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# SPECTROSCOPIC ON-LINE MONITORING OF RADIOCHEMICAL STREAMS

## NEET Review
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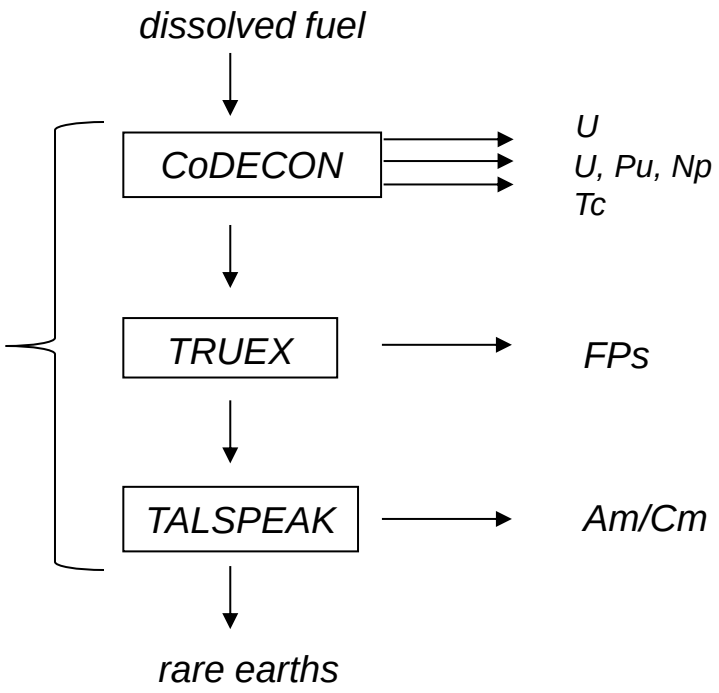
# Process Monitoring Can Be Achieved Throughout the Flowsheet




*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*

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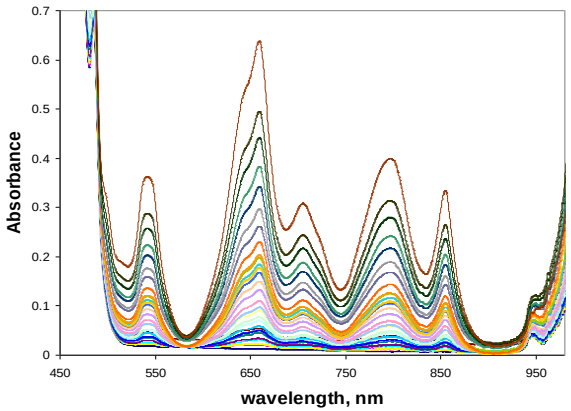
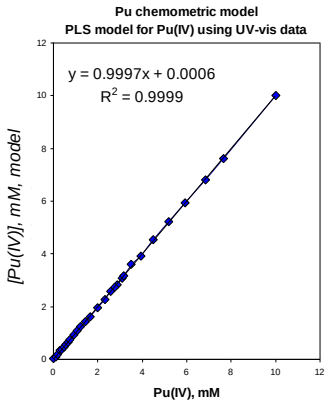
# Methodology for on-line process monitor development: from proof-of-concept to final output

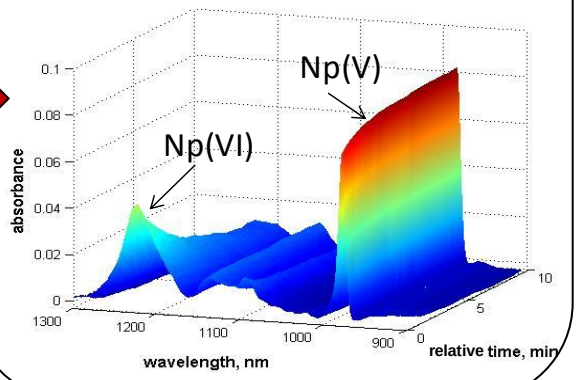
## *Static measurements: Model training database*



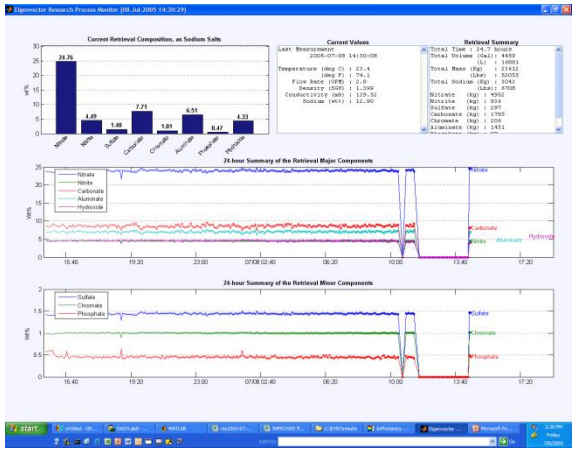

## *Chemometric model development*




## *On-line model verification and translation*




## *Real-time on-line concentration data display*



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

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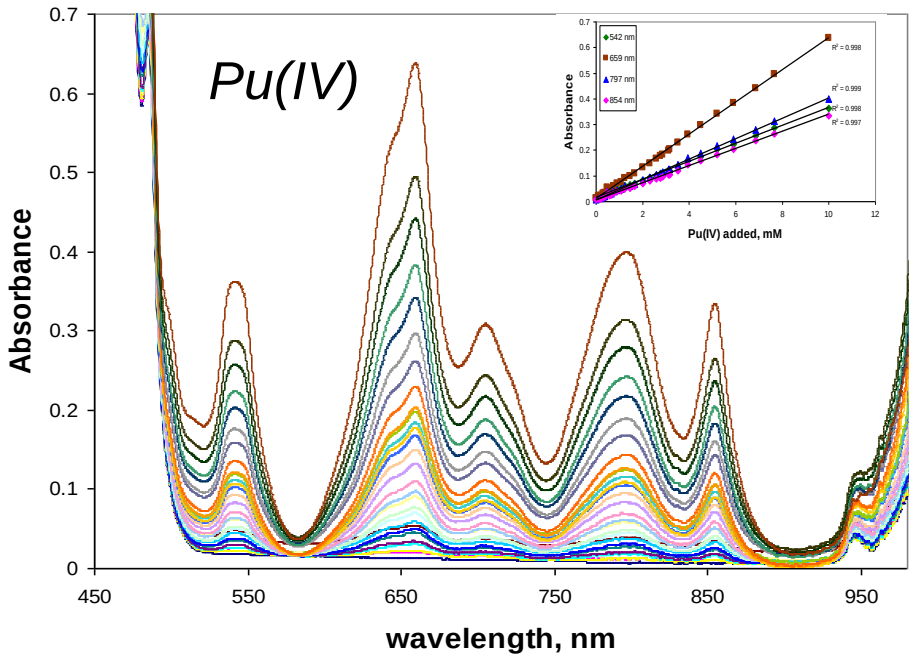
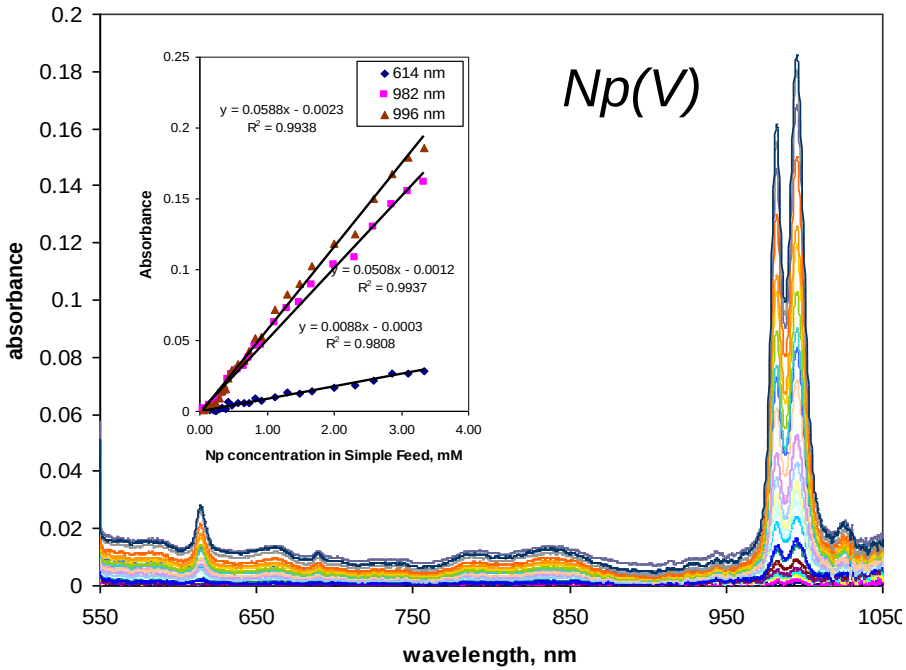
# Vis-NIR measurements for Pu and Np model development

- *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 $UO_2(NO_3)_2$ in 0.8 M $HNO_3$*
- *$UO_2(NO_3)_2$ does not interfere with Pu(IV) measurements*

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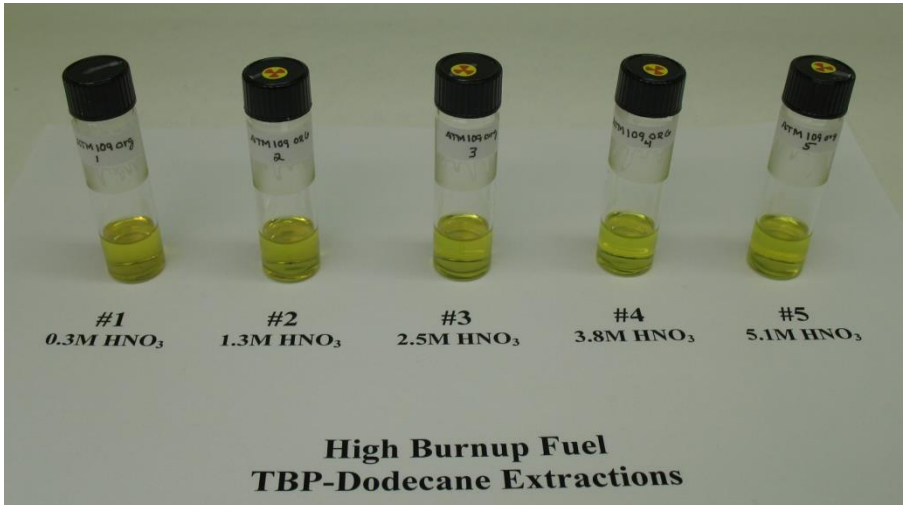
# Proof-of-Concept : Applicability of spectroscopic methods for commercial BWR ATM-109 fuel measurements

- **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* |
|---|---|---|---|---|
| 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

*Bryan et al. Radiochim. Acta, 2011.*

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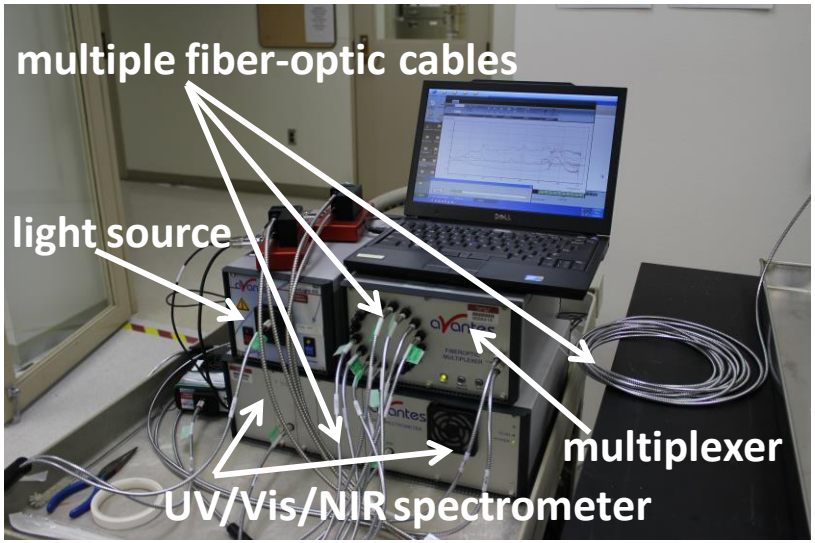
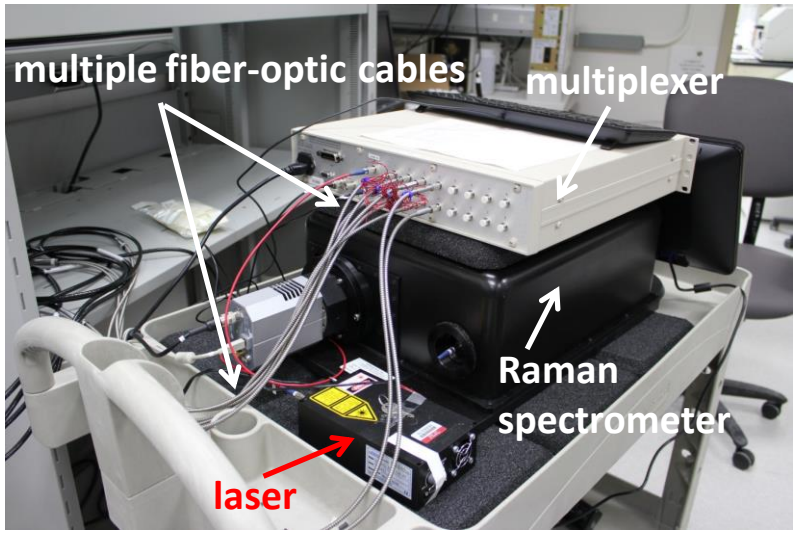
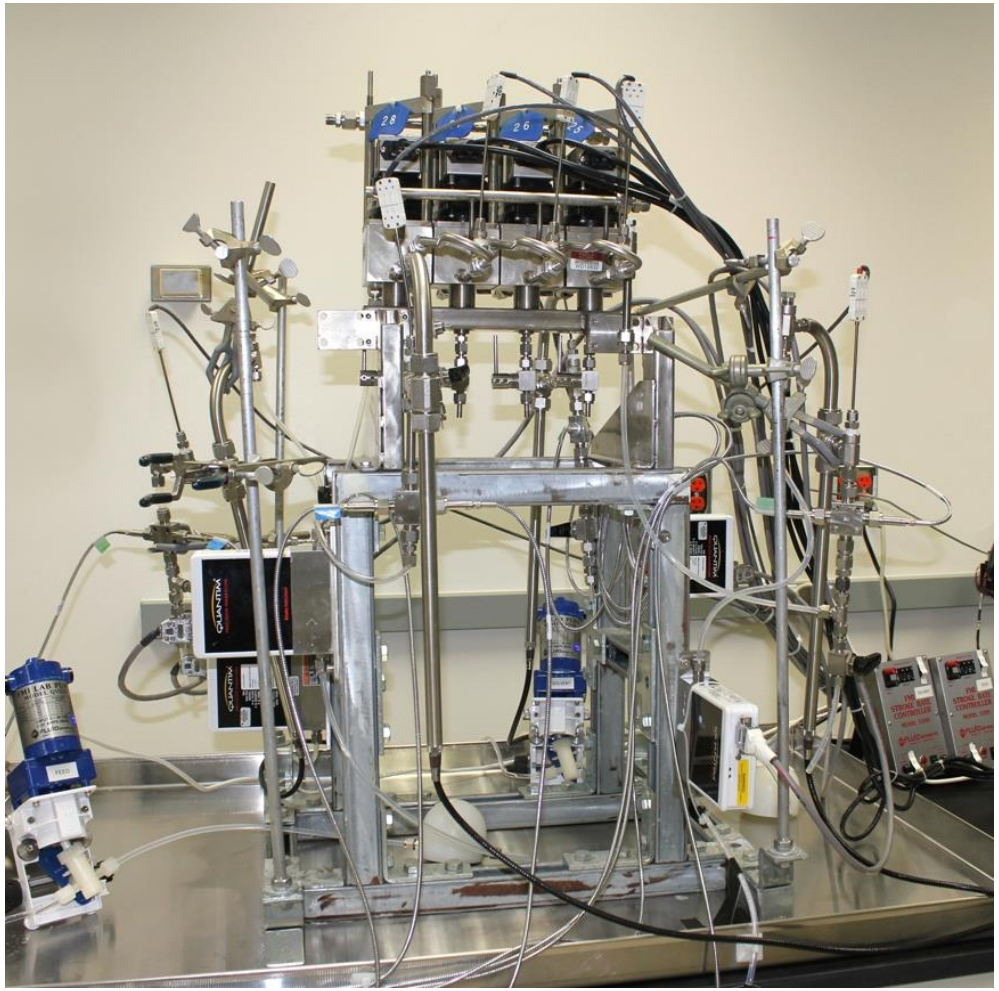
# Vis-NIR and Raman Multiplexer allows for multiple, simultaneous sensor locations on contactor system



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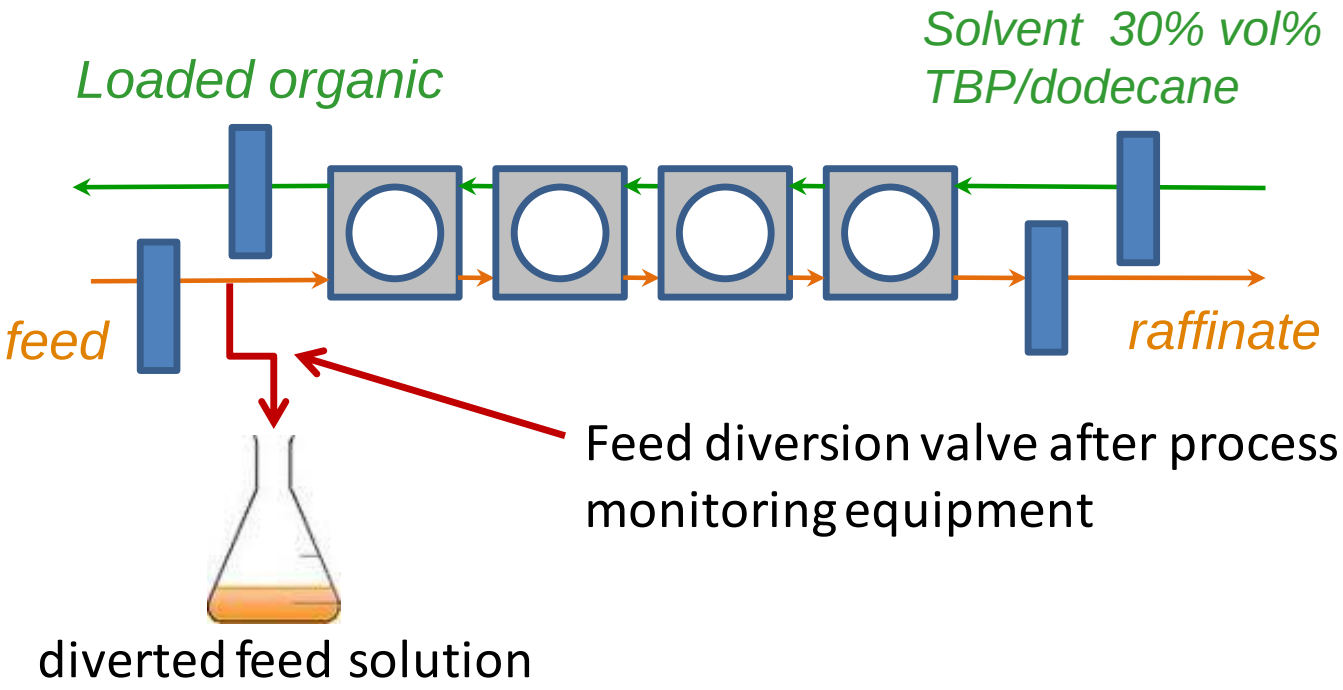
# Centrifugal contactor: *flow diversion experiment*




## *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*

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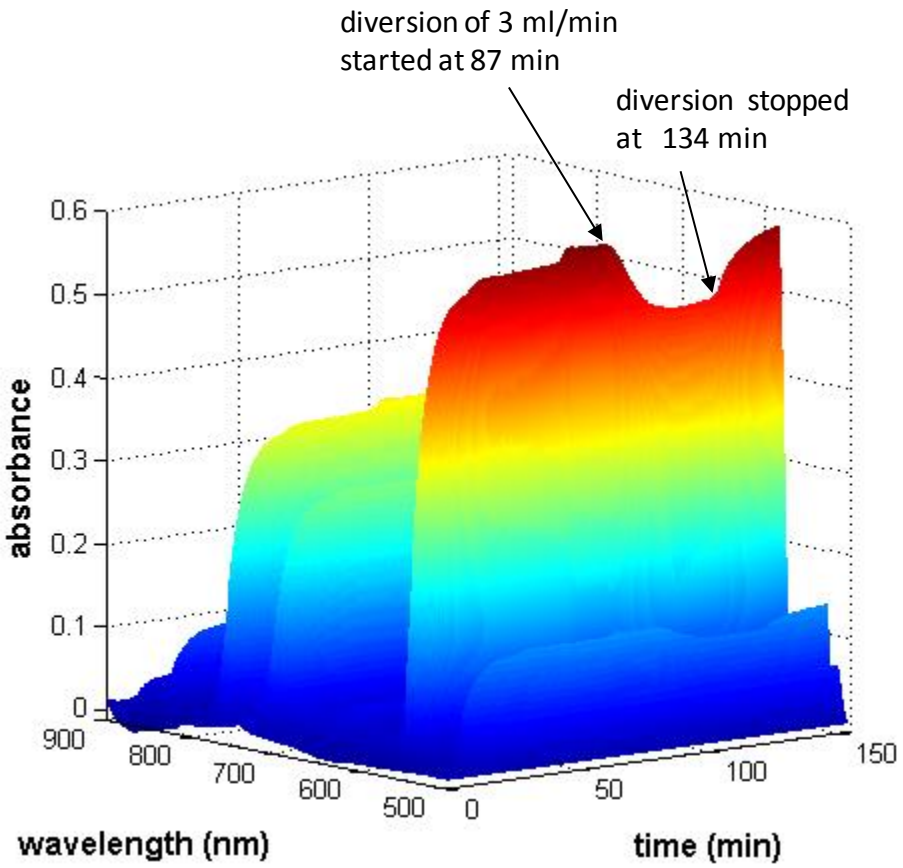
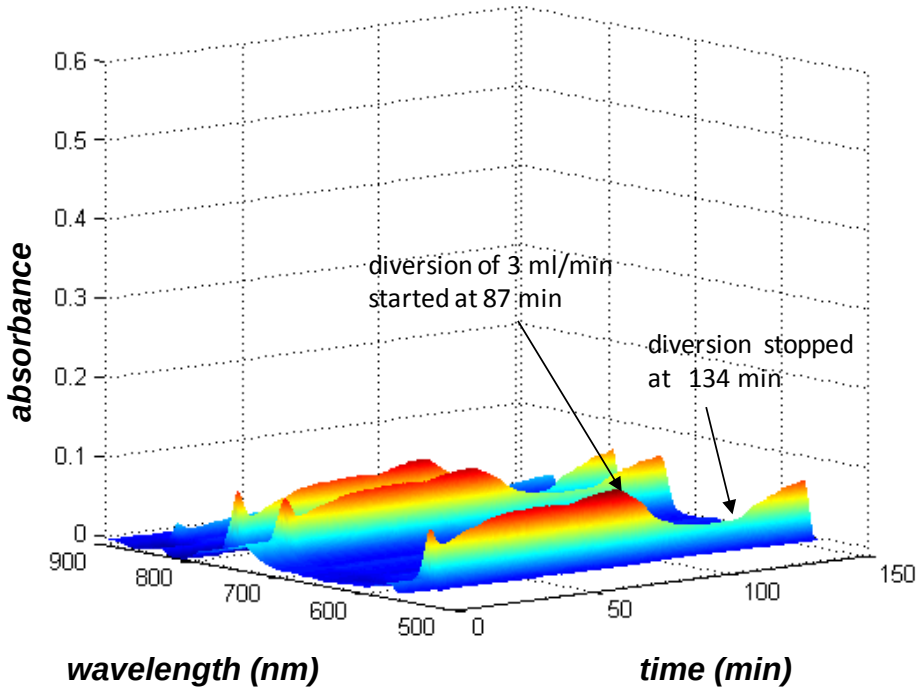
# Spectroscopic measurements for diversion detection

***organic product (TBP/dodecane) phase***




***raffinate (aqueous) phase***



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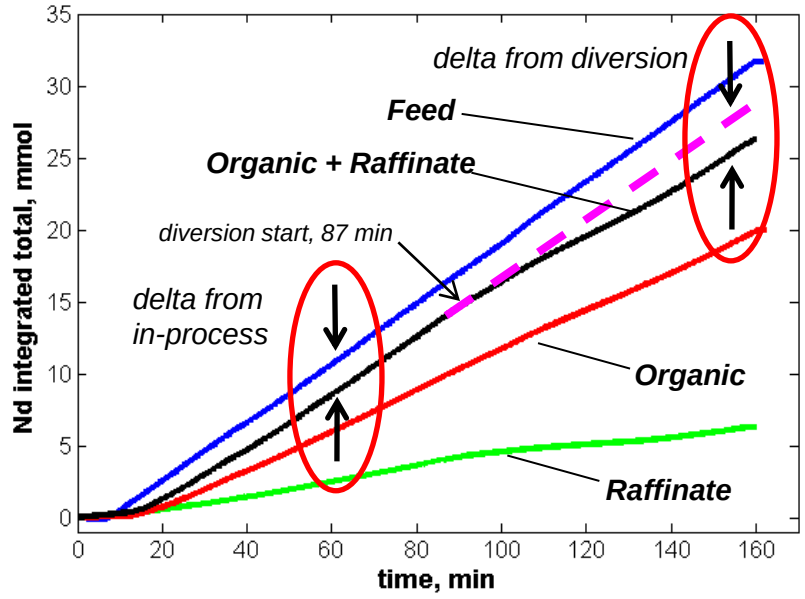
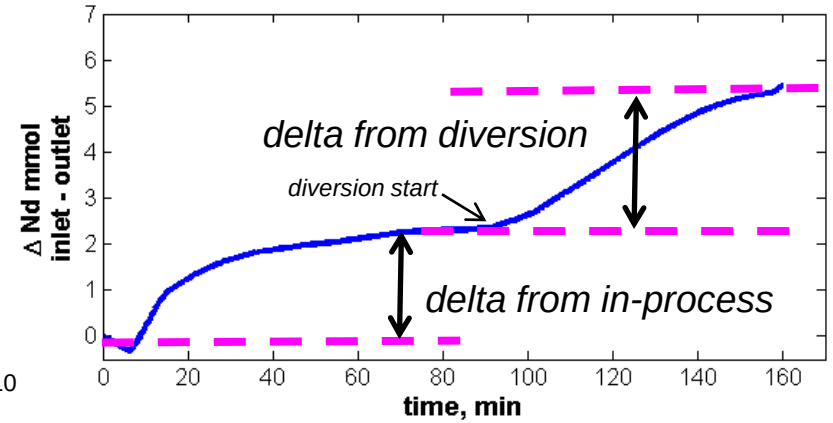
# Diversion quantification: mass flow plus spectroscopic measurement




***Excellent agreement between process monitor and mass balance measurements***

***2.9 x 10$^{-3}$ mol Nd$^{3+}$*** *diverted based on mass balance*

***3.0 x 10$^{-3}$ mol Nd$^{3+}$*** *diverted based on process monitor analysis*

***delta from diversion***

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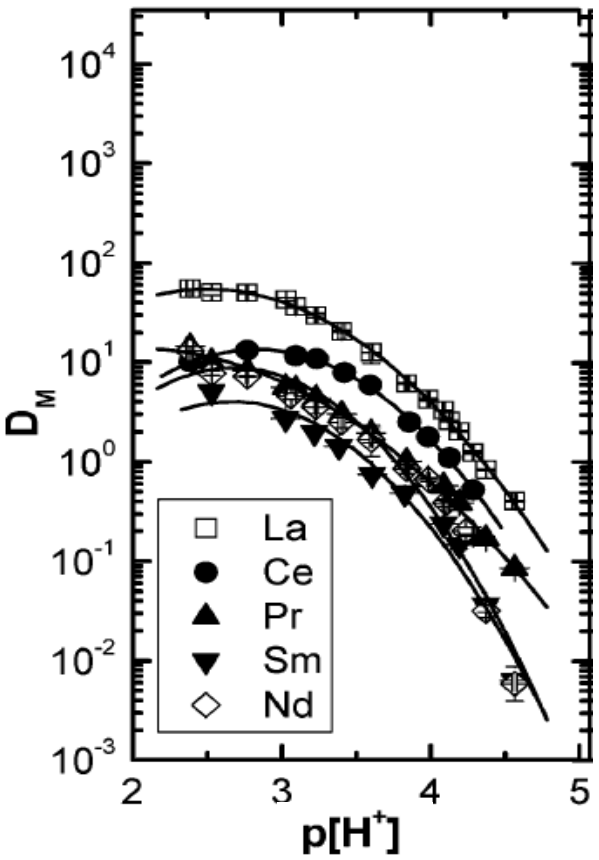
# Motivation for weak acid (pH 2 – 6) measurements using spectroscopic signatures

**Aqueous phase: 1 M total $NO_3^-$, 1 mM total [Ln] + [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*

*Nilsson and Nash, Solv. Extr. Ion Exch., 27, 354-377, 2009*

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# pH monitoring: Weak Acid Measurements

- **TALSPEAK and Advanced-TALSPEAK as Model Systems**
- **Raman Spectroscopic measurements for pH monitoring**

***Lactic acid system***

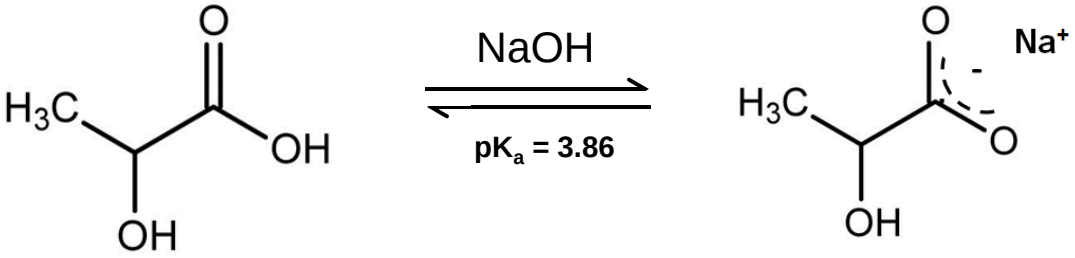
- *Lactate, 0.25 - 1.0 M*
- *Ionic Strength, 0.5 - 3.0 M*
- *pH = 1.2 - 5*

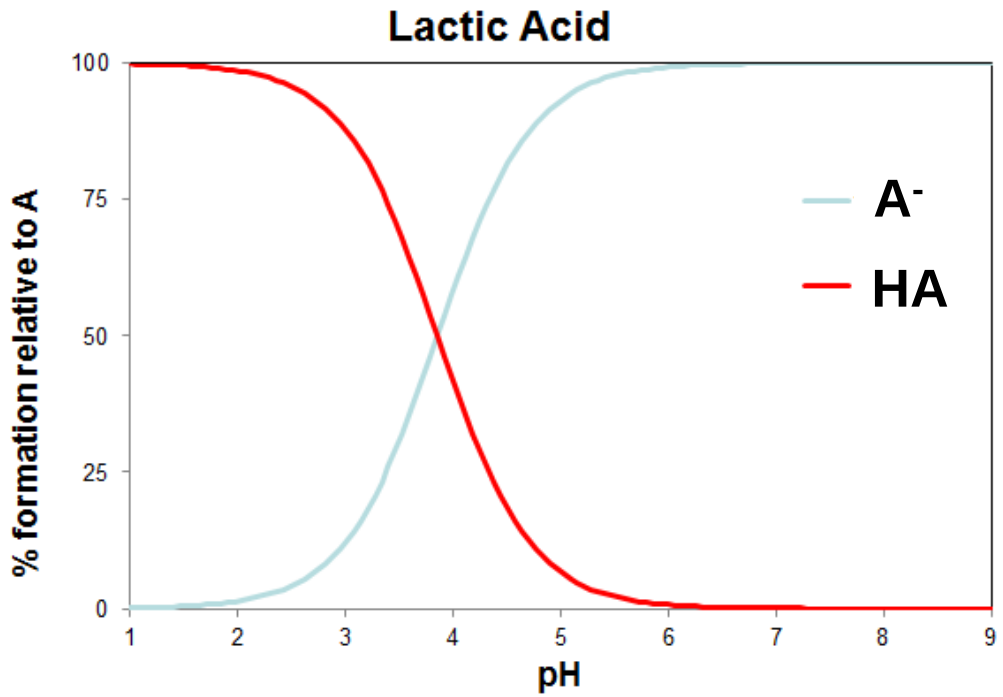
***Citric acid system***

- *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
  - $[Ln]_{tot}$, ~ 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

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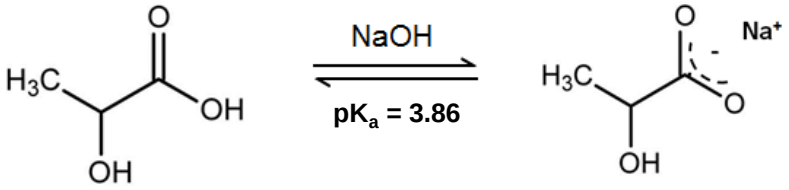
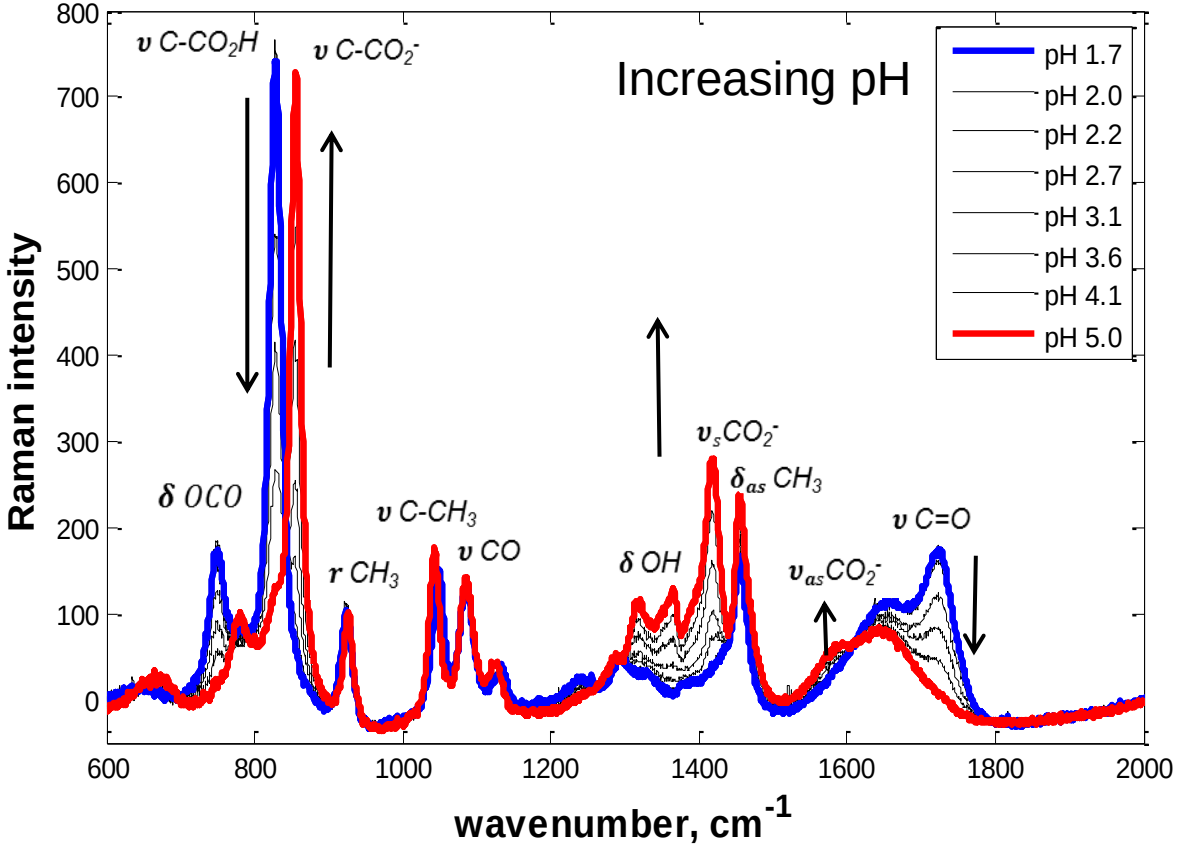
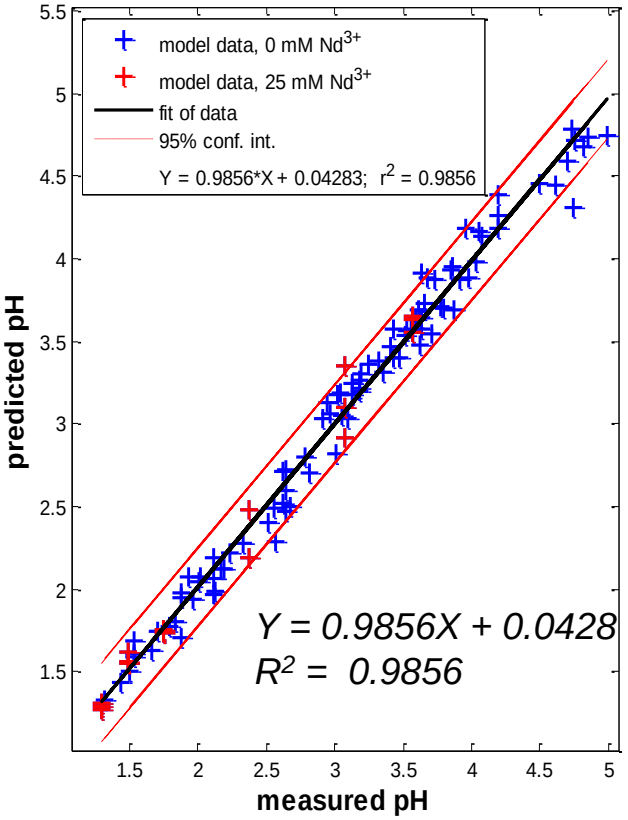
# pH monitoring: Weak Acid Measurement trend with increasing pH




## Carboxylate effects

- free acid (-$CO_2H$) to anion (-$CO_2^-$)



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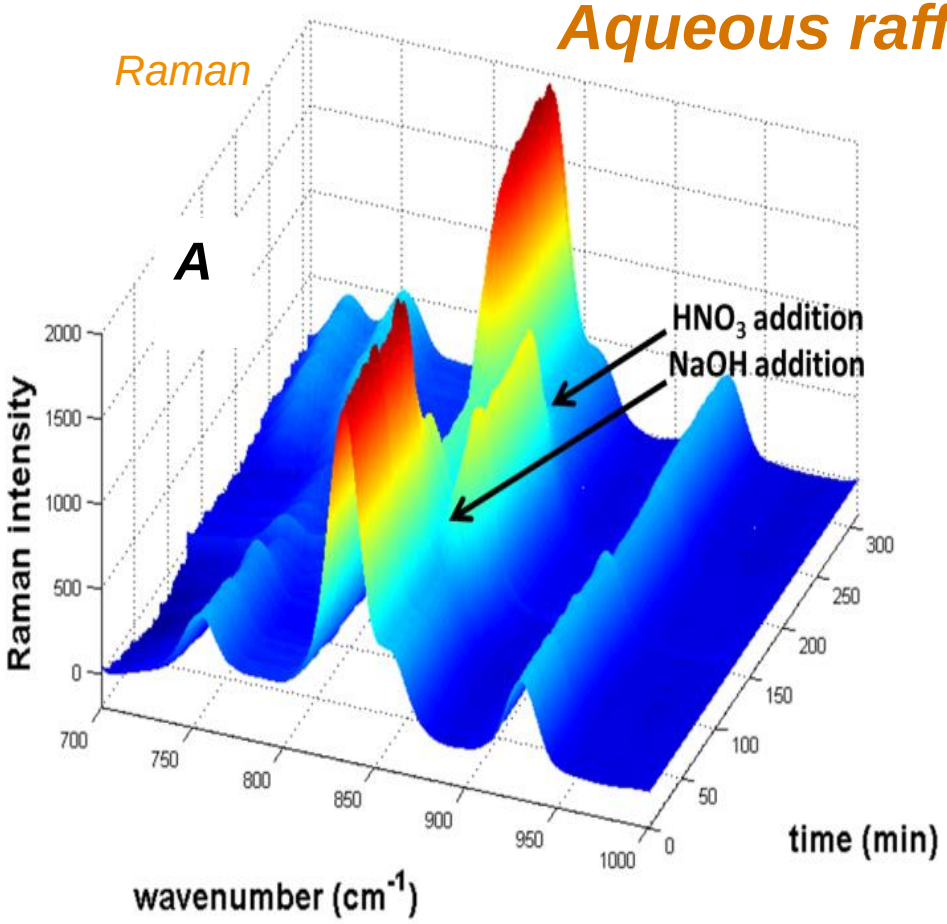
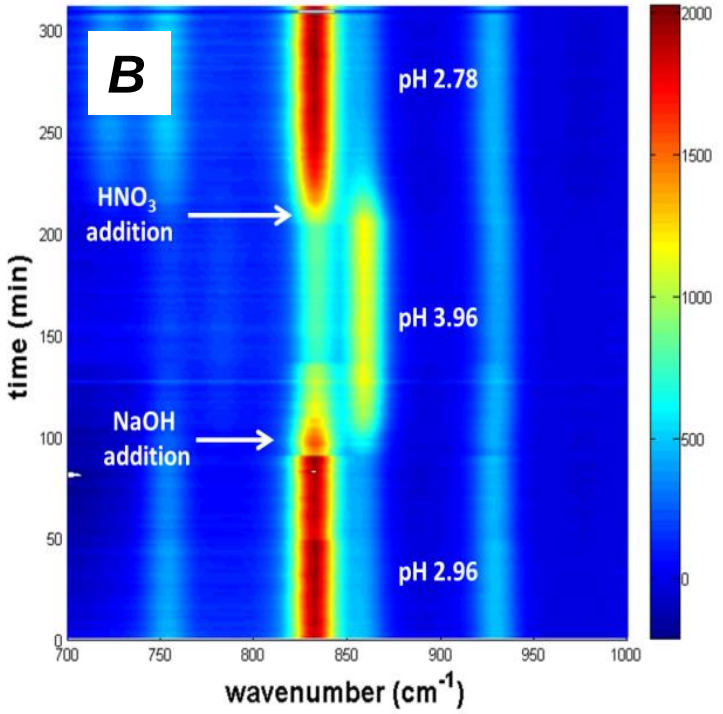
# pH Results based on Raman Spectroscopy

## *Aqueous raffinate*

*Raman*



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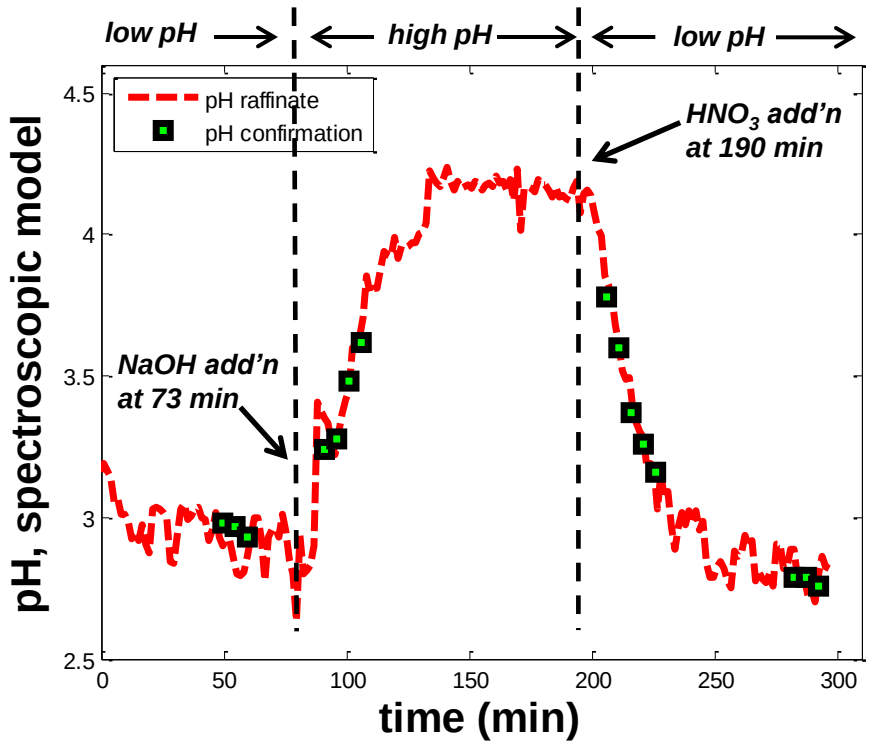
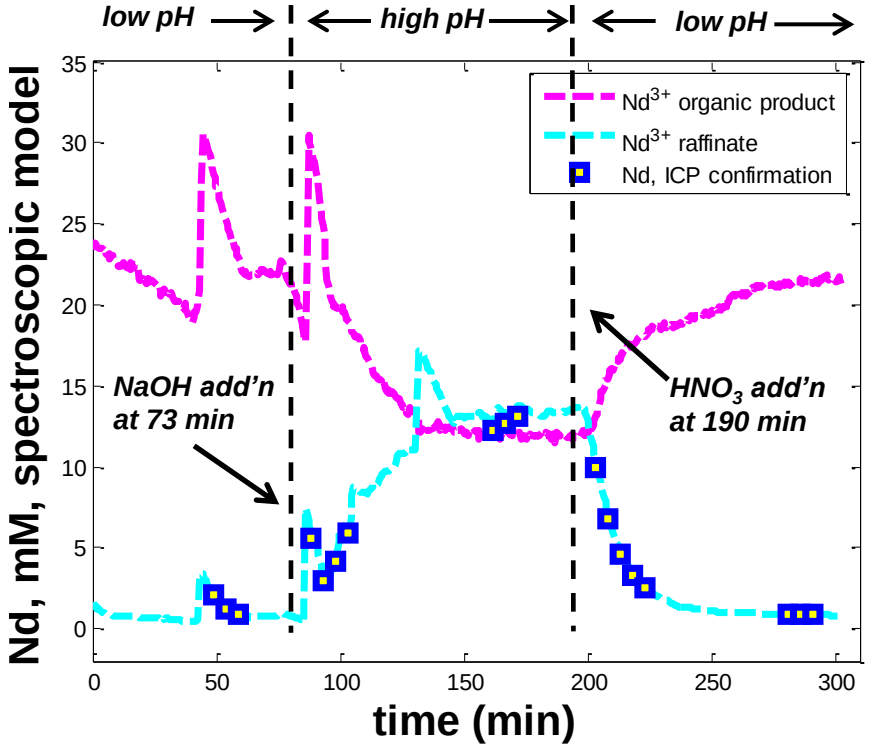
# pH and Nd3+ successfully monitored by Raman and vis-NIR spectroscopy during flow contactor test

*The change in $Nd^{3+}$ extraction was successfully monitored in both raffinate and organic product phases when the pH was modified with NaOH and $HNO_3$ additions.*

*When pH was increased, the extraction of $Nd^{3+}$ decreased, as predicted.*



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# 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 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 ($Nd^{3+}$) monitoring demonstrated with TALSPEAK system

- **Future plans for on-line process monitoring**
  - Collaborative demonstration on commercial (larger) scale :
    - *H-Canyon (SRS), others*

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# Acknowledgements


- **U.S. Department of Energy (DOE)**
  - Fuel Cycle Research and Development (FCR&D), Separations Campaign (NE)
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- **PNNL's Sustainable Nuclear Power Initiative (SNPI)**