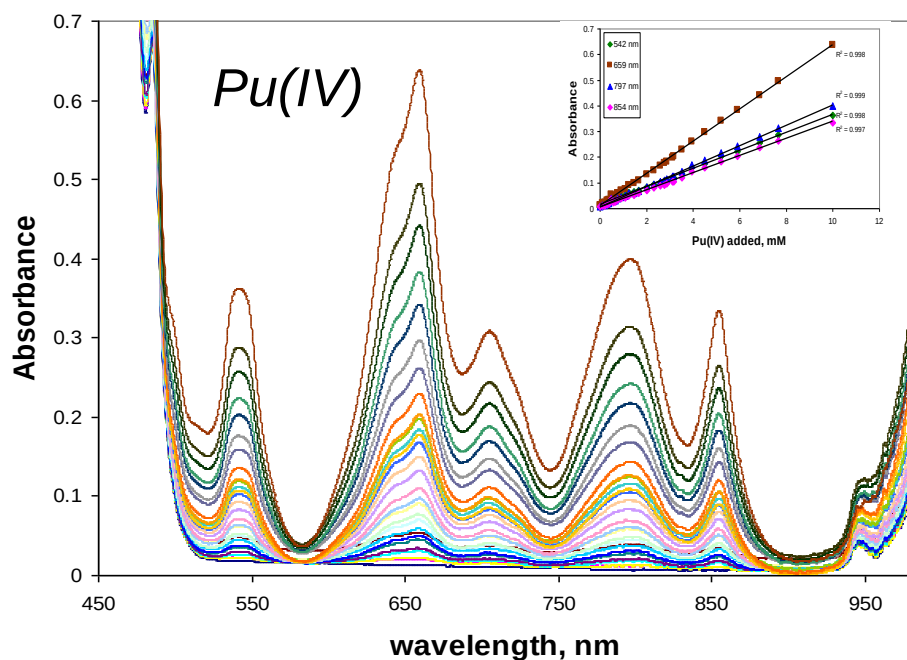
Real-time on-line concentration data display



*Integrated software for data collection,
processing, storage and archiving*

Vis-NIR measurements for Pu and Np model development

- *Pu and Np concentration can be quantified over wide range of process chemistry conditions*

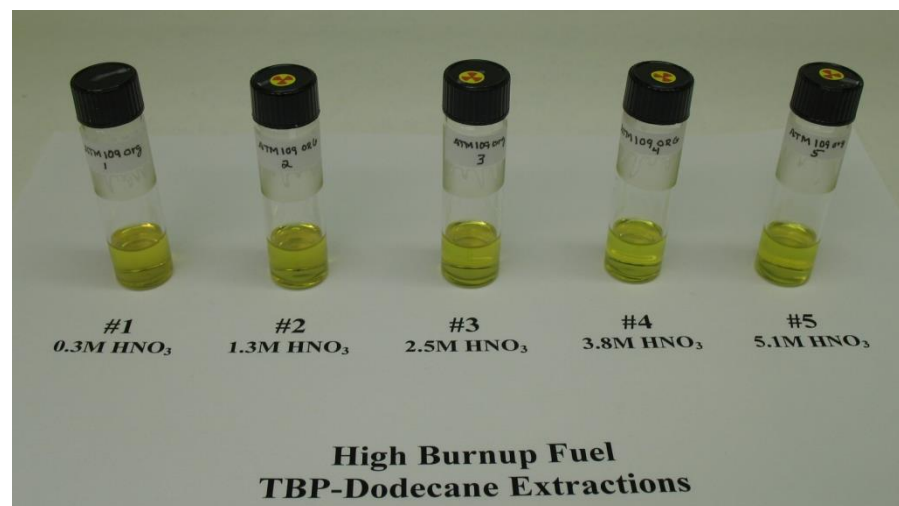


- *Pu(IV) concentration variable 0.1 to 10 mM*
- *Np(V) concentration, variable 0.05 to 3.3 mM*
- *Feed composition: 1.3 M $\text{UO}_2(\text{NO}_3)_2$ in 0.8 M HNO_3*
- *$\text{UO}_2(\text{NO}_3)_2$ does not interfere with Pu(IV) measurements*



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*
ICP-MS	0.721	8.99E-03	4.7E-04	8.40E-02
Spectroscopy	0.719	8.90E-03	4.7E-04	1.10E-02
Spectroscopic / ICP ratio	0.99	0.99	1.0	1.3

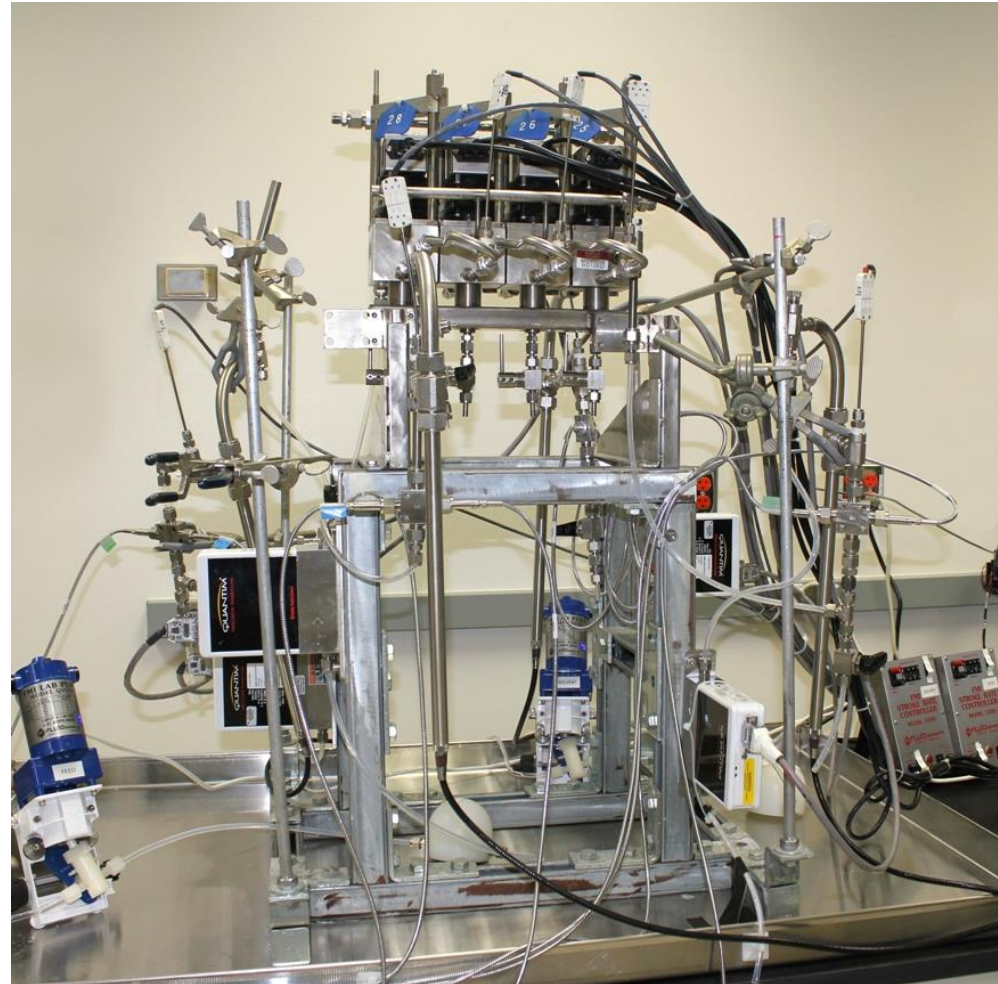
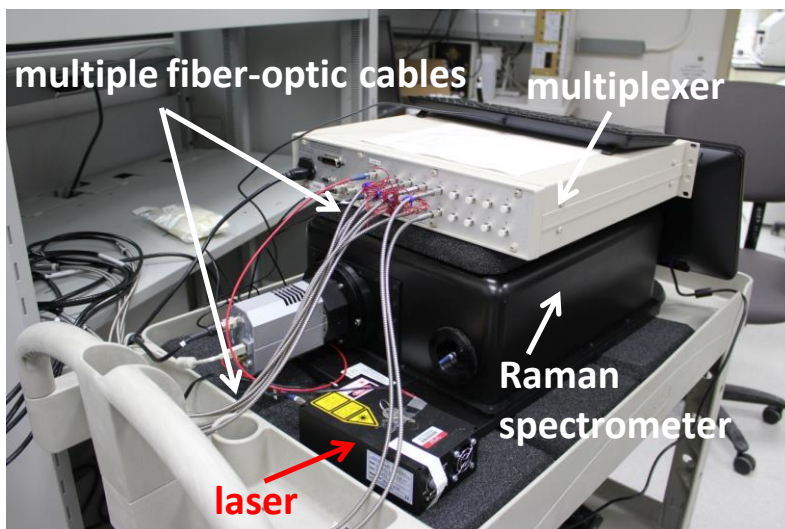
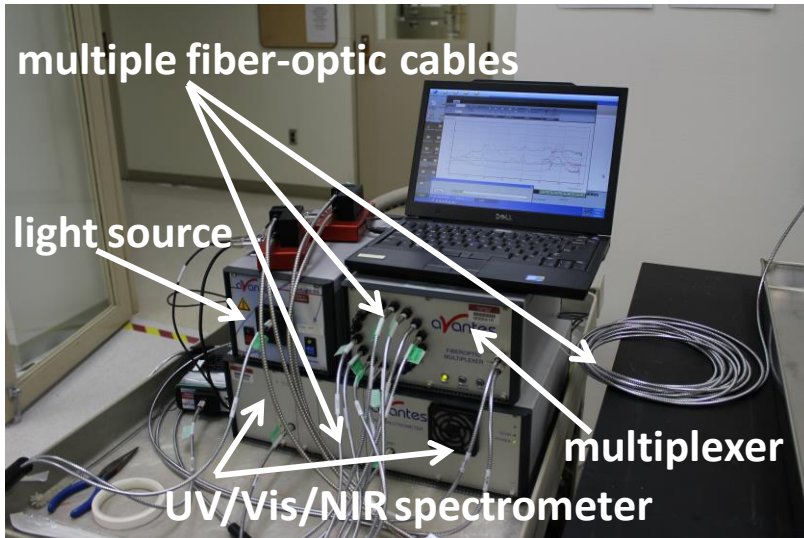
*concentrations in Molar units



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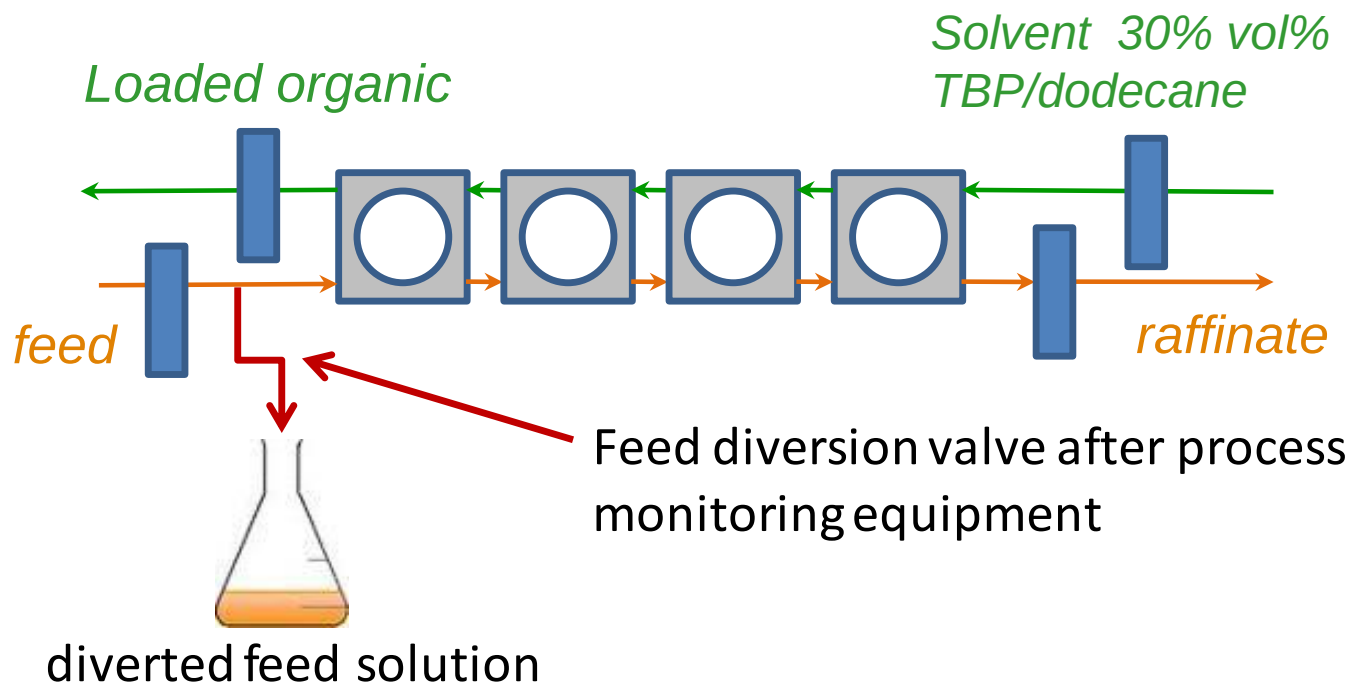
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Vis-NIR and Raman Multiplexer allows for multiple, simultaneous sensor locations on contactor system





Centrifugal contactor: *flow diversion experiment*



► *test conditions*

- centrifugal contactors; 2-cm, 3600 rpm
- Aqueous phase: 11 mL/min
- Organic phase: 11 mL/min

• *Diversion experiment*

- 3 mL/min of feed during flow test

- Spectroscopic probes and flow meters attached to feed, raffinate, and organic product streams

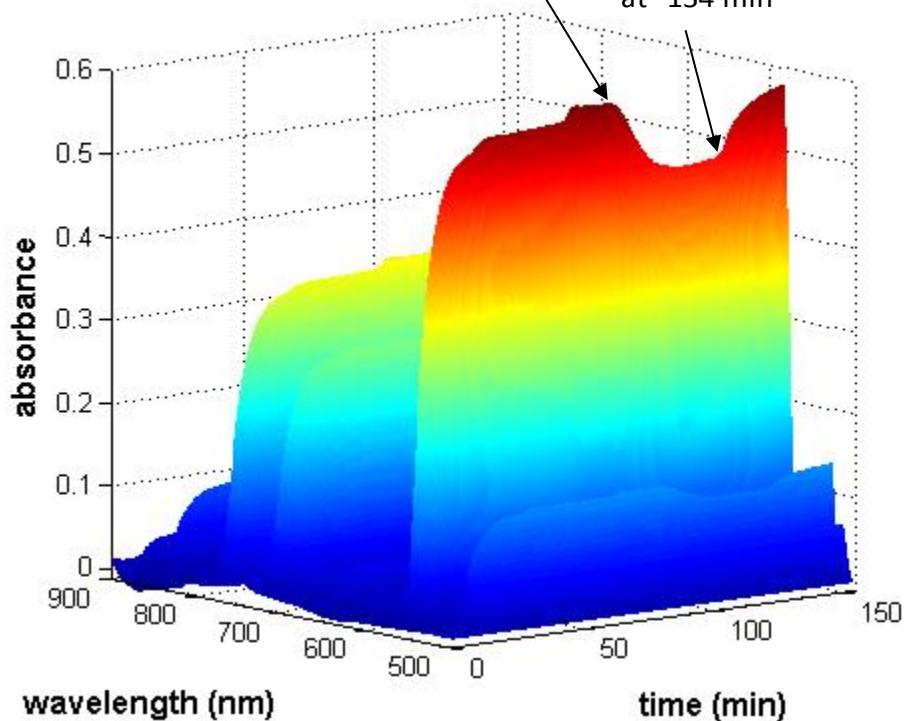


Spectroscopic measurements for diversion detection

organic product (TBP/dodecane) phase

diversion of 3 ml/min
started at 87 min

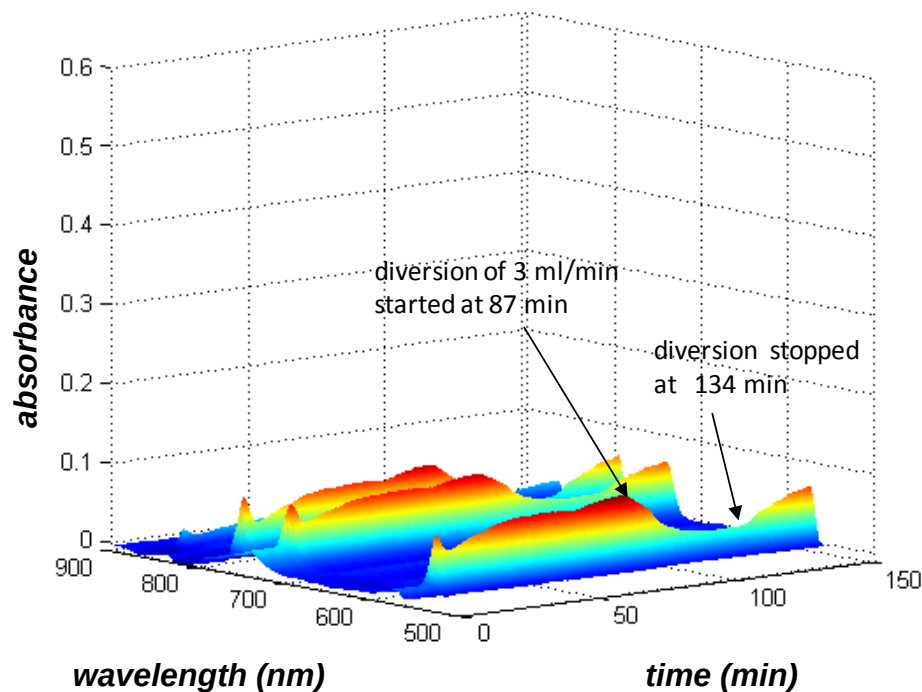
diversion stopped
at 134 min



raffinate (aqueous) phase

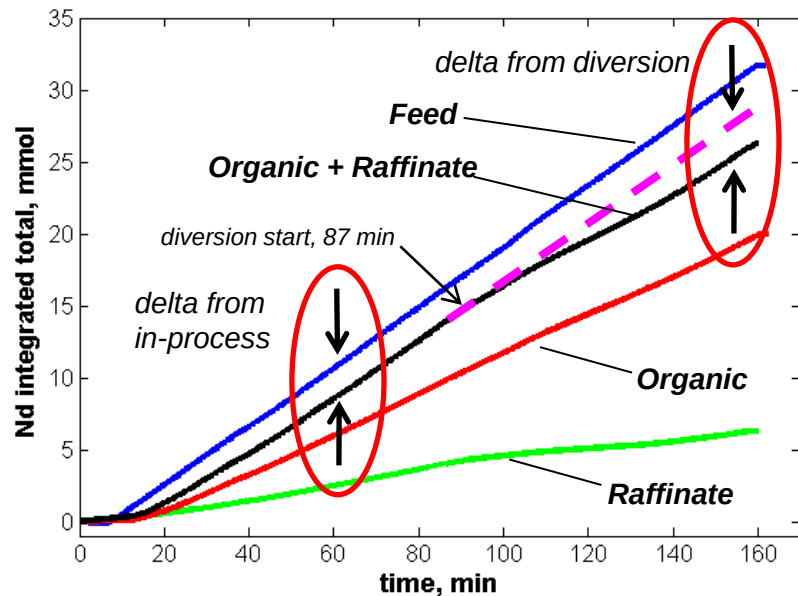
diversion of 3 ml/min
started at 87 min

diversion stopped
at 134 min





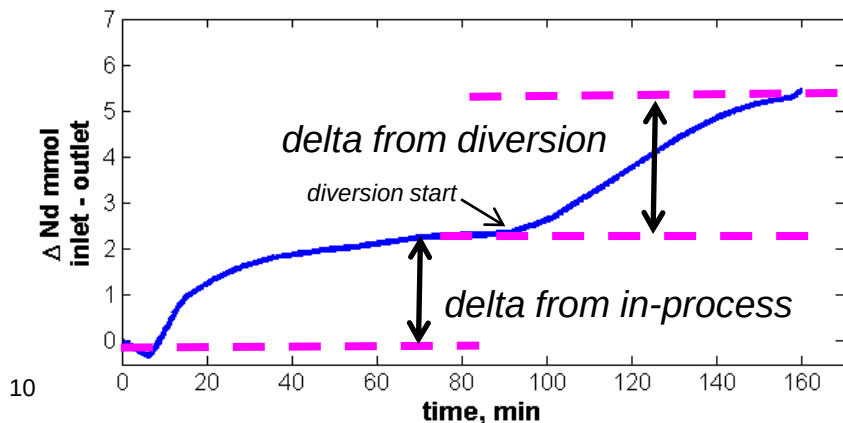
Diversion quantification: mass flow plus spectroscopic measurement



Excellent agreement between process monitor and mass balance measurements

$2.9 \times 10^{-3} \text{ mol Nd}^{3+}$ diverted based on mass balance

$3.0 \times 10^{-3} \text{ mol Nd}^{3+}$ diverted based on process monitor analysis



delta from diversion

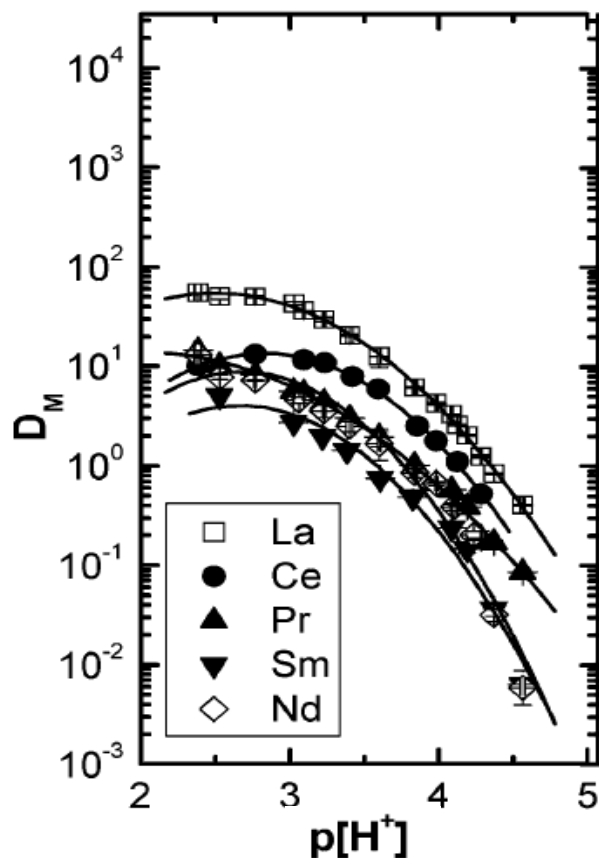




Motivation for weak acid (pH 2 – 6) measurements using spectroscopic signatures

Aqueous phase: 1 M total NO_3^- , 1 mM total $[\text{Ln}] + [\text{Y}]$,
1 M lactic acid, 0.05 M DTPA at various acidity.

Organic phase: 0.5 M HDEHP in 1,4-DIPB



- *pH control is critical in TALSPEAK separations*
- *spectroscopic determination of pH desirable*
- *Simultaneous spectroscopic determination of lanthanides also desirable*
- *activities coordinated with Sigma Team for Minor Actinide Separations*



pH monitoring: Weak Acid Measurements

■ TALSPEAK and Advanced-TALSPEAK as Model Systems

■ Raman Spectroscopic measurements for pH monitoring

Lactic acid system

- Lactate, 0.25 - 1.0 M
- Ionic Strength, 0.5 - 3.0 M
- pH = 1.2 - 5

Citric acid system

- Citrate, 0.1 - 1.0 M
- Ionic Strength, 0.5 - 3.0 M
- pH = 1.2 - 6

■ Effects of lanthanides and stripping complexants in aqueous phase

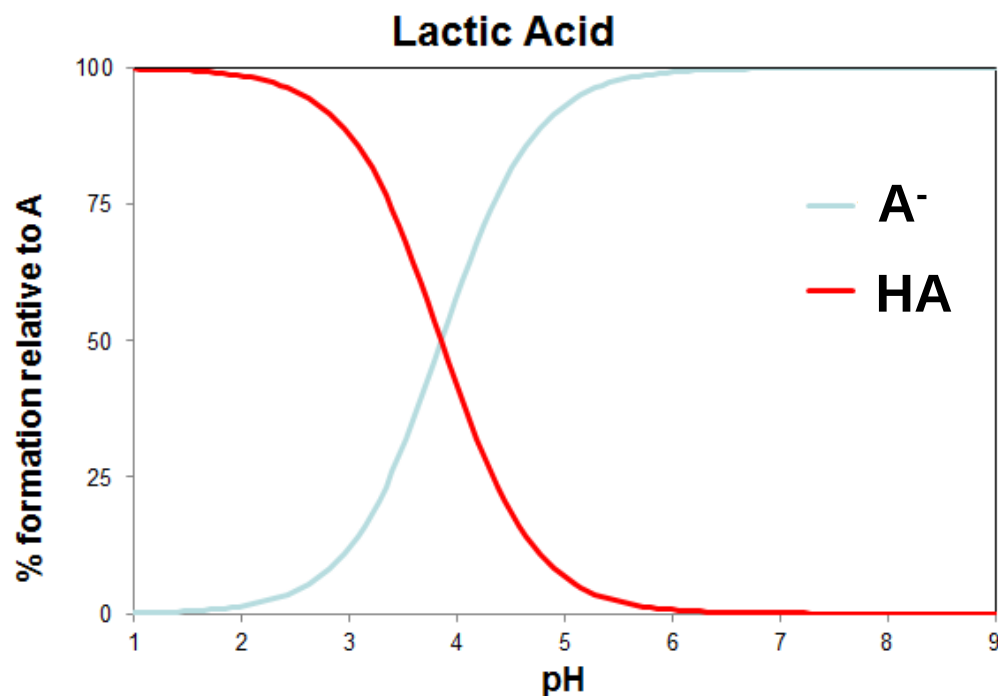
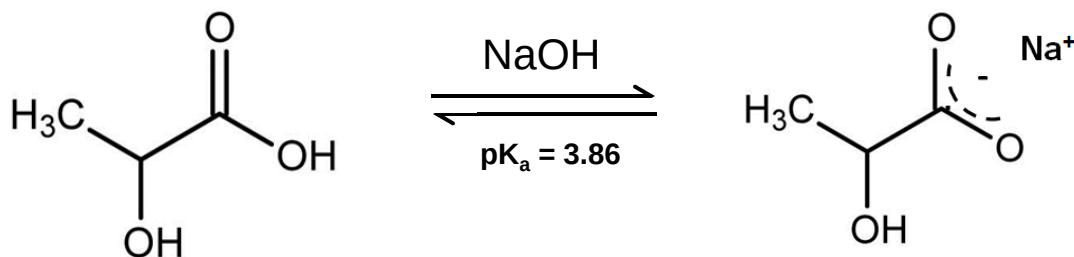
- DTPA, 0.01 – 0.05 M
- HEDTA, 0.05 – 0.25 M
- $[\text{Ln}]_{\text{tot}}$, ~ 20mM

■ Effects of complexants in organic phase

- HDEHP and HEH[EHP] / *n*-dodecane



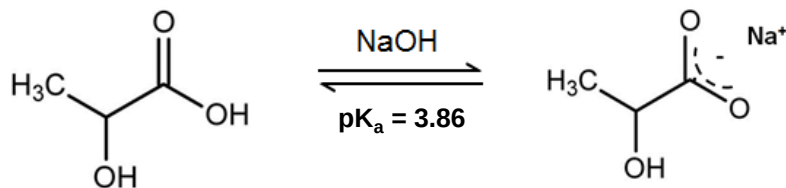
Lactic acid buffer system



- ▶ Carboxylate group modified by pH changes
 - free acid ($-CO_2H$) to anion ($-CO_2^-$)
 - Bending of $-COH$
- ▶ Can be used as spectroscopic probe of system pH

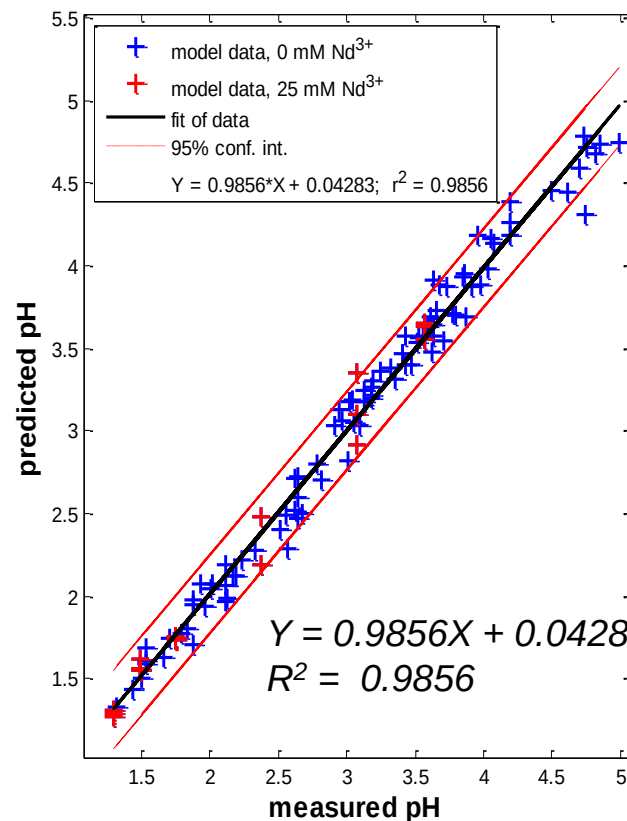
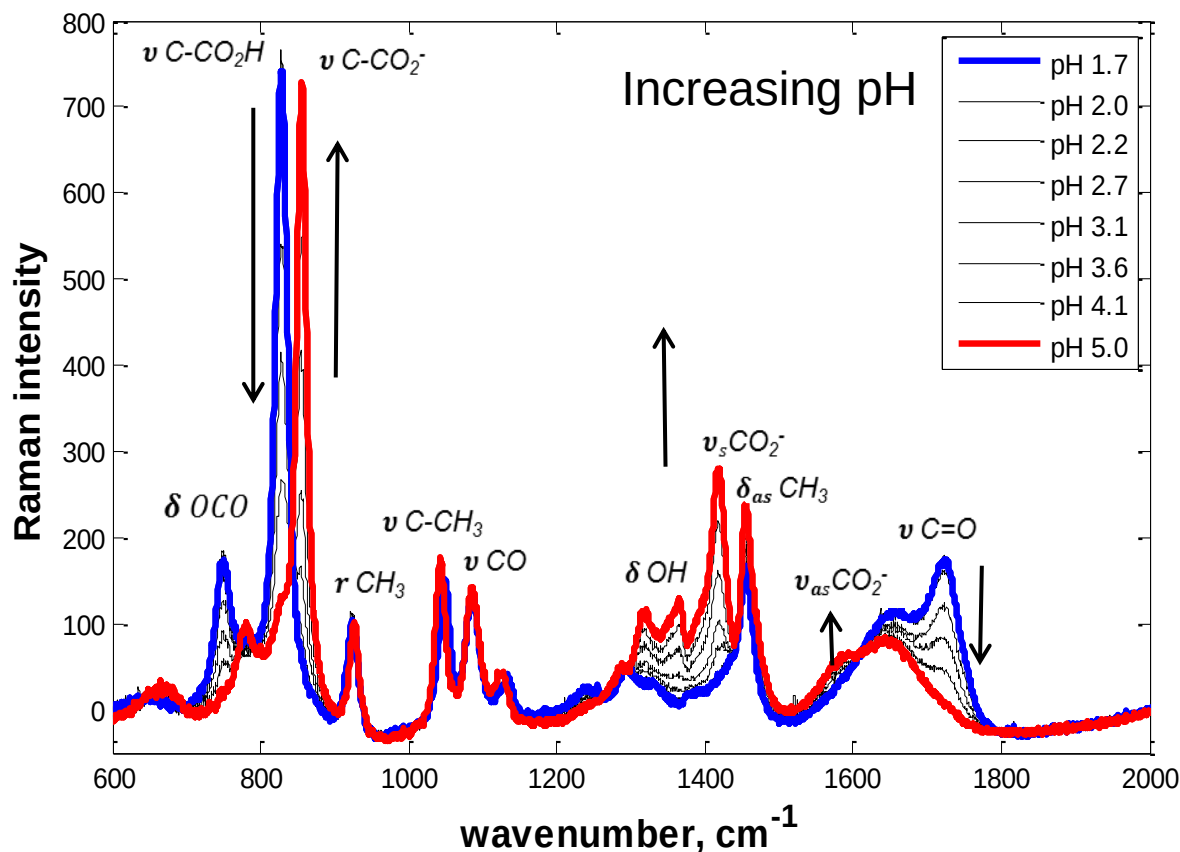


pH monitoring: Weak Acid Measurement trend with increasing pH



Carboxylate effects

■ free acid (-CO₂H) to anion (-CO₂⁻)

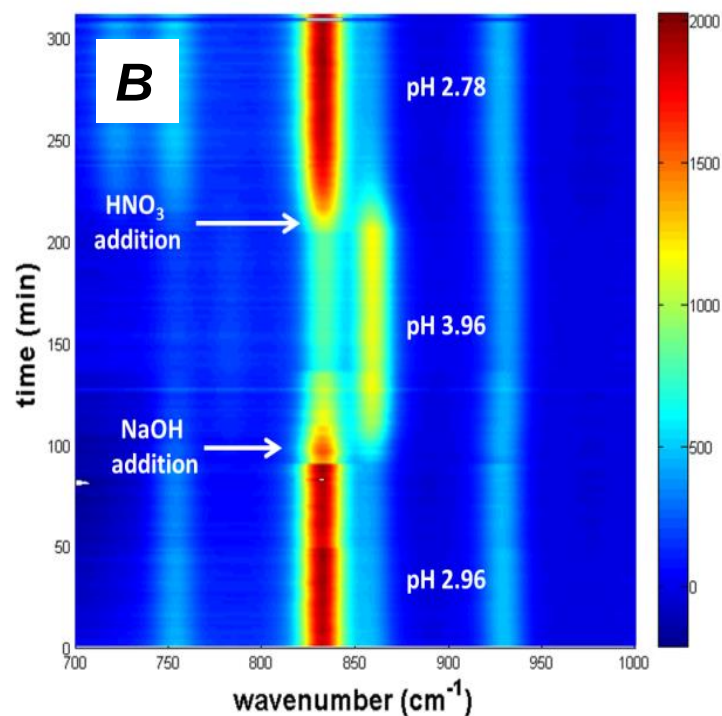
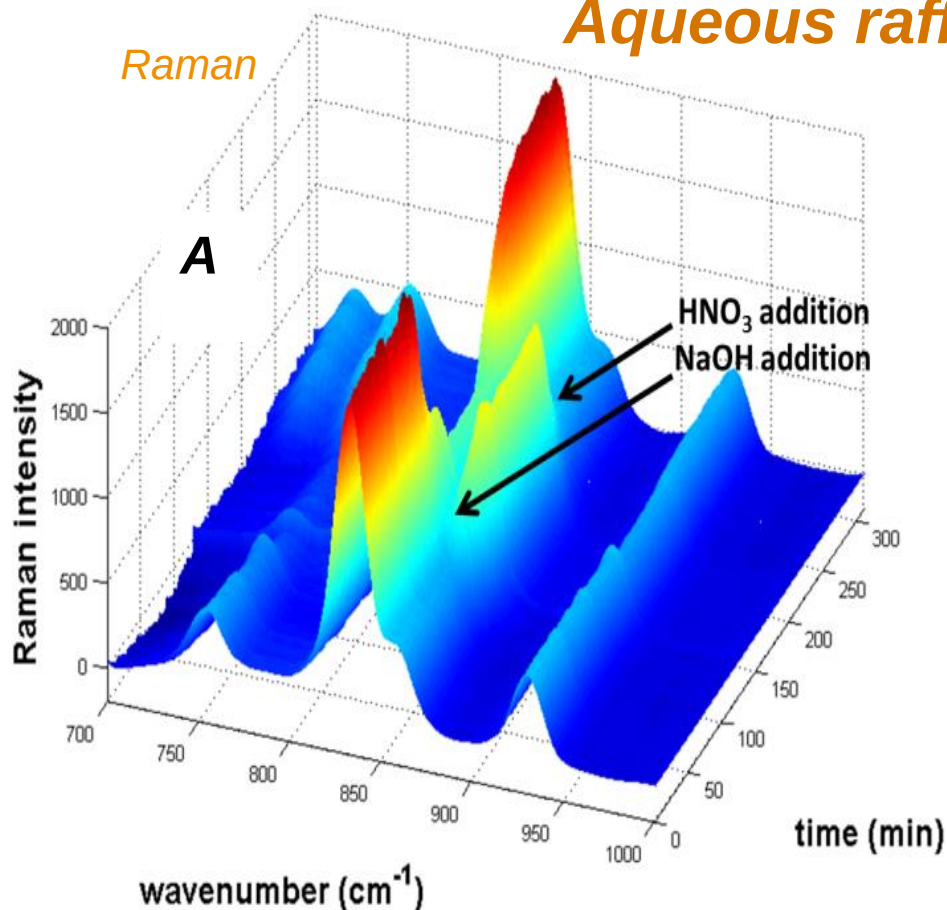




pH Results based on Raman Spectroscopy

Aqueous raffinate

Raman

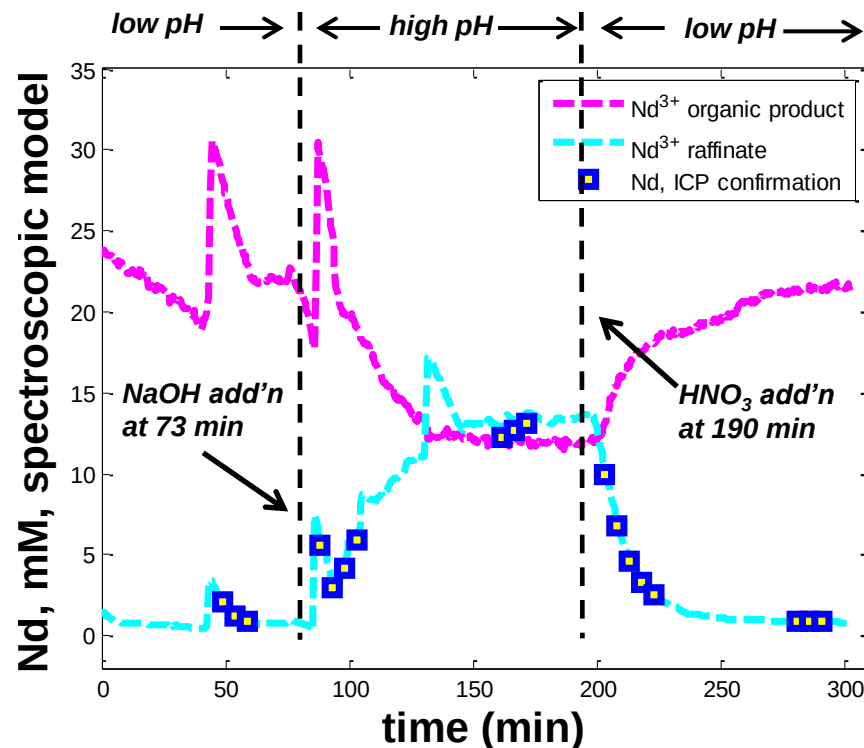
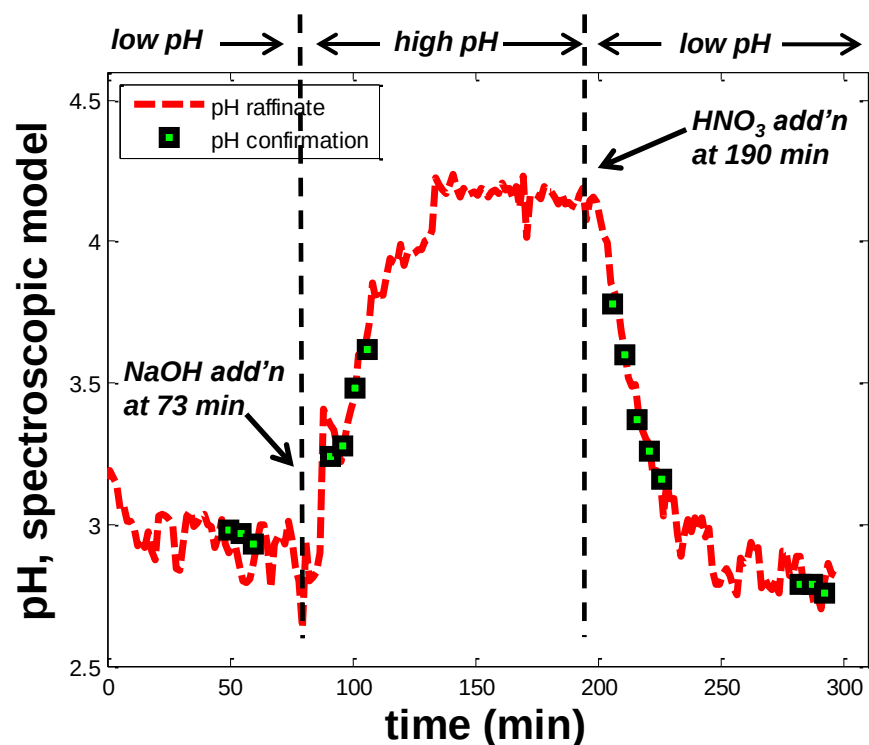




pH and Nd³⁺ successfully monitored by Raman and vis-NIR spectroscopy during flow contactor test

The change in Nd³⁺ extraction was successfully monitored in both raffinate and organic product phases when the pH was modified with NaOH and HNO₃ additions.

When pH was increased, the extraction of Nd³⁺ decreased, as predicted.





■ 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 HNO₃ concentrations, for both aqueous and organic phases*
 - *Vis/NIR for on-line monitoring of Np(V/VI), Pu(IV/VI), Nd(III)*

■ Demonstrated mass balance in on-line contactor system using spectroscopic process monitoring

- During real-time centrifugal contactor TBP/dodecane extraction
- Diversion of feed was quantitatively detected within contactor system
- pH monitoring and simultaneous Ln (Nd³⁺) monitoring demonstrated with TALSPEAK system

■ Future plans for on-line process monitoring

- Collaborative demonstration on commercial (larger) scale :
 - *H-Canyon (SRS), others*



■ U.S. Department of Energy (DOE)

- Fuel Cycle Research and Development (FCR&D), Separations Campaign (NE)
- NNSA Office of Nonproliferation and International Security (NA-24)

■ PNNL's Sustainable Nuclear Power Initiative (SNPI)