Spectroscopic Based Process Monitor for Continuous Real-Time Analysis of High Level Radioactive Waste Components and Monitoring for Control and Safeguarding of Radiochemical Streams

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La Grande, Oregon
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Outline

- Background of Hanford Site
- Process Monitor for Continuous Real-Time Analysis of High Level Radioactive Waste Components
- Monitoring for Control and Safeguarding of Radiochemical Streams

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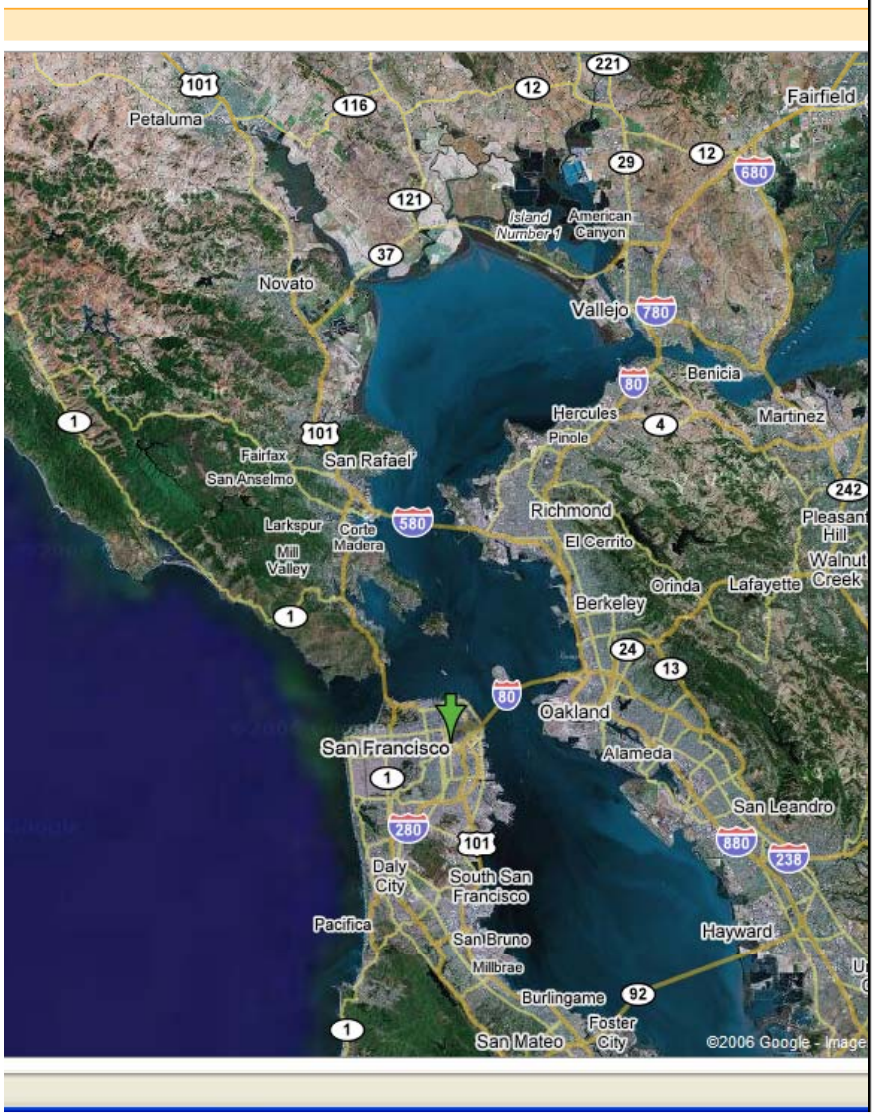
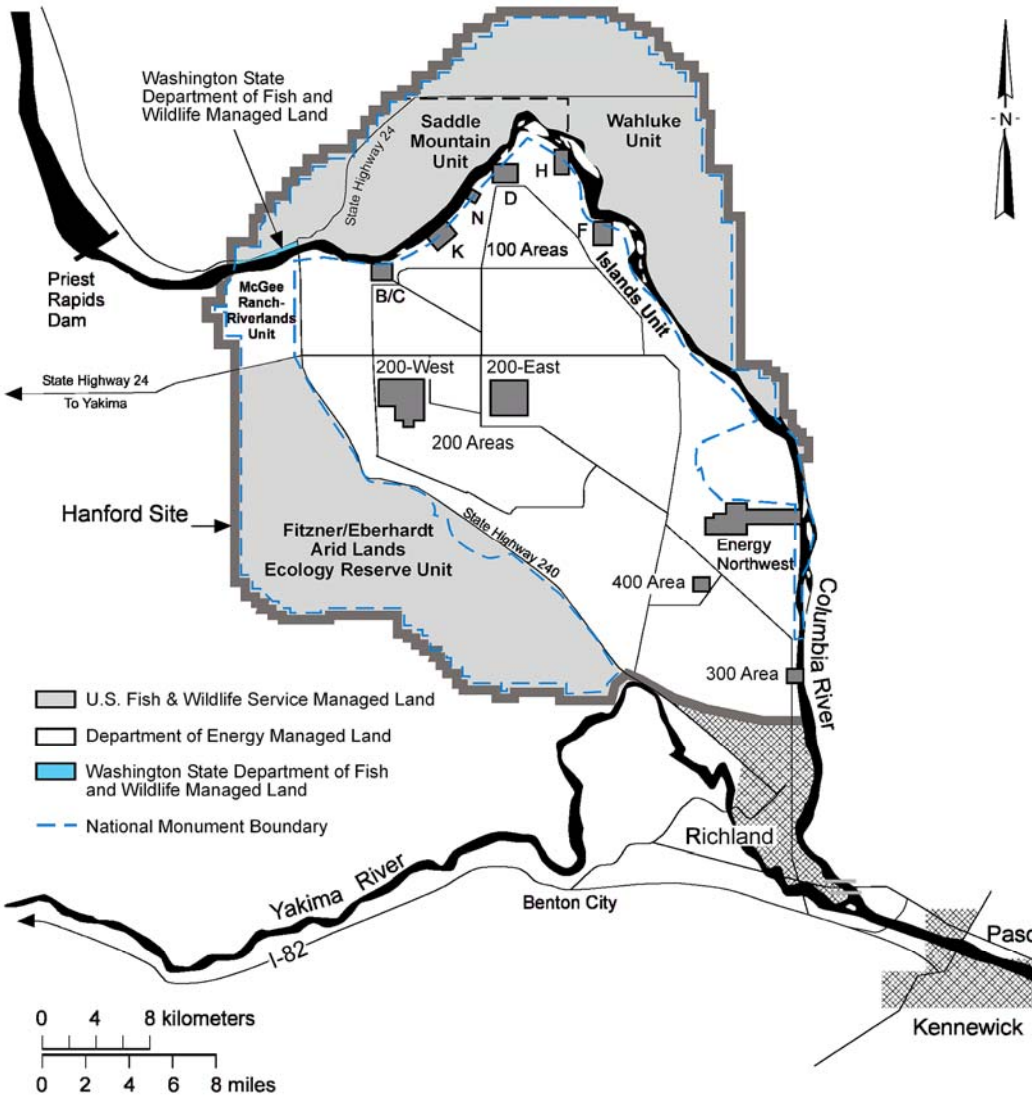
Hanford Site relative to San Francisco Bay Area

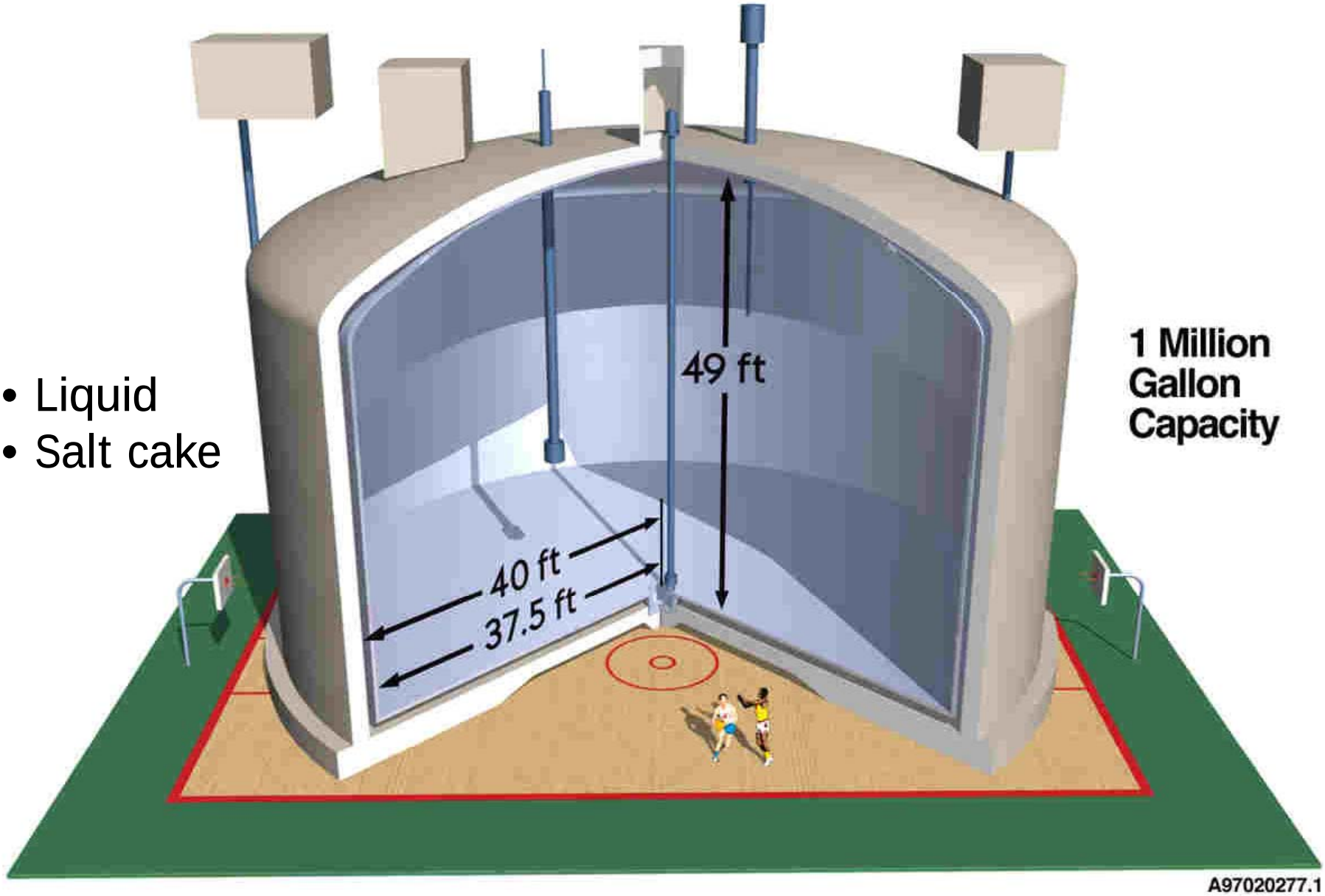
(same scale)



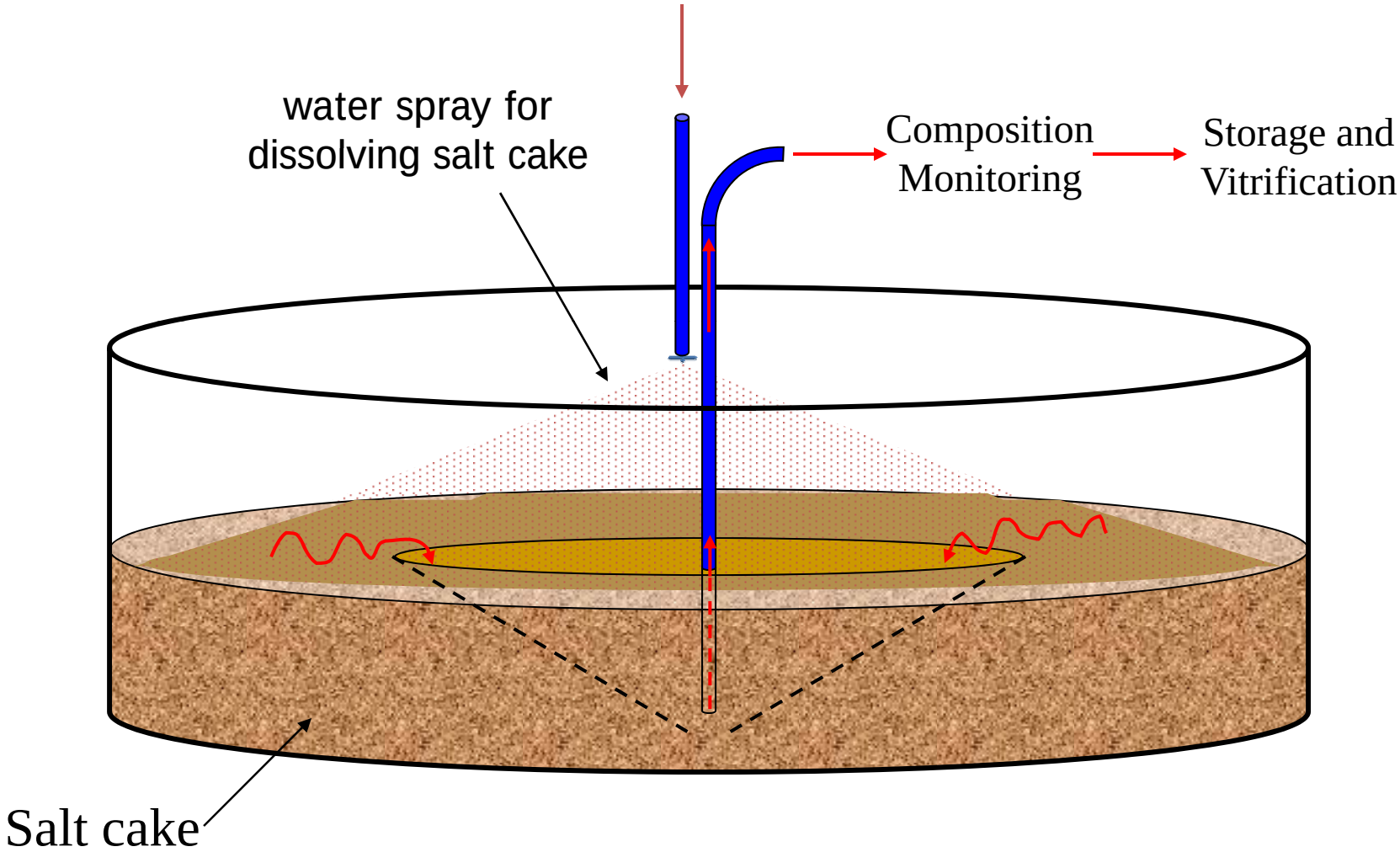


Hanford Double Shell Tank

- Liquid
- Salt cake



Waste Retrieval from Nuclear Waste Storage Tanks



Photograph of Interior of Single Shell Hanford Tank

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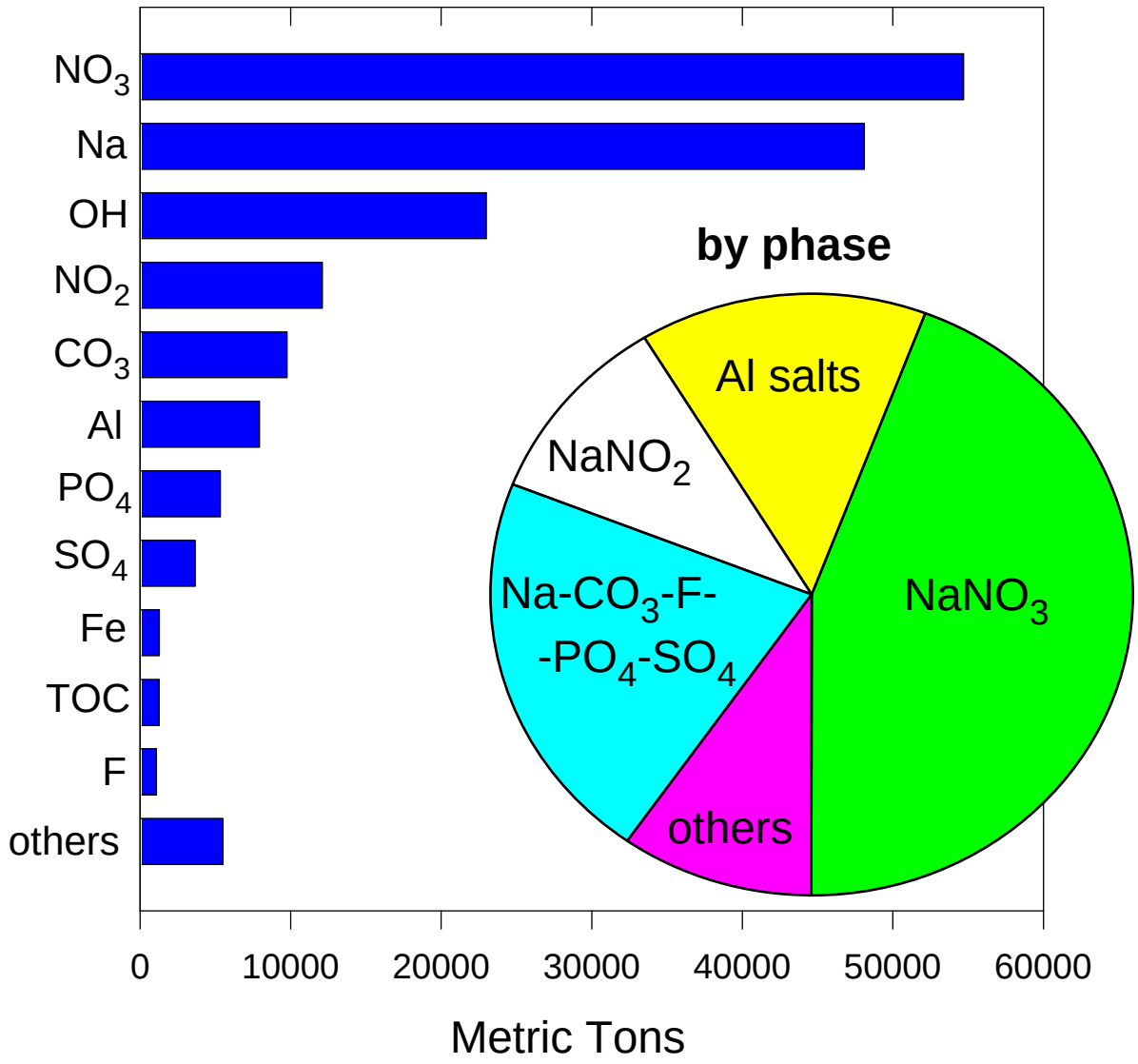
Tank Farm Chemical Inventory



Current Retrieval Capability

- Flow
- Gamma monitor
- Grab samples

On-line Real-time Process Monitor

- Continuous real-time monitoring of retrieval composition
  - Immediate status and composition of retrieval
  - Retrieval summary from start of processing
- Process monitor benefits process performance
  - cost savings
  - doesn't require personnel involvement to grab samples
  - doesn't interrupt continuous retrieval
  - easily adaptable for variable waste applications

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Process Monitor Features

- Instrumentation was configured for remote monitoring (spoolpiece, fiber optic, cables)
  - Coriolis and conductivity meters
    - Straight data readout; density, flow, conductivity
  - Raman
    - Output spectral files
- Methodology of data processing
  - Chemometric data treatment
  - Two independent chemometric models
    - Total sodium concentration (conductivity, density, temp)
    - 8 individual sodium salt concentrations (Raman spectra)

      NO_3^-, NO_2^-, PO_4^{3-}, CO_3^{2-}, CrO_4^{2-}, OH^-, SO_4^{2-}, $Al(OH)_4^-$
- Data acquisition
- Data storage-archiving
- Display
- MatLab-based software to process, store, and display data

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Measurements needed for the development of chemometric model

Raman signal, conductivity, and density depend upon:

- Solution composition and ionic strength
  - Measure solutions of individual Na salts and mixtures in wide concentration range
- Temperature
- Presence of bubbles and solid particulates

Instrument performance at variable flow rate

- Measure solutions in static mode and under variable flow rate

Acceptance Test:

- Verify chemometric model using early and late feed simulant solutions

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Static Measurements

- 86 solutions were prepared and measured by Raman, Coriolis, and conductivity sensors at room and several elevated temperatures.
- Solids as $Fe(OH)_3$ or bentonite were added to the selected solutions and measured.
- Preliminary chemometric model was developed using static measurements.
- Single component and multiple mixture standards used

component	concentration range
NO_3^-	4 – 40 wt%
NO_2^-,	3 – 34 wt%
PO_4^{3-},	1.5 – 15 wt%
CO_3^{2-},	1.5 – 15 wt%
CrO_4^{2-},	0.8 – 8 wt%
OH^-,	1 – 20 wt%
SO_4^{2-},	2 – 20 wt%
$Al(OH)_4^-$	0.8 – 8 wt%

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Flow Mesurements

- Total 6 flow tests were performed:
  - 5 tests used laboratory bench-top flow loop;
  - 1 test combined field manifold and laboratory flow loop.
- Flow rate studied; 2 - 20 GPM range.
- Temperature was varied from 15 to 50°C.
- N_2 Bubbles were introduced into flow system at controlled variable rates up to 6% of the solution flow rate.
- Effect of $Fe(OH)_3$ solids was studied; up to 1% solids loading.
- Revised Raman chemometric model incorporated flow measurements.
- Sodium model for prediction of total Na concentration was developed based on conductivity / density / temperature measurements.

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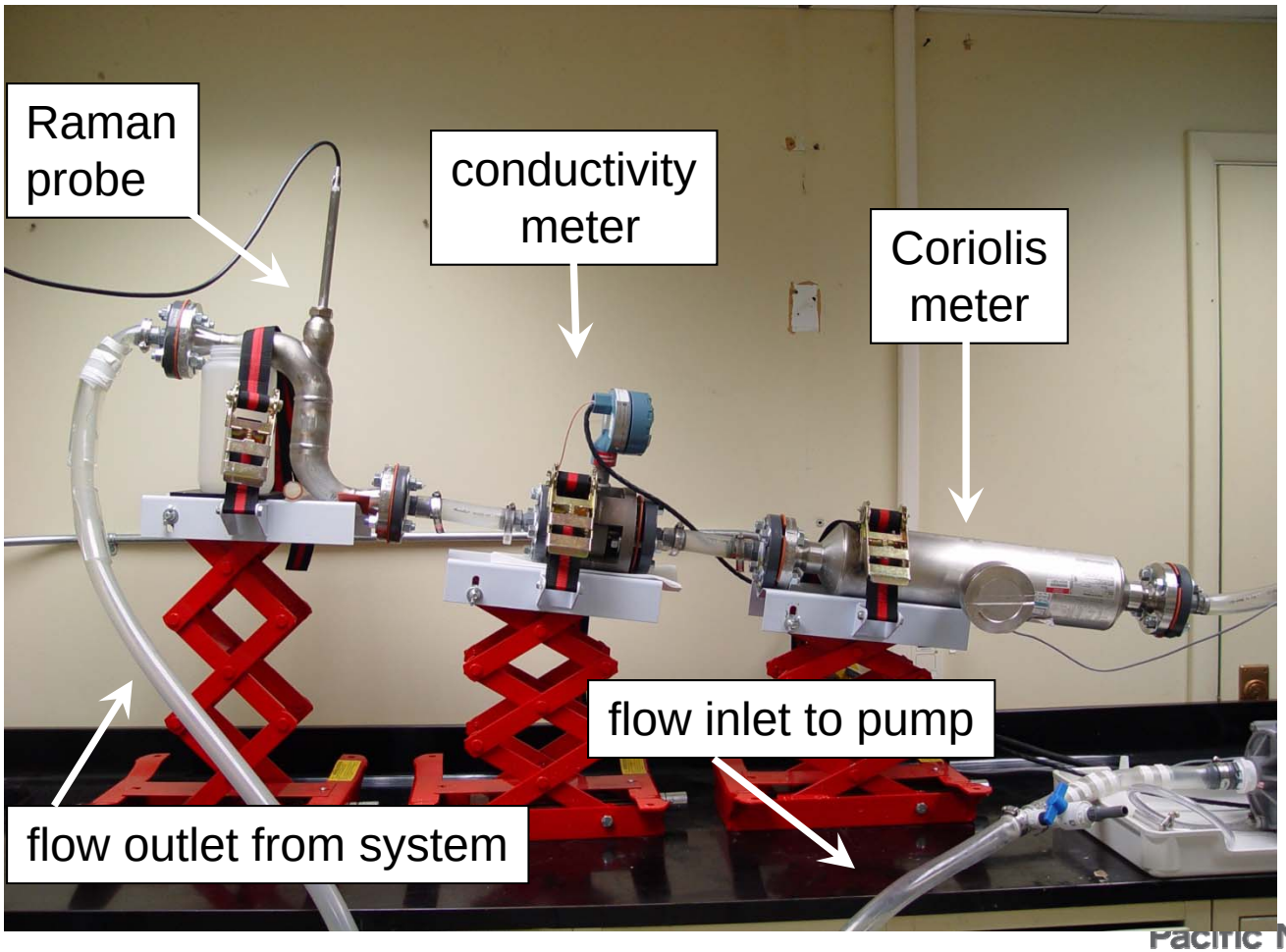
Photo of Process Monitor Equipment



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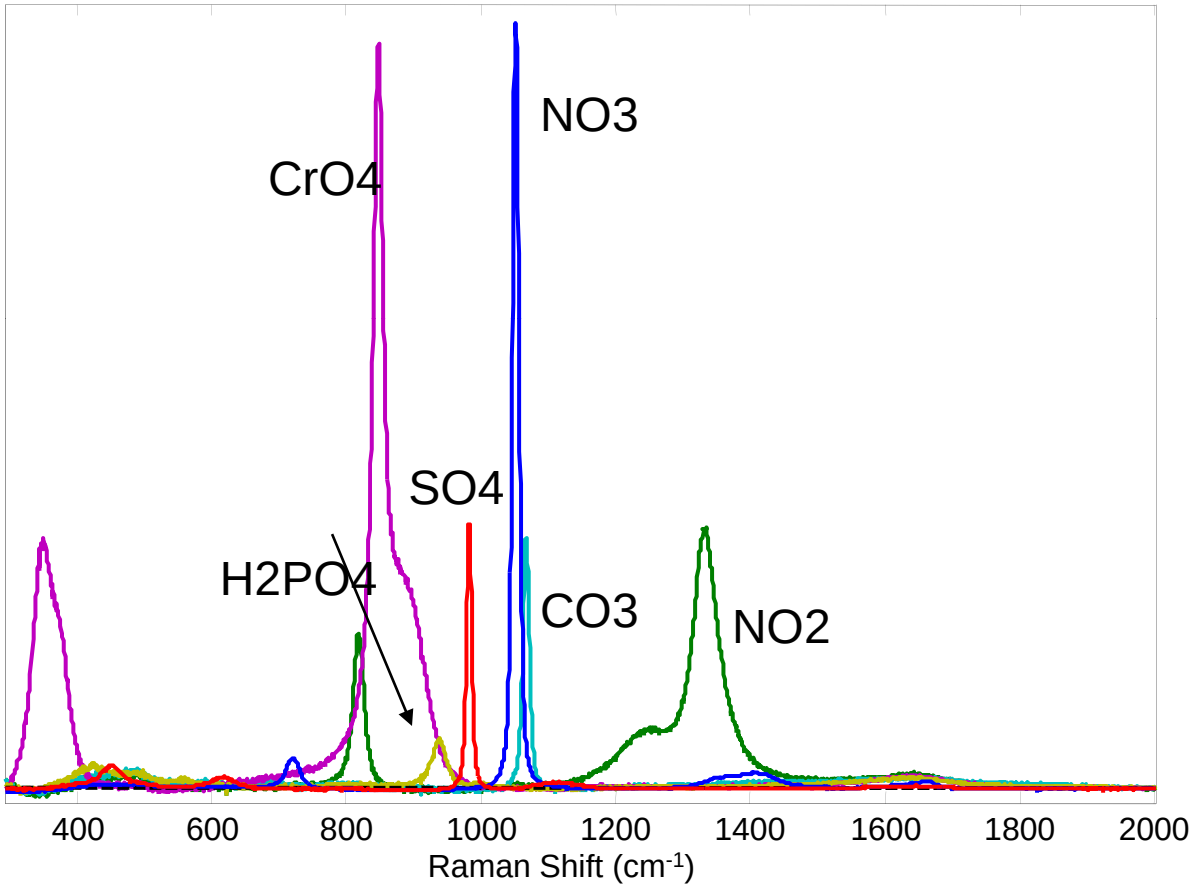
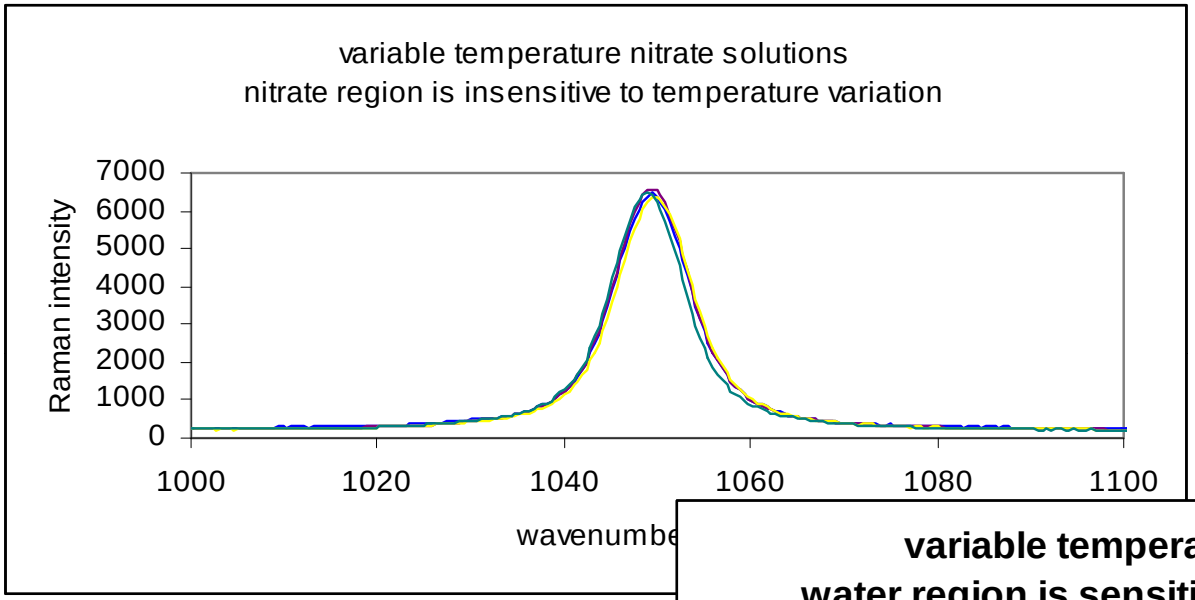
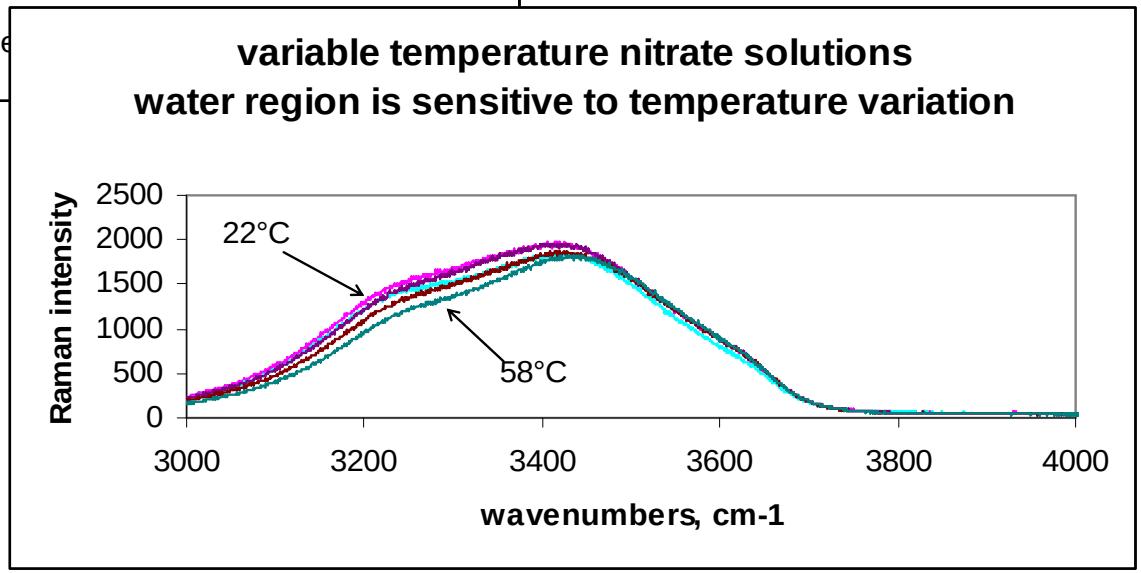
Raman Spectra of Ionic Species

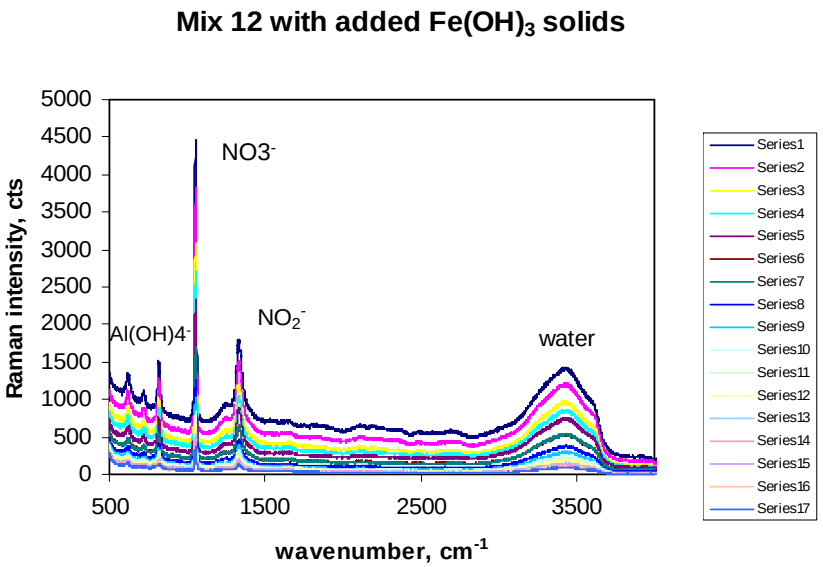


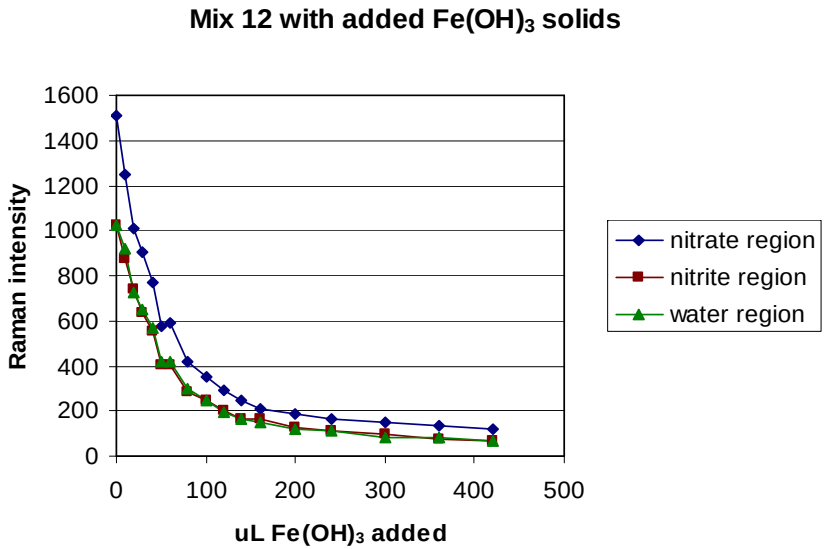
Temperature influence on spectra





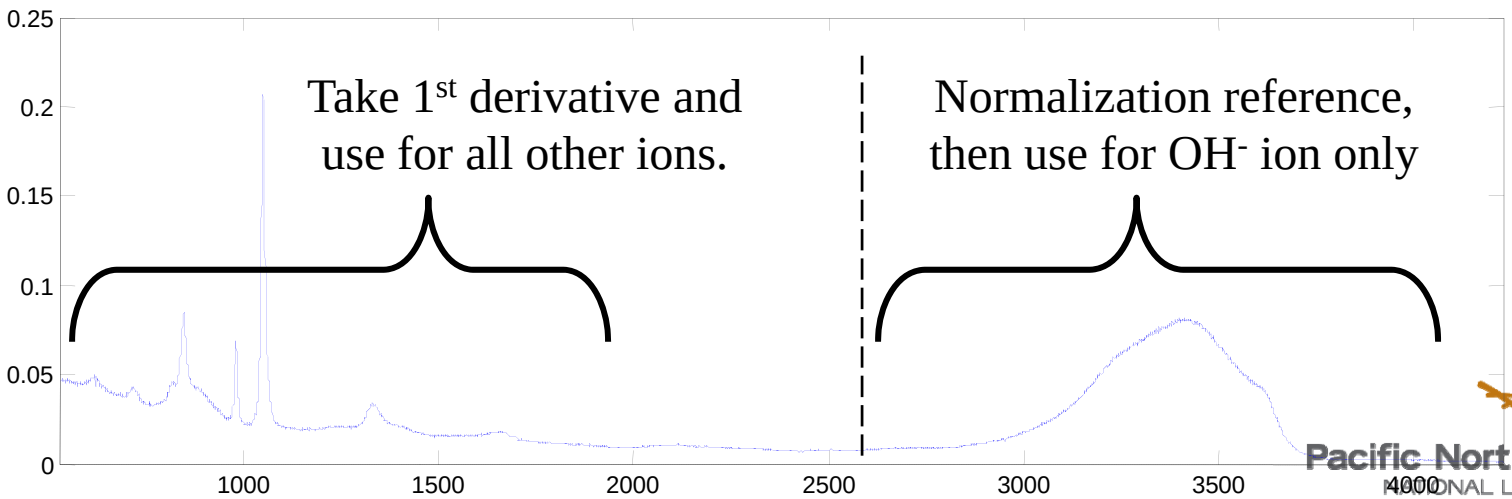
Added Solids Reduce Raman Signal





Raman Model

- Primary Ions use Classical Least Squares-based model Calibration steps
  - Normalize to OH stretch (to correct for intensity variations) then use 1st derivative (to reduce impact of luminescence backgrounds)
  - Use only low spectral range (salts 517-1836 cm-1; OH- >2670 cm-1)
  - Estimate "pure component spectra" (what each species would look like if it were alone in solution) for each ionic species
  - Allow more than one possible spectrum from each species (because some spectral peaks shift in highly concentrated solutions). Allows approximation and handling of "non-linear" spectral behavior
  - Include additional "background" spectra (estimates of interferences) to account for other backgrounds



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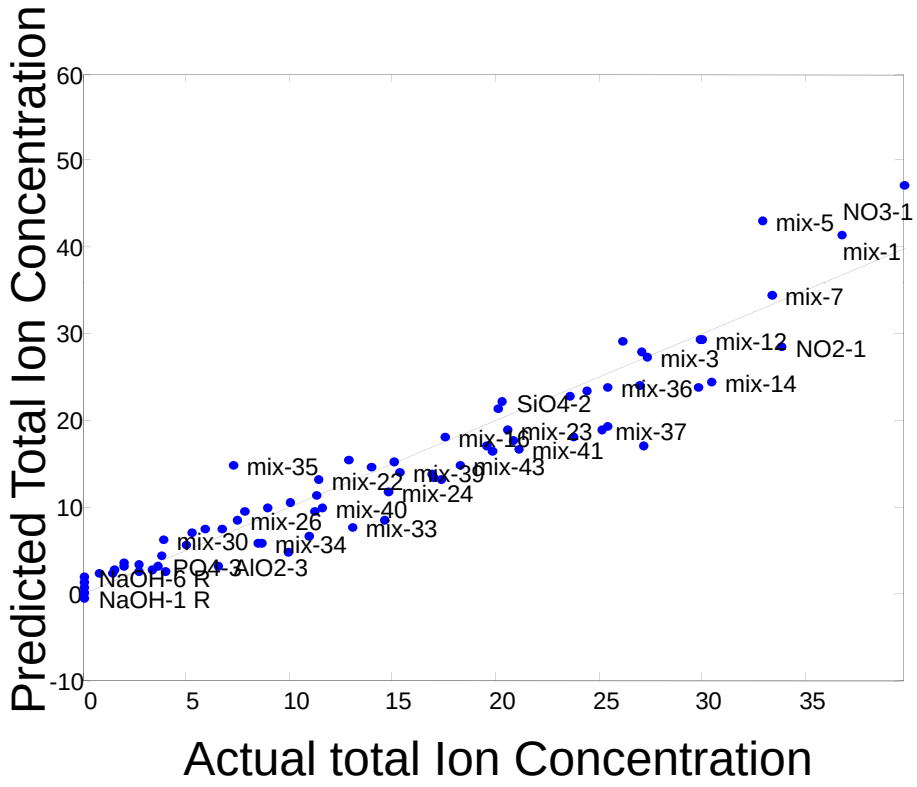
Raman Model Prediction of Concentrations



➢total ion concentration displayed (sum of all calculated species)

Sodium Model

- Measure: Density (x_1), Conductivity (x_2), Temperature (x_3)
- Create non-linear combination of these variables to the data (x_1^2, x_2^2, x_3^2, x_1x_2, x_1x_3, … , x_1/x_2, x_1/x_3 , x_2/x_1, x_2/x_3, ...) Gives a total of 15 variables.
- Use Genetic Algorithm to select "best" variables (those that give lowest error of cross-validation from PLS model)

  Results include 5 variables: density, density^2, density*conductivity, conductivity*temperature, density/conductivity
- Use Partial Least Squares (PLS) and Locally-Weighted Regression (LWR) to predict sodium concentration.

  LWR builds "local" regression model from calibration data which looks most like the unknown.
- Chemometric model developed by Eigenvector Research, Inc.

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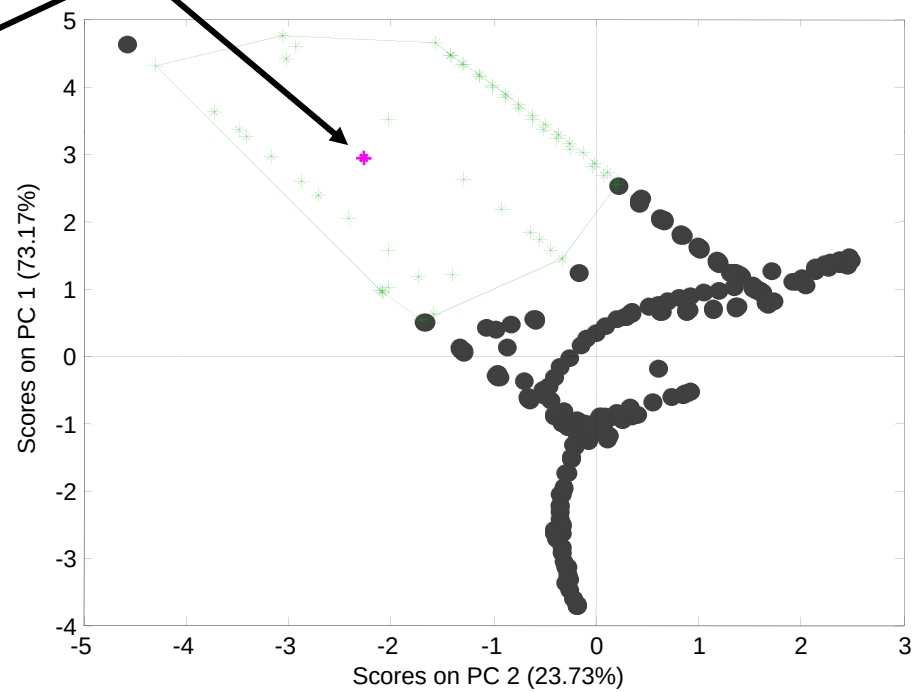
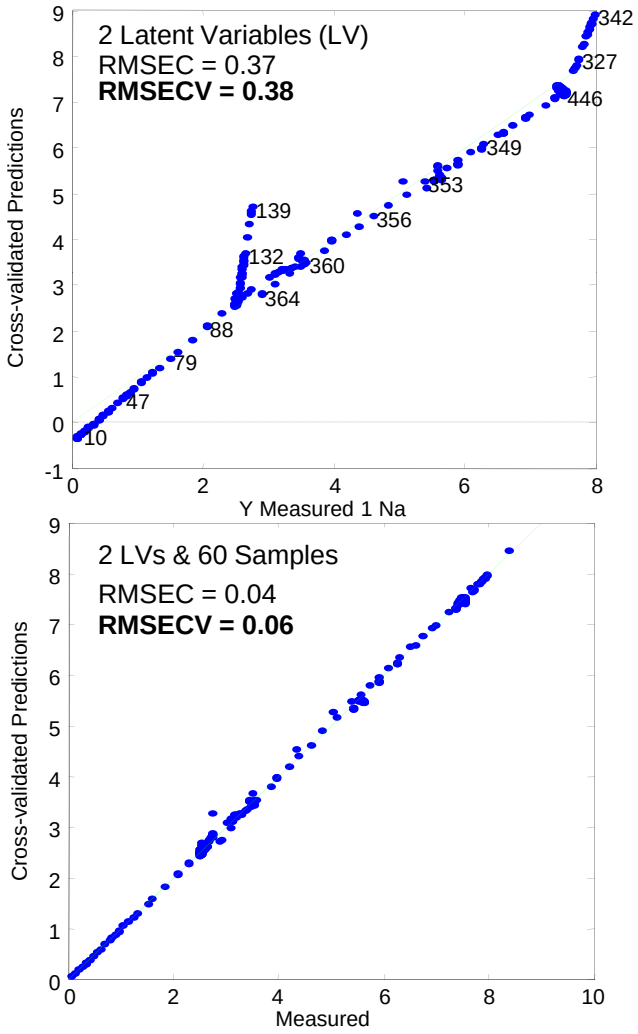
Locally Weighted Regression Models

1. Given PCA model of all calibration data and an unknown sample, select the 60 calibration samples closest to the unknown (green samples).
2. Use ONLY these samples to build Principal Component Regression model (from whole-data scores) and predict.
3. Refine sample selection based on estimated Y and known Y from calibration samples.

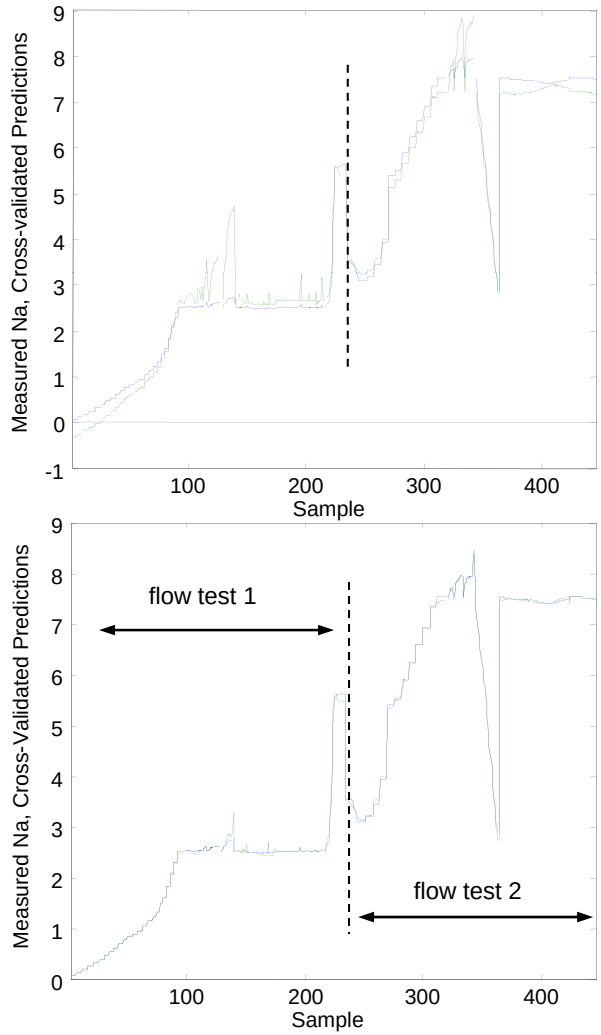


Calibration Results
PLS vs. LWR

Calibration Plots



Calibration Data vs Time



PLS
~ 0.38M error

Variable
- composition
- temperature
- gas addition
- flow rate
- solids addition

Data (blue)
Fit (green)

LWR
~ 0.06M error

Compositions of S109 Feed Simulants Used in Acceptance Tests

Analyte	Early Feed		Late Feed	
	M	%Wt	M	%Wt
Density	1.42		1.15	
OH	1.67	4.70 as NaOH	0.021	0.073 as NaOH
TOC	<0.03		<0.03	
TIC	0.61	4.55 as Na2CO3	0.24	2.21 as Na2CO3
Al	0.52	4.32 as NaAl(OH)4	0.044	0.45 as NaAl(OH)4
Cr	0.079	0.92 as Na2CrO4	0.018	0.26 as Na2CrO4
Fe	0.0001		<0.00002	
K	0.026		0.009	
Na	7.87	12.75	2.62	5.24
P	0.025		0.052	
S	0.13		0.17	
Si	0.0005		<0.0002	
F	<0.016		0.098	
Acetate	NA		NA	
Cl	0.08	0.33 as NaCl	0.009	0.051 as NaCl
NO2	0.86	4.18 as NaNO2	0.073	0.44 as NaNO2
NO3	3.98	23.82 as NaNO3	1.59	11.75 as NaNO3
PO4	0.025	0.29 as Na3PO4	0.055	0.78 as Na3PO4
SO4	0.14	1.40 as Na2SO4	0.17	2.10 as Na2SO4
Oxalate	<0.031		0.011	
Cs (µg/mL)	2.3		0.23	

Chemometric Prediction of Component Concentrations for S109 Feed Simulants

Analyte	%Wt Analytical	Saltpred %Wt Prediction					Detection Limit %Wt (M)
		Average		Absolute Range	Relative Error %	Absolute Deviation %Wt	
A) Early Feed, Total of 2028 Measurements							
NaOH	4.70	4.85	(0.25)	3.8 – 5.9	3.2	0.15	0.38 (0.09)
Na_2CO_3	4.55	5.02	(0.13)	4.4 – 5.4	10	0.47	0.093 (0.009)
$NaAl(OH)_4$	4.32	4.72	(0.11)	4.4 – 5.1	9.3	0.40	0.30 (0.025)
Na_2CrO_4	0.92	0.96	(0.02)	0.92 – 0.99	4.3	0.04	0.021 (0.001)
$NaNO_2$	4.18	4.22	(0.04)	4.1 – 4.3	1.0	0.04	0.19 (0.03)
$NaNO_3$	23.82	23.47	(0.17)	23.0 – 24.0	1.5	- 0.35	0.033 (0.004)
Na_3PO_4	0.29	0.35	(0.04)	0.21 – 0.64	21	0.06	0.29 (0.02)
Na_2SO_4	1.40	1.43	(0.01)	1.4 – 1.5	2.1	0.03	0.047 (0.003)
Na	12.75	12.87	(0.04)	12.8 – 13.0	1.0	0.12	
B) Late Feed, Total of 779 Measurements							
NaOH	0.073	0.0	(0.29)	0.0 – 1.1		- 0.073	0.38 (0.09)
Na_2CO_3	2.21	2.31	(0.04)	2.2 – 2.5	4.5	0.10	0.093 (0.009)
$NaAl(OH)_4$	0.45	0.41	(0.03)	0.28 – 0.52	8.9	- 0.04	0.30 (0.025)
Na_2CrO_4	0.26	0.19	(0.01)	0.17 – 0.29	27	- 0.07	0.021 (0.001)
$NaNO_2$	0.44	0.33	(0.02)	0.23 – 0.41	25	- 0.11	0.19 (0.03)
$NaNO_3$	11.75	11.89	(0.10)	11.4 – 12.3	1.2	0.14	0.033 (0.004)
Na_3PO_4	0.78	0.75	(0.05)	0.20 – 1.2	3.8	- 0.03	0.29 (0.02)
Na_2SO_4	2.10	2.0	(0.02)	2.0 – 2.3	4.8	- 0.10	0.047 (0.003)
Na	5.24	5.38	(0.10)	3.9 – 5.9	2.7	0.14	

Acceptance Test Criteria:
20% relative error or ±0.5% absolute error

Two solutions of extreme compositions were tested

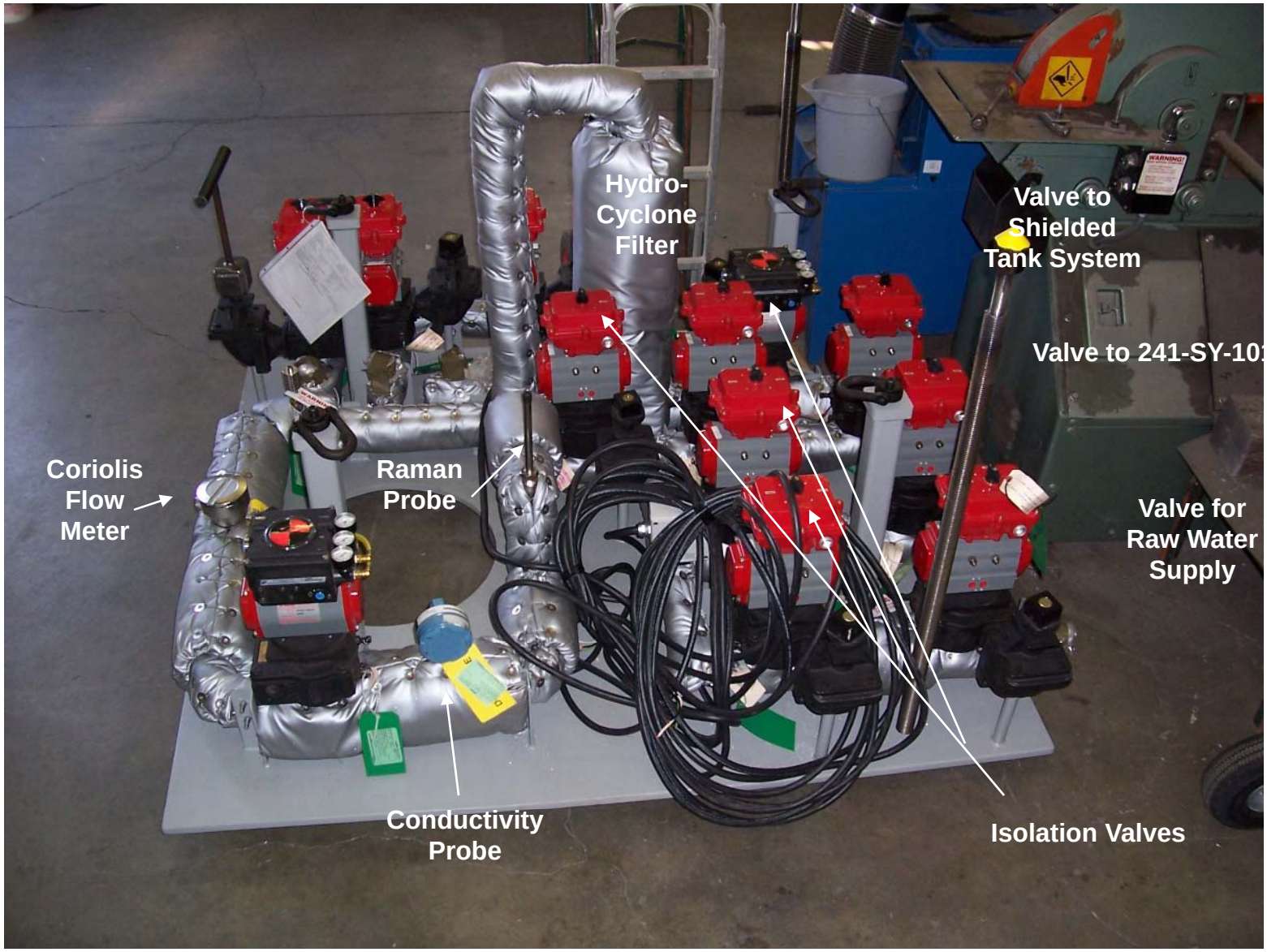
Test included real time evaluation of ~2800 independent measurements collected over 24 h time interval

Acceptance test criteria met

Field Manifold Verification Test

- Compare field manifold system with laboratory system
  - Assemble combined flow system
  - Connect combined flow system with pump and 55 gallon feeding/receiving reservoir
  - Connect laboratory instruments and field instruments to independent data acquisition systems and computers
- Verify of the electronic components
- Compare instrument performance
  - using 5 wt% $NaNO_3$ solution
  - continuously changing the composition of the test solution
- Test chemometric models using data independently collected by laboratory and field systems
- Test software for the data acquisition, processing, storage, and archival

Assembled Process monitor manifold



Field Manifold Verification Test

Field Manifold Verification Test Results

- Field unit calibrated using previously calibrated laboratory unit
- Field system instrumental performance was comparable to laboratory system
- Composition change of test solutions was successfully monitored by both systems
- Software performed equally well for field and laboratory systems

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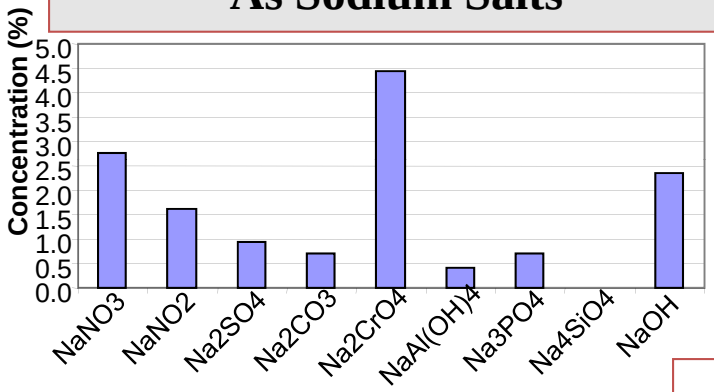
Schematic presentation of the software computer display

Current Retrieval Composition, As Sodium Salts



Current Values

Time of last measurement

Temp, F and C

Flow rate, GPM

Density, SGU

Conductivity, mS

Current wt% Na

Retrieval Summary

Time, (days)

Volume, in gallons and liters

Total Mass,in pounds and Kg

Sodium,in pounds and Kg

NaNO3	NaNO2
Na2SO4	Na2CO3
Na2CrO4	Na
Na3PO4	NaOH

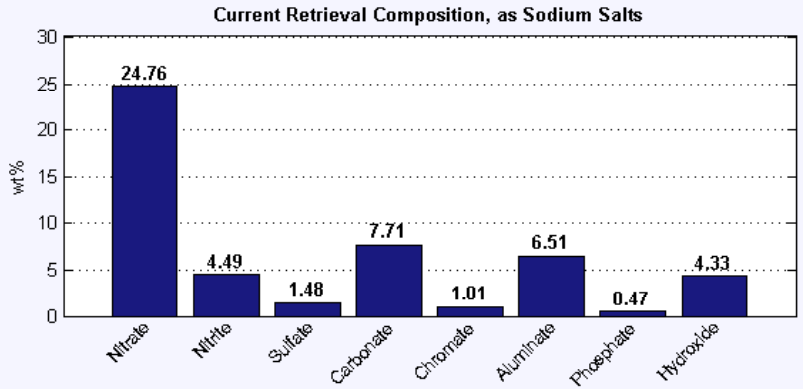
24-Hour Summary of Retrieval Major Components

Given as trend plot wt% vs time

24-Hour Summary of Retrieval Minor Components

Given as trend plot wt% vs time

Eigenvector Research Process Monitor (08-Jul-2005 14:30:29)



Current Values

```
Last Measurement
        2005-07-08 14:30:08

Temperature (deg C) : 23.4
            (deg F) : 74.1
    Flow Rate (GPM) : 2.8
      Density (SGU) : 1.399
  Conductivity (mS) : 139.52
      Sodium (wt%)  : 12.90
```

Retrieval Summary

```
Total Time : 24.7 hours
Total Volume (Gal): 4459
             (L)  : 16881
Total Mass (Kg)   : 23612
           (Lbs)  : 52055
Total Sodium (Kg) : 3043
             (Lbs): 6708
Nitrate    (kg) : 4952
Nitrite    (kg) : 936
Sulfate    (kg) : 297
Carbonate  (kg) : 1785
Chromate   (kg) : 206
Aluminate  (kg) : 1451
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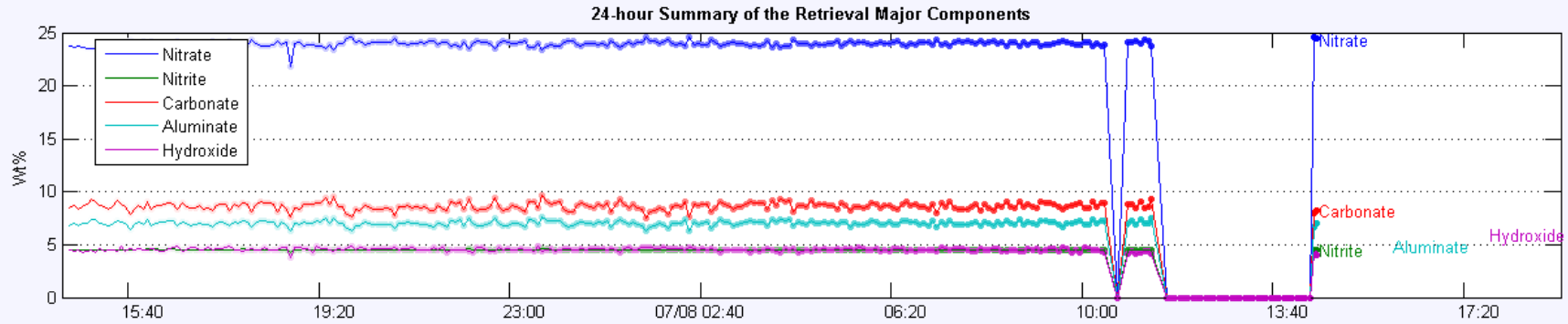

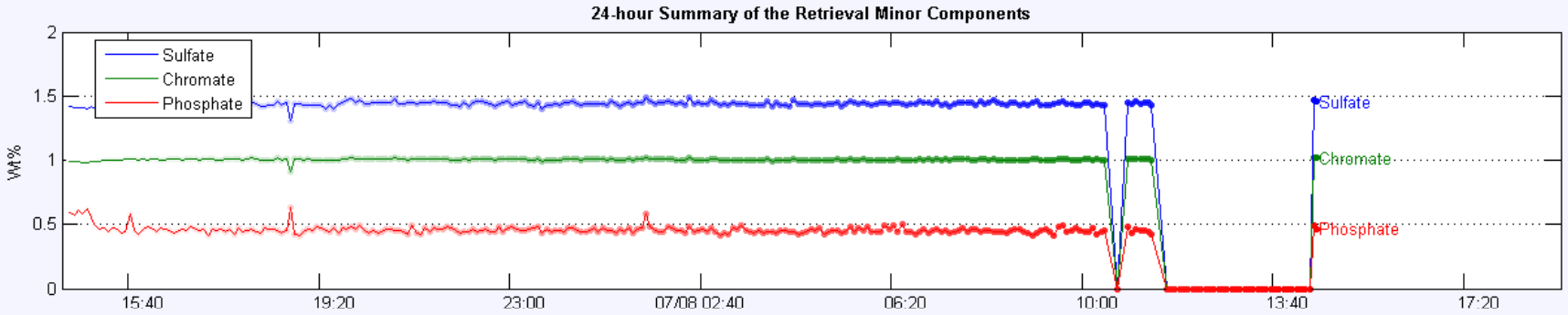

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Address | Go

On-Line Monitoring for Control and Safeguarding of Radiochemical Streams at Spent Fuel Reprocessing Plant

- Application of past on-line process monitoring experience to UREX flowsheet
- Spectroscopic measurements of selected fuels and fuel simulants
- Evaluation of detection limits
- Initial development of quantitative PLS models for U, Pu, and Np
- Demonstration of process monitoring using commercial fuel
- Instrumentation of a centrifugal contactor system with Raman and vis-NIR spectroscopic probes

Approach:
Online Spectroscopic Measurements

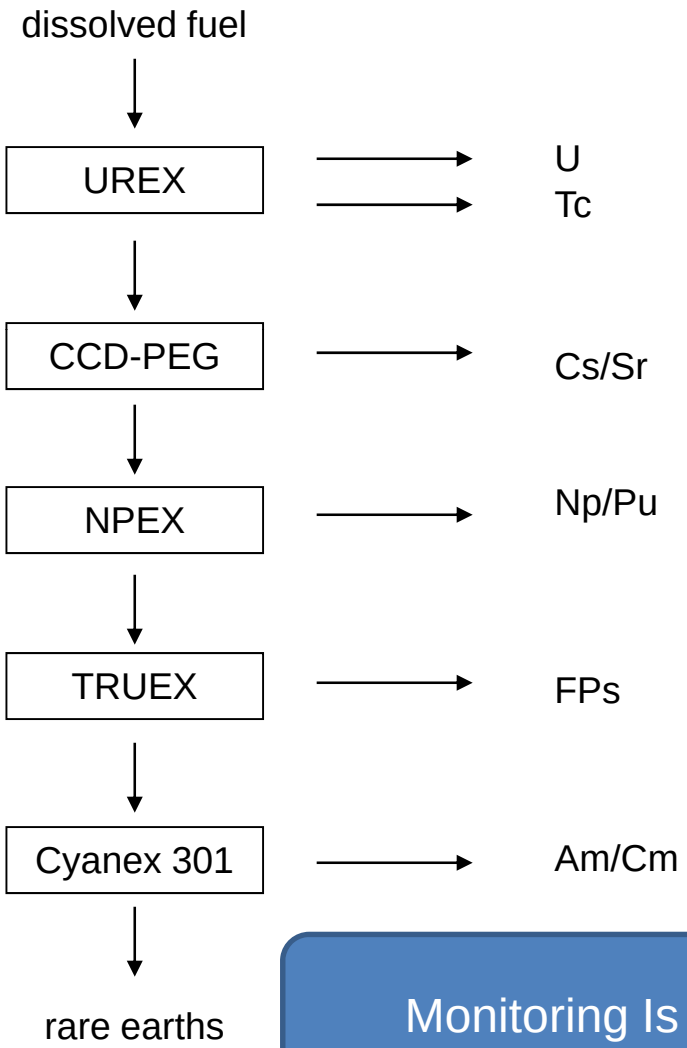
- **Raman** measurements of
  - Actinide oxide ions
  - Organics: solvent components and complexants
  - Inorganic oxo-anions (NO_3^-, CO_3^{2-}, OH^-, SO_4^{2-}, etc)
  - Water, acid (H^+), base (OH^-)

- **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**
  - Real-time, online monitoring of high-level nuclear waste
  - Raman spectroscopy, flow, temperature, conductivity, density

Process Monitoring Can Be Achieved Throughout the Flowsheet



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

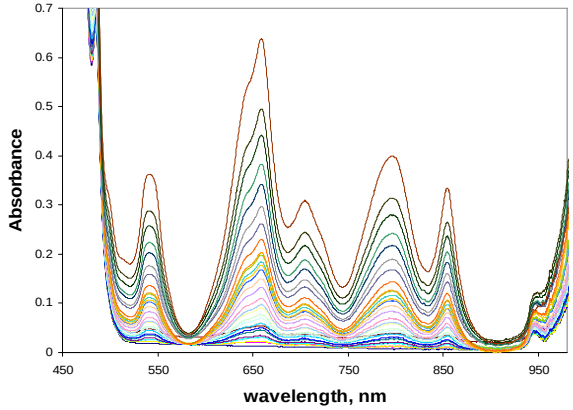
Every flowsheet contains Raman and/or UV-vis-NIR active species

Coriolis and conductivity instruments can be used on all process streams

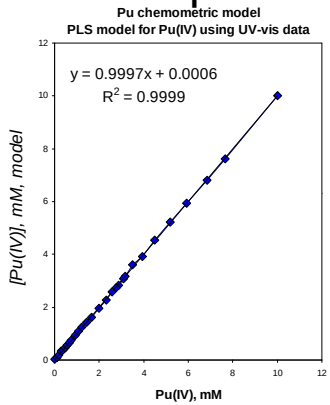
Monitoring Is Not Flowsheet Specific

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

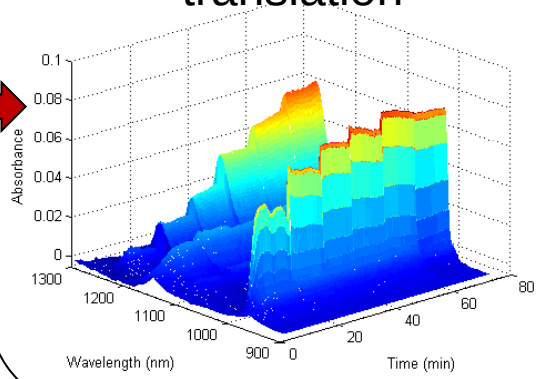
Static measurements: Model training database



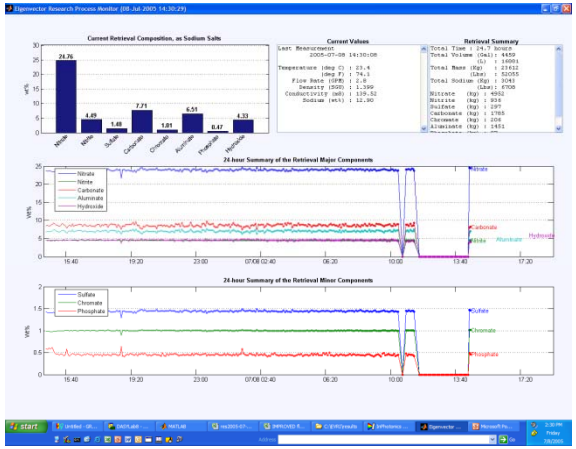
Chemometric model development



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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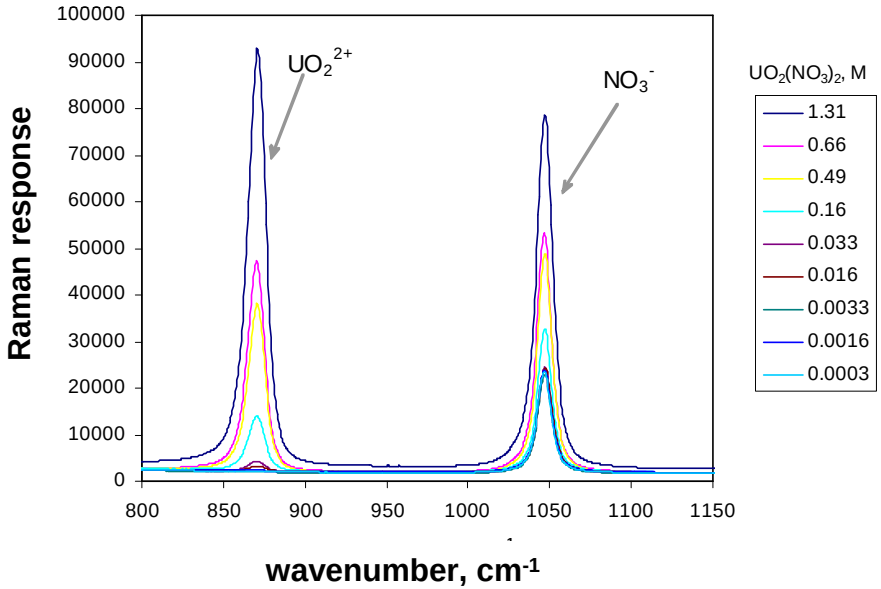
Raman Spectroscopy for Monitoring Uranyl and Nitrate ions

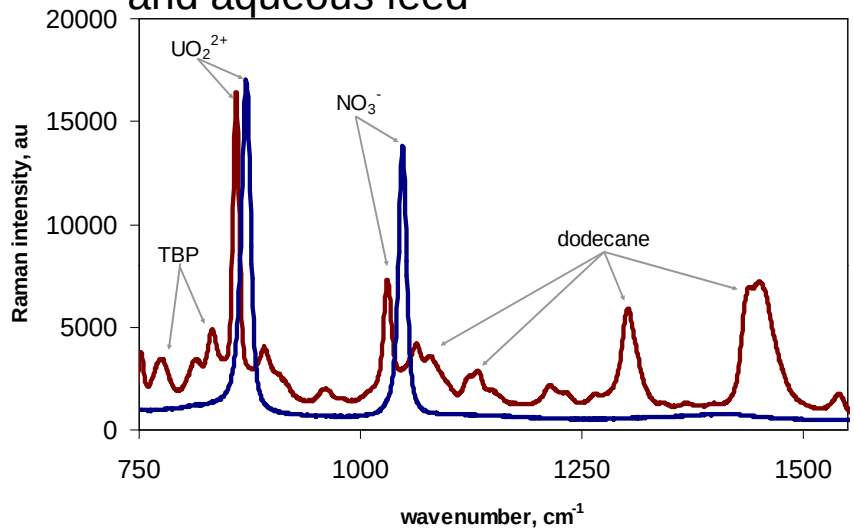
- Raman spectroscopy allows for quantification of UO_2^{2+} and NO_3^- in aqueous and organic phases

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

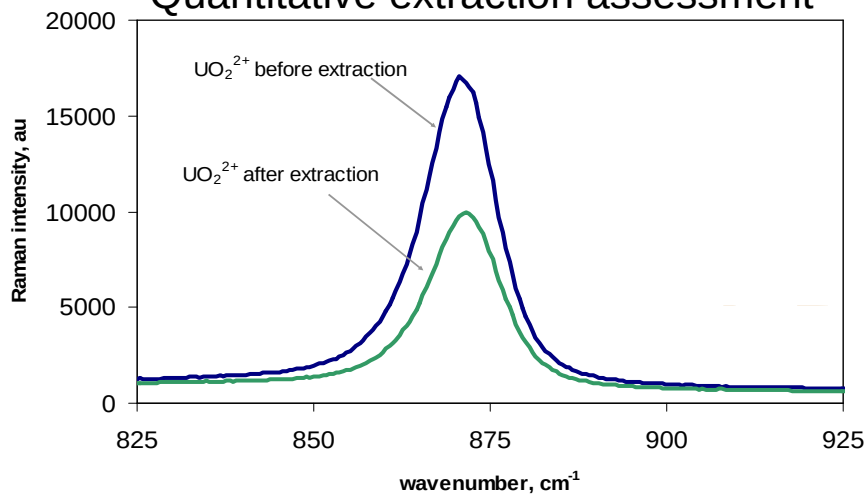


Detection limits:
3.1 mM for UO_2
2.6 mM for NO_3

Comparison of loaded TBP/dodecane and aqueous feed

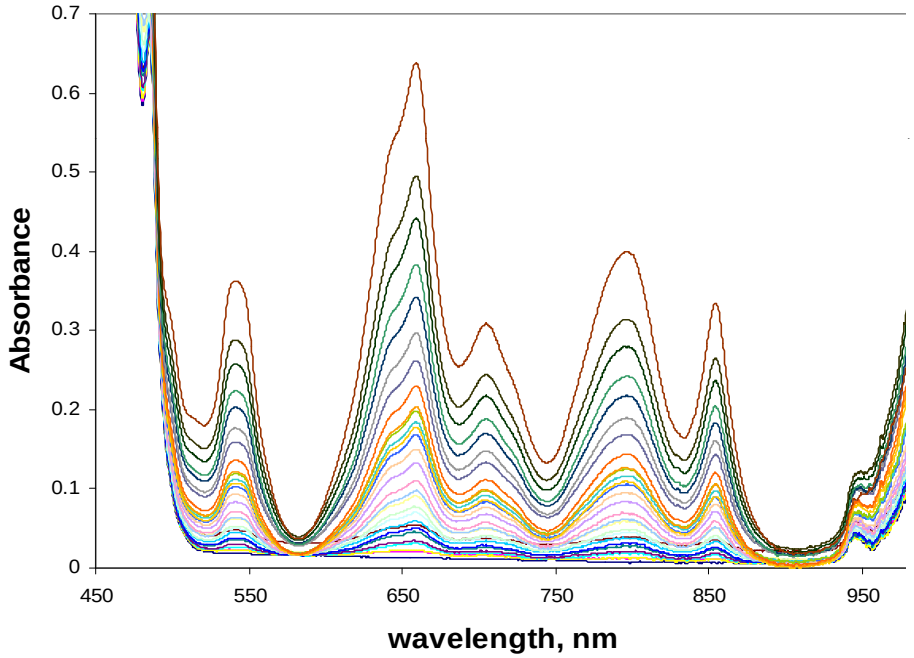


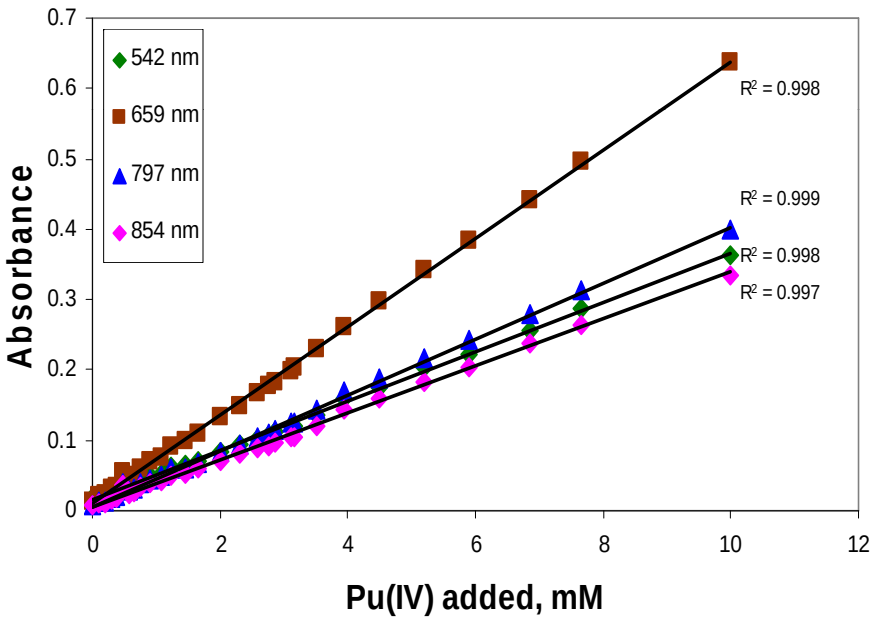
Quantitative extraction assessment



Vis-NIR spectra of variable Pu(IV) in fuel feed simulant

- Pu(IV) concentration can be quantified over wide range of process chemistry conditions



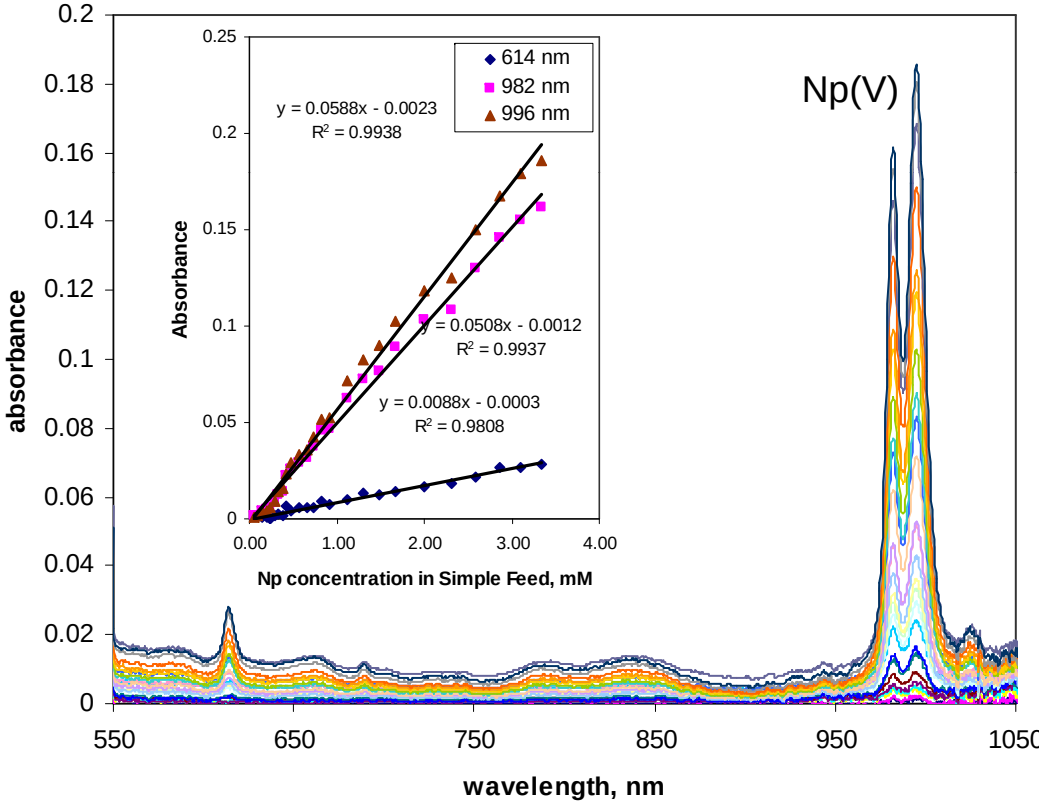


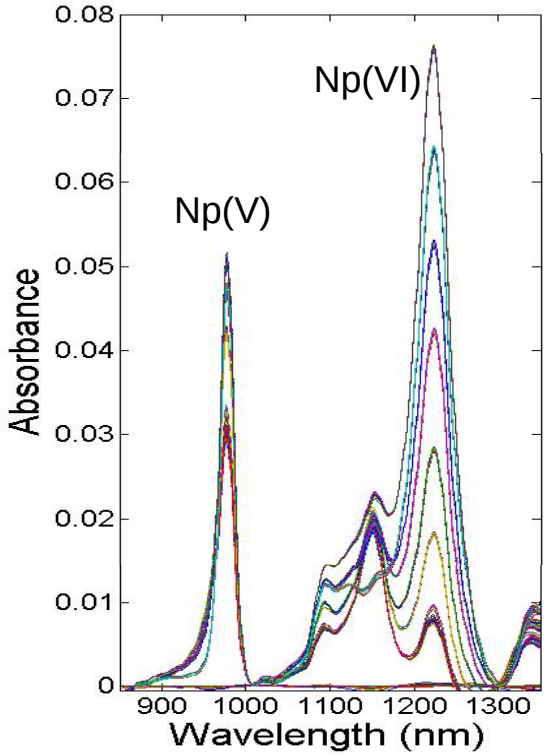
- Pu(IV) concentration variable 0.1 to 10 mM
- Feed composition: 1.3 M $UO_2(NO_3)_2$ and 0.8 M HNO_3
- $UO_2(NO_3)_2$ does not interfere with Pu(IV) measurements

Detection limit: 0.08 mM for Pu(IV) using 659 nm band

Vis-NIR spectra of Np(V) and Np(VI) in fuel feed simulant

- Np(V) and Np(VI) concentration can be quantified over wide range of process chemistry conditions





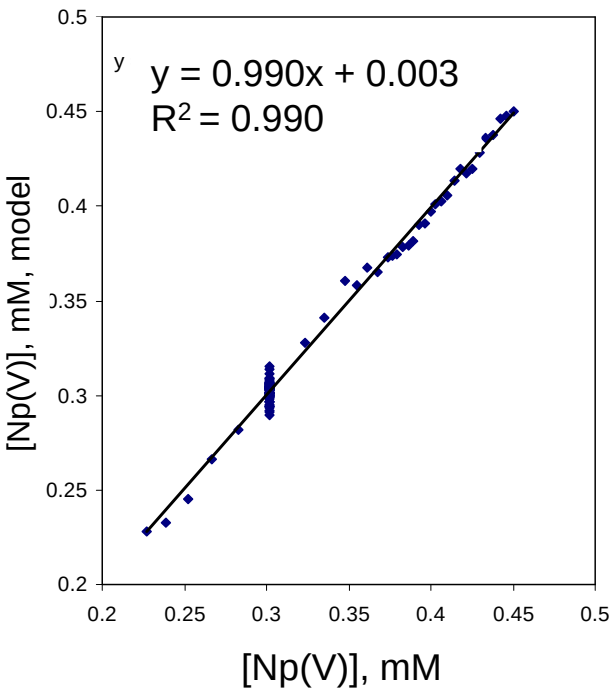
- Np(V): variable 0.05 to 3.3 mM
- Feed composition: 1.3 M $UO_2(NO_3)_2$ in 0.8 M HNO_3

- Np(V): variable 0 to 0.1 mM
- Np(VI): variable 0 to 0.75 mM
- Feed composition: 0.3 M HNO_3

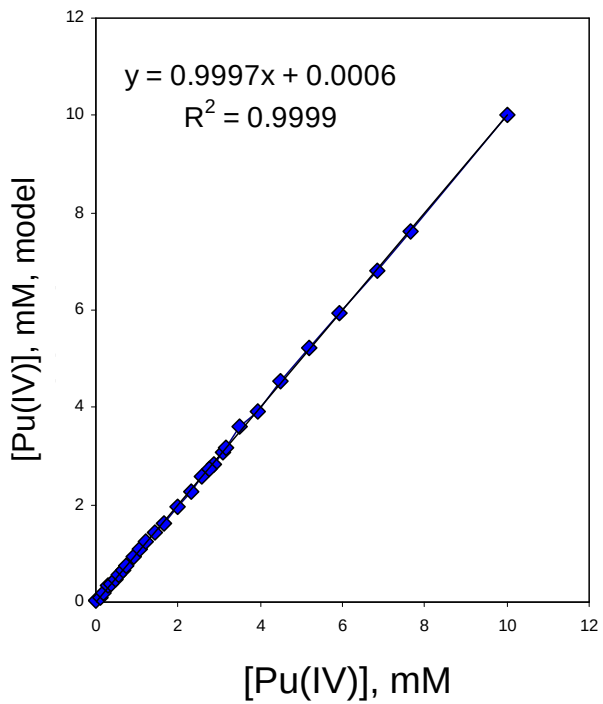
Chemometric PLS models for quantitative analysis: Pu(IV), Np(V) and UO_2^{2+} (Raman and vis-NIR)

Use Static spectral database for process monitor model development
Linear fit with slope = 1 indicates agreement between actual and predicted values, and successful model performance

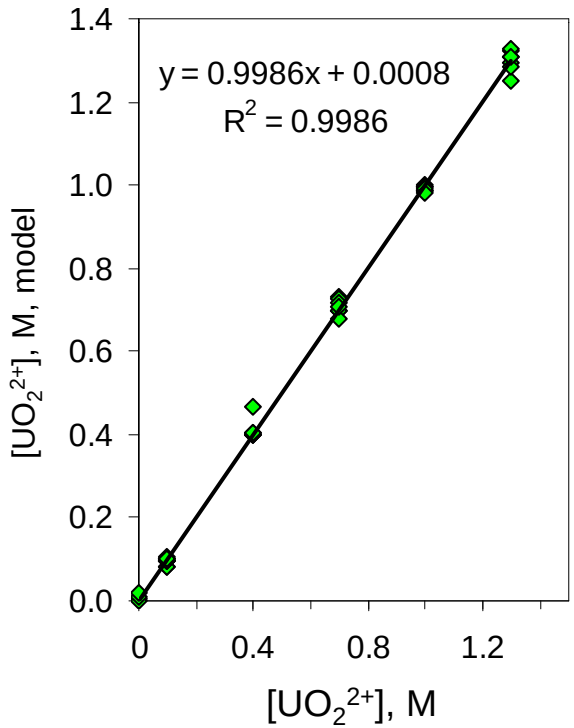
Np(V) model



Pu model



UO_2 model



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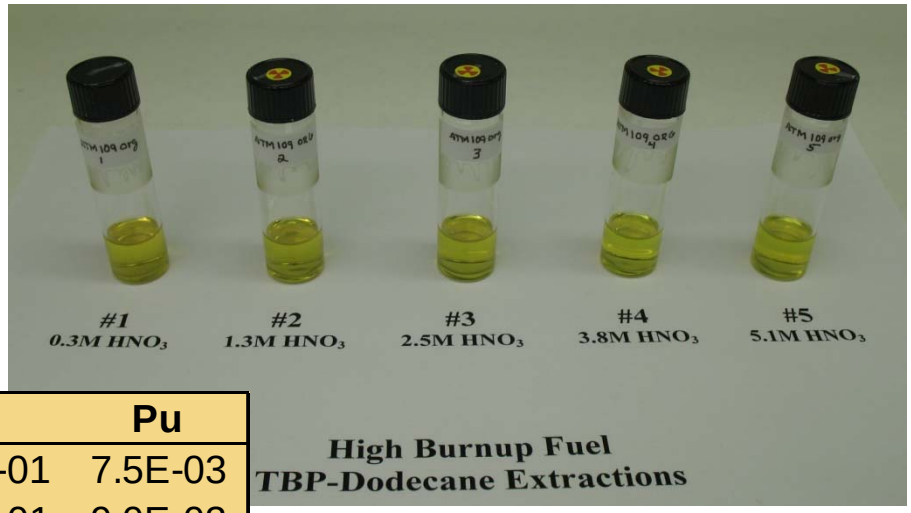
Proof-of-Concept : Applicability of spectroscopic methods for commercial BWR fuel measurements

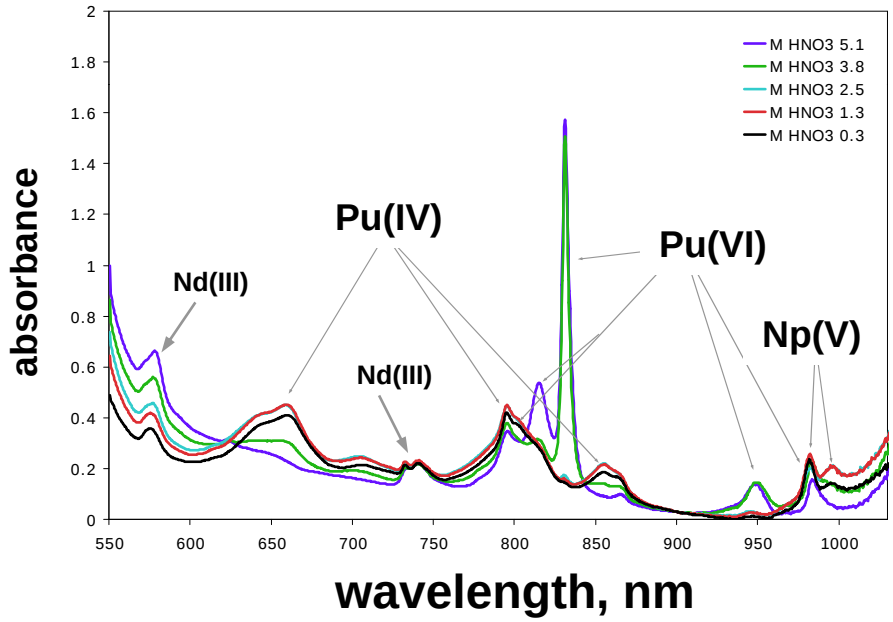
- Commercial fuels available at PNNL for demonstration
  - ATM-105, BWR, Cooper Nuclear Power Plant; 18 MWd/kg; low burnup
  - ATM-109, BWR, Quad Cities I reactor; 70 MWd/kg; high burnup
- Fuel dissolved in HNO_3
  - Feed adjusted to 5 nitric acid strengths (0.5 to 5M) and 0.7M U(VI)
- Performed batch contact on each aqueous feed with 30 vol% TBP-dodecane
- Feed, Organic, Raffinate phases successfully measured by
  - Raman, Vis-NIR
- Excellent Agreement between ORIGEN code, spectroscopic, and analytical measurement



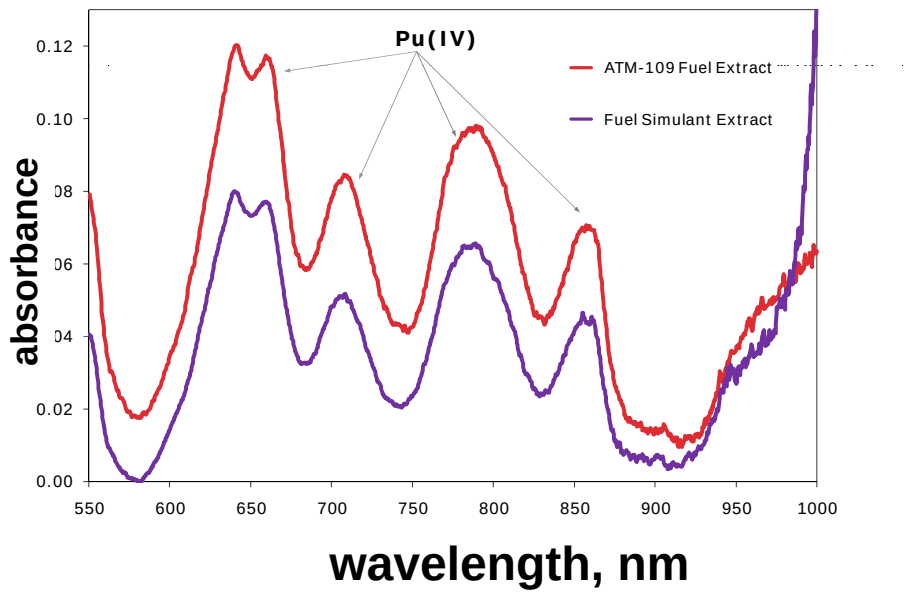
ATM-109	Nd	Np	U	Pu
ORIGEN	1.1E-02	4.6E-04	7.2E-01	7.5E-03
ICP-MS	8.4E-03	4.7E-04	7.2E-01	9.0E-03
Spectroscopic	5.4E-03	3.0E-04	7.3E-01	9.6E-03
ORIGEN / ICP ratio	***1.3***	***1.0***	***1.0***	***0.8***
ORIGEN / Spectroscopic	***1.9***	***1.5***	***1.0***	***0.8***

Examples of Vis-NIR spectra: BWR Fuel Feed and TBP/dodecane extraction phase

high burnup ATM-109 aqueous feed



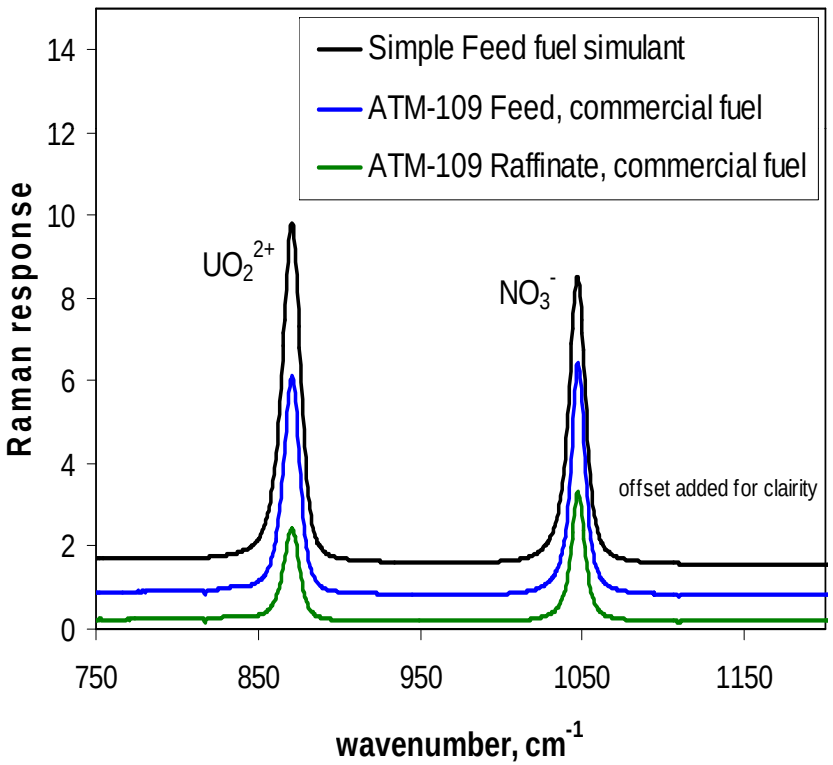
ATM-109 TBP/dodecane phase



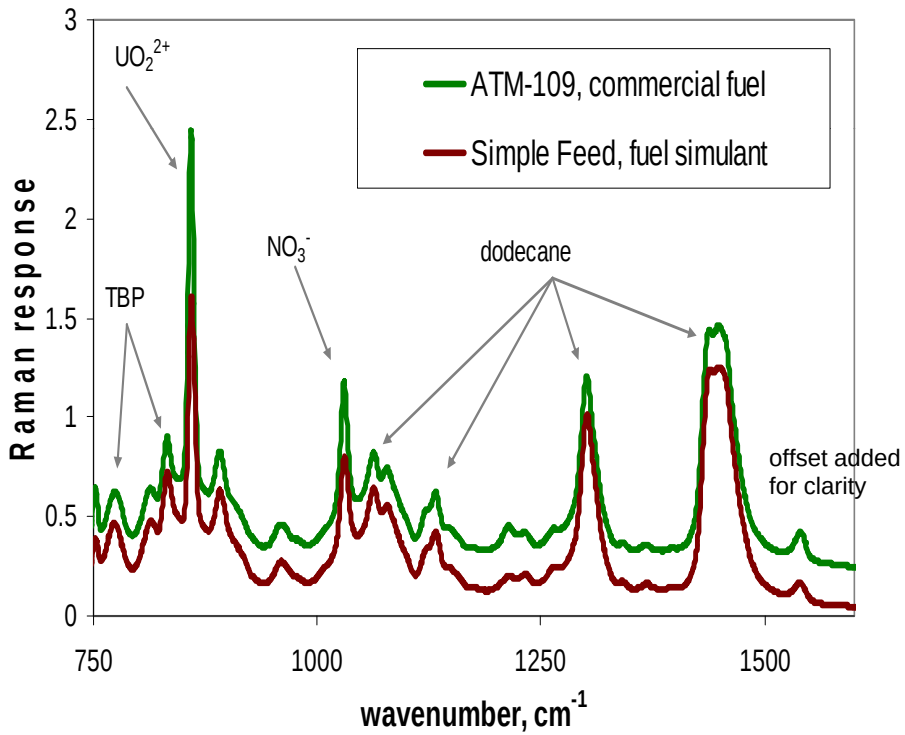
Red - ATM-109 high burn-up, extract
Blue - Simlant feed extract

Raman spectra of High-Burnup BWR Fuel, ATM-109

Aqueous phase:
ATM-109 feed, raffinate, and simulant



TBP/dodecane phase:
ATM-109 fuel and simulant



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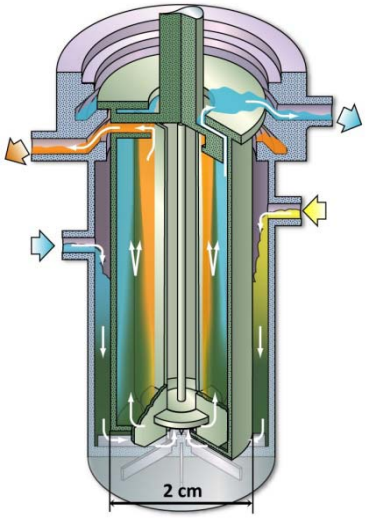
Flow Testing with PNNL's Solvent Extraction Test Apparatus (SETA)

- Sixteen 2-cm centrifugal contactors
- Instrumented with Raman and UV-VIS-NIR spectroscopic probes
- Computer-controlled operation
- Vessels mounted on balances → accurate tracking of material flow
- Instrumentation ports, connections points → long-range flexibility



PNNL' s centrifugal contactors can be additionally instrumented to support instrumentation evaluation and modeling validation

Cold run of centrifugal contactors: Test on-line Raman and Vis-NIR instrumentation

Cold test conditions

- centrifugal contactors; 2-cm, 3600 rpm
- Aqueous phase: 12 ml/min
- Organic phase: 18 ml/min

Aqueous feed

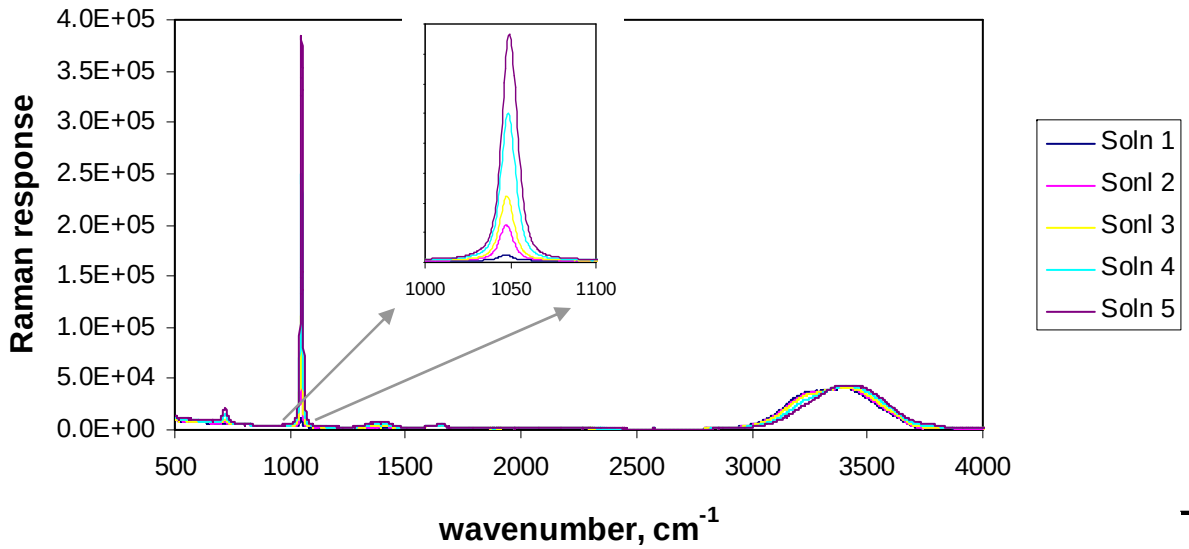
ID	HNO_3, M	NO_3, M	Nd, mM
Soln 1	0.1	0.1	0
Soln 2	0.1	0.6	2
Soln 3	0.1	1.1	5
Soln 4	0.1	2.6	10
Soln 5	0.1	4.1	14

Organic Phase

30%TBP/dodecane

Spectroscopic monitoring of Raffinate stream only

Raman spectra of Solutions 1-5

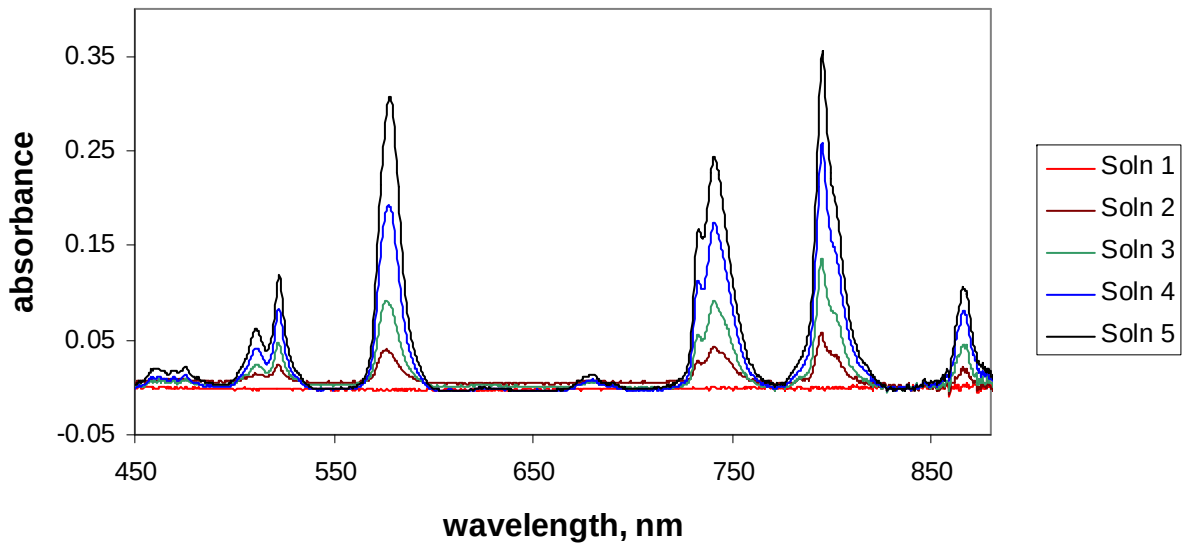


Raman is diagnostic for nitrate ion

Aqueous feed

ID	HNO_3, M	NO_3, M	Nd, mM
Soln 1	0.1	0.1	0
Soln 2	0.1	0.6	2
Soln 3	0.1	1.1	5
Soln 4	0.1	2.6	10
Soln 5	0.1	4.1	14

Visible Spectra of Solutions 1-5



Vis-NIR is diagnostic for Nd^{3+} ion

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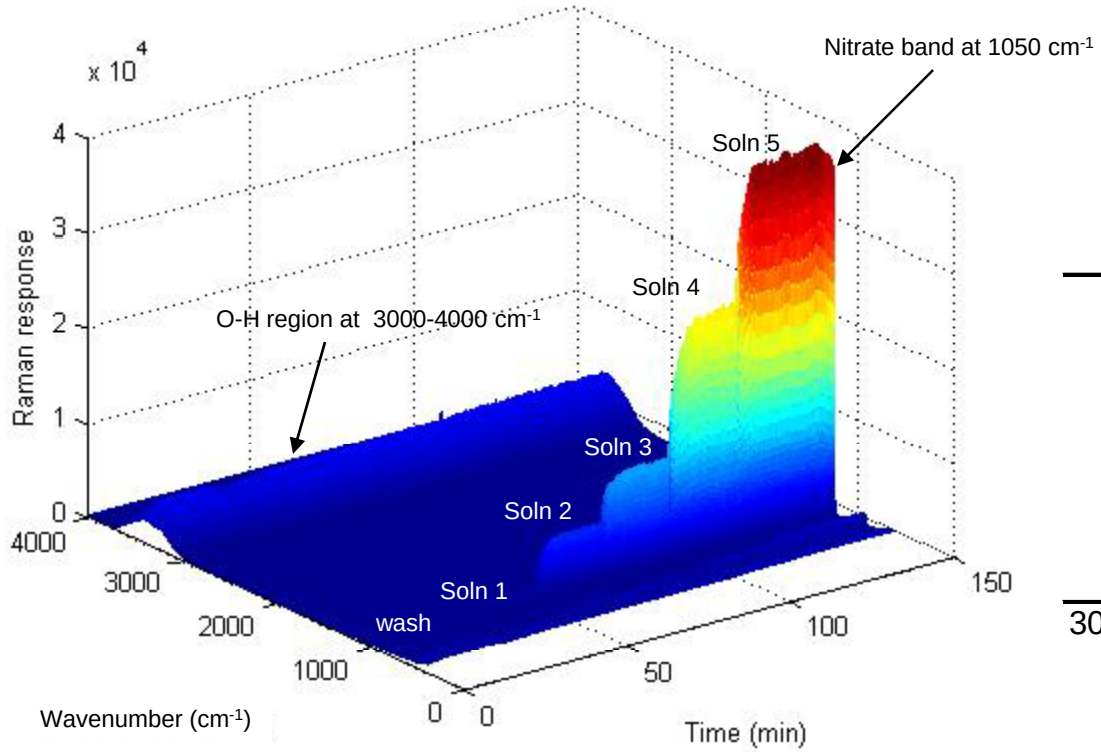
Raman process monitor spectral response of Raffinate stream



Cold test solutions

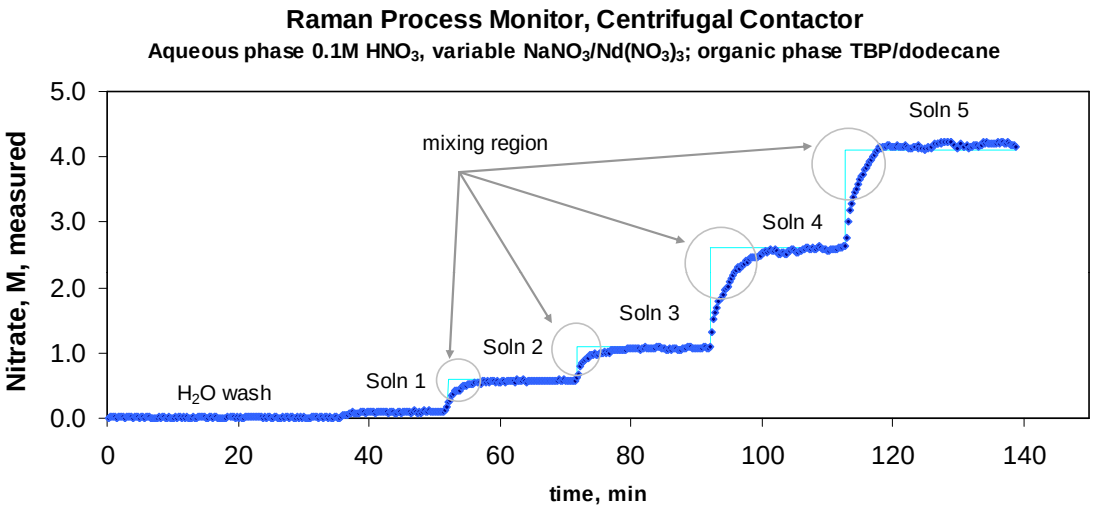
Aqueous feed

ID	HNO_3, M	NO_3, M	Nd, mM
Soln 1	0.1	0.1	0
Soln 2	0.1	0.6	2
Soln 3	0.1	1.1	5
Soln 4	0.1	2.6	10
Soln 5	0.1	4.1	14

Organic Phase

30%TBP/dodecane

PLS model results of Raman and Visible Process Monitoring of Centrifugal Contactor Raffinate

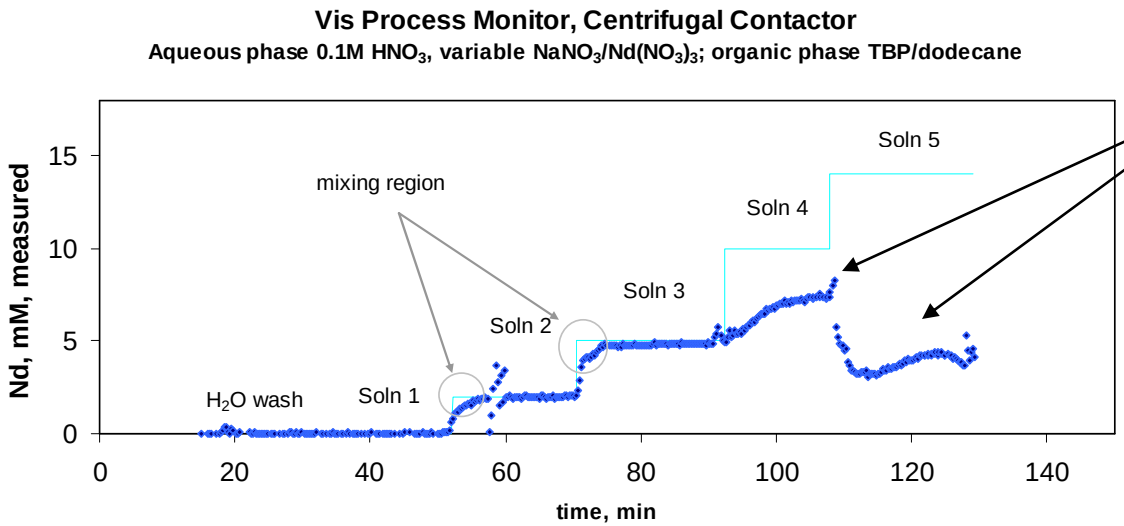


Aqueous feed

ID	HNO_3, M	NO_3, M	Nd, mM
Soln 1	0.1	0.1	0
Soln 2	0.1	0.6	2
Soln 3	0.1	1.1	5
Soln 4	0.1	2.6	10
Soln 5	0.1	4.1	14

Organic Phase

30%TBP/dodecane



Drop in Nd^{3+} is due to extraction

Nd concentration in:

- raffinate
- aqueous feed

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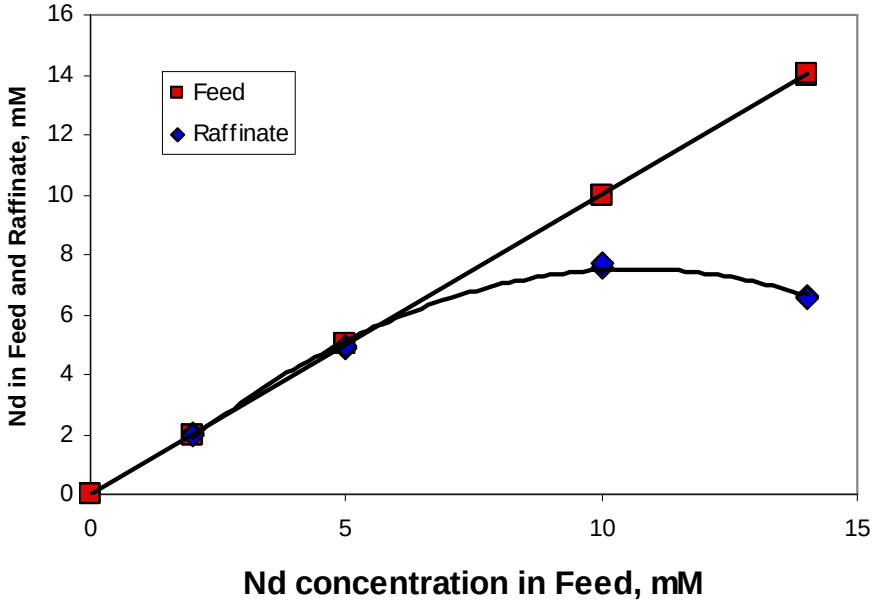
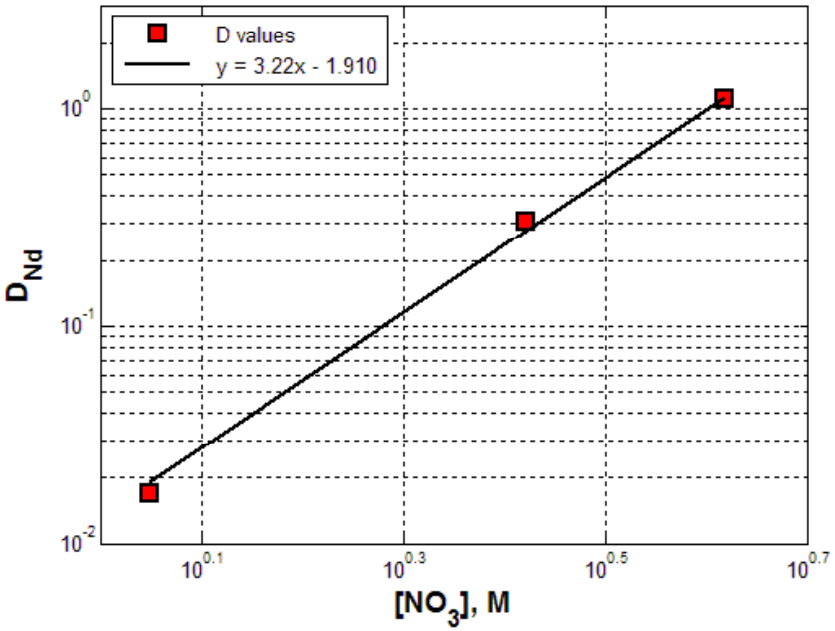
Batch contact distribution experiment for $Nd(NO_3)_3$ in variable Nitrate with TBP/dodecane





Aqueous feed

ID	HNO_3, M	NO_3, M	Nd, mM
Soln 1	0.1	0.1	0
Soln 2	0.1	0.6	2
Soln 3	0.1	1.1	5
Soln 4	0.1	2.6	10
Soln 5	0.1	4.1	14

Slope analysis of 3.2 confirms Nd^{3+} extraction

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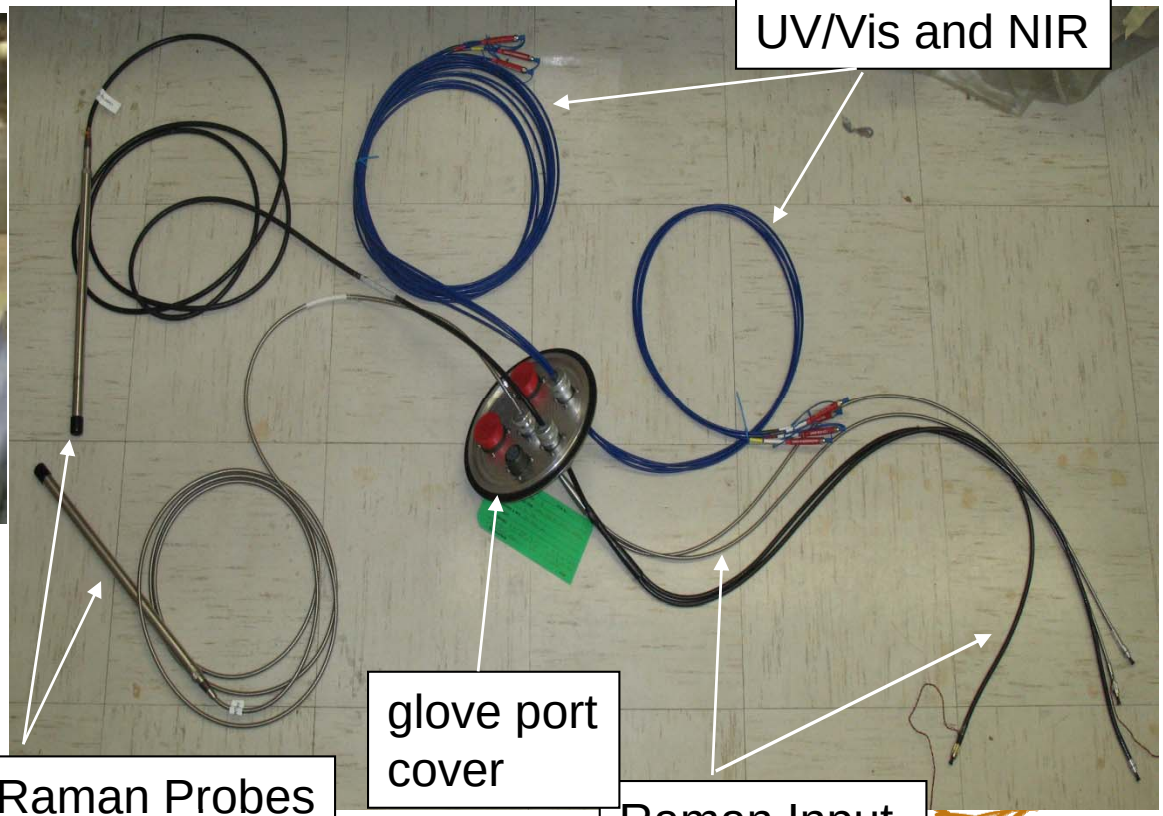
Centrifugal Contactor System Instrumented with Raman and VIS-NIR Spectroscopic Probes

centrifugal contactors installed within glovebox



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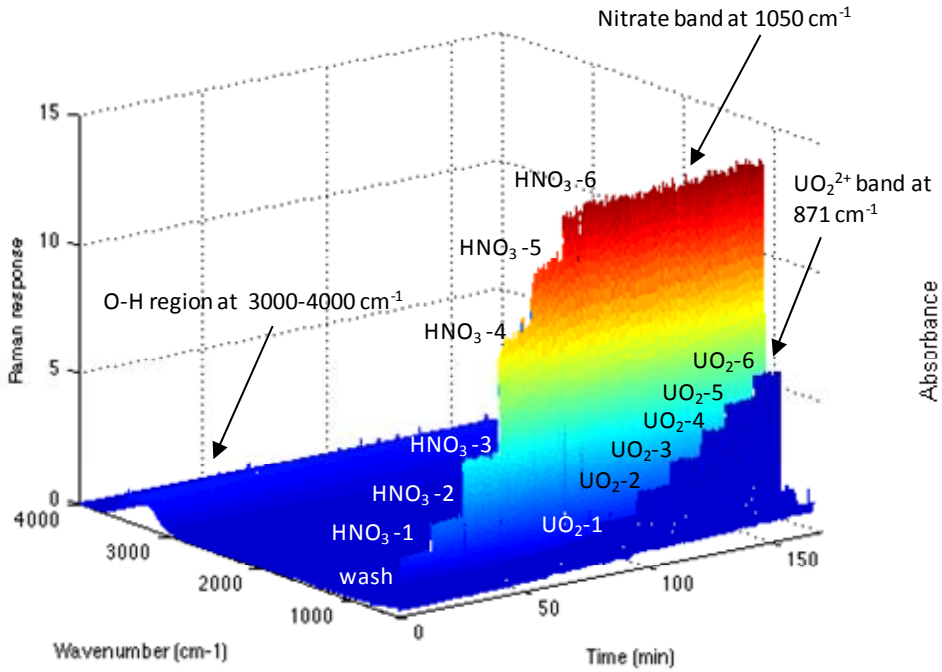
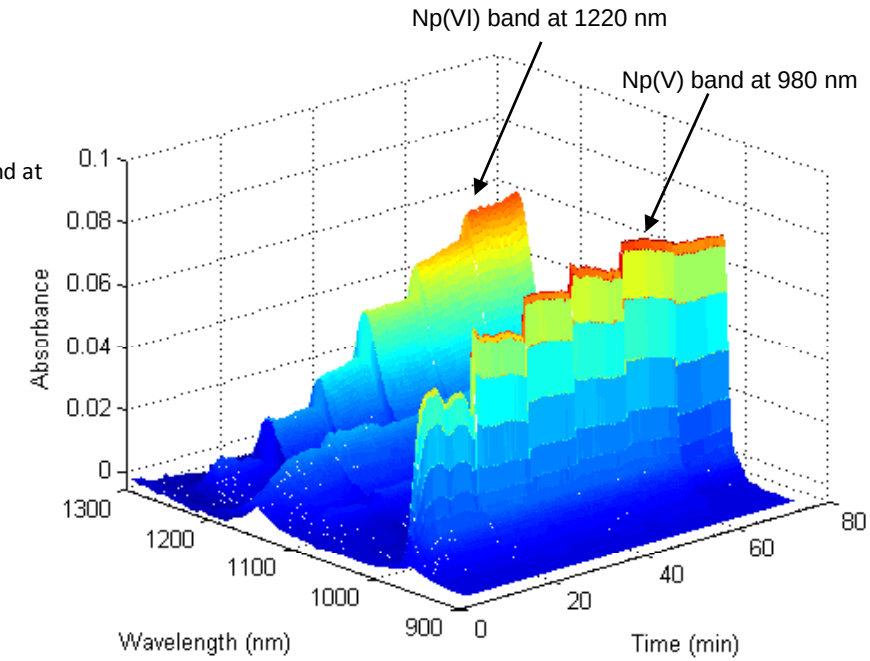
Flow Test:
Raman and VIS-NIR Monitoring of Fuel Simulants

Raman data



VIS-NIR data



Data collected on-line in real-time using running contactor system

Feed contains variable Np(V, VI), HNO_3 and $UO_2(NO_3)_2$

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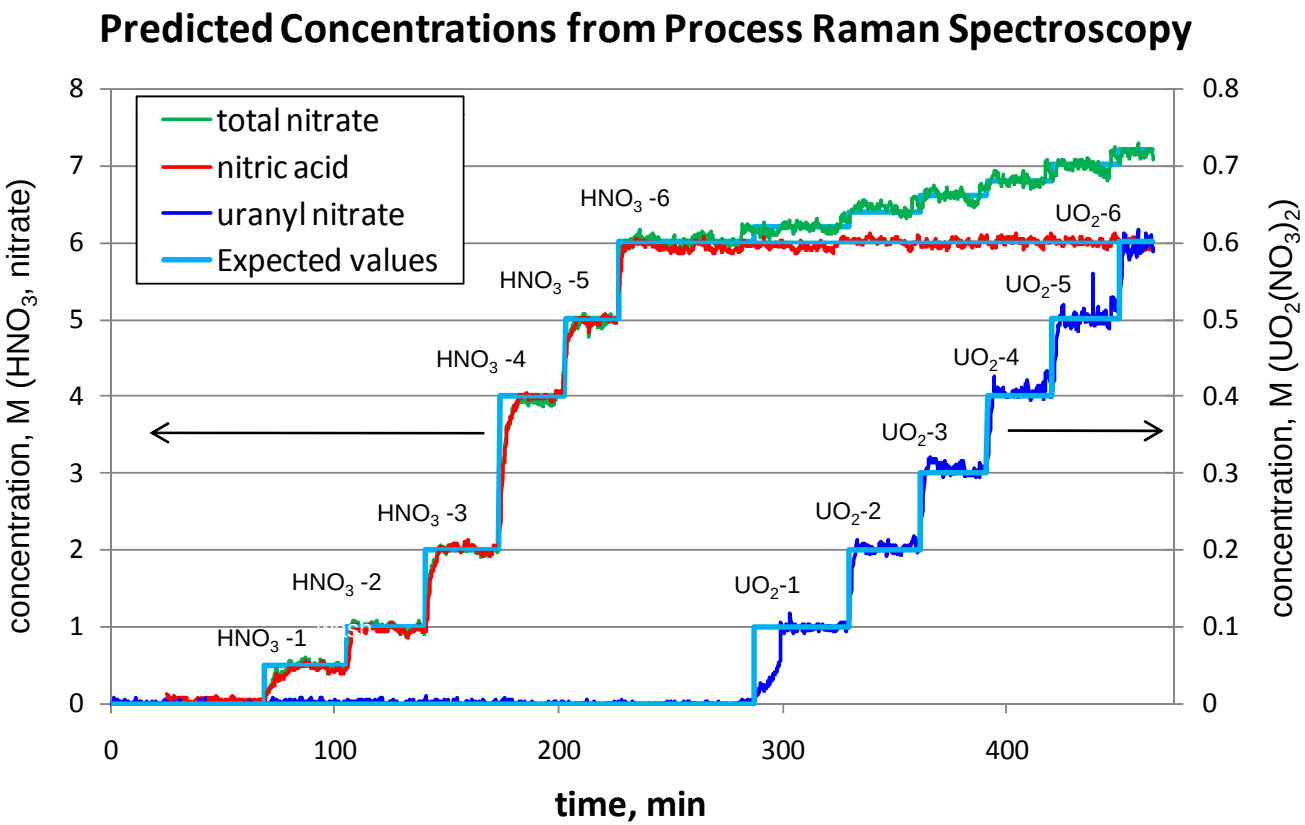
Chemometric model translation to flow test: Agreement between Measured and Predicted Raman on-line measurements

PLS model developed on static measurements successfully predict concentrations of U(VI), HNO_3, and nitrate under flow conditions in real-time



Fuel Feed Simulant, M

ID	HNO_3	$UO_2(NO_3)_2$	NO_3 total
HNO_3-1	0.5	0	0.5
HNO_3-2	1	0	1.0
HNO_3-3	2	0	2.0
HNO_3-4	4	0	4.0
HNO_3-5	5	0	5.0
HNO_3-6	6	0	6.0
UO_2-1	6	0.1	6.2
UO_2-2	6	0.2	6.4
UO_2-3	6	0.3	6.6
UO_2-4	6	0.4	6.8
UO_2-5	6	0.5	7.0
UO_2-6	6	0.6	7.2

Conclusions

- **Methods: Using simulants and BWR Spent Fuel**
  - Confirmed validity of PNNL's chemometric modeling approach using both static and flow testing
  - Demonstrated Raman spectroscopy for on-line monitoring of U(VI), nitrate, and HNO_3 concentrations, for both aqueous and organic phases
  - Demonstrated Vis/NIR for on-line monitoring of Np, Pu, Nd
- **Testing Facility: PNNL's Centrifugal Contactor Apparatus**
  - Glovebox installation of 16 *spectroscopically instrumented* centrifugal contactors
  - Performance of equipment (contactor and spectroscopic) verified
- **Technical Challenges**
  - Demonstrate applicability of outlined approach for complex simulants and commercial fuels on-line
    - interferences from fission products and optically active species
    - range of fuel types and flowsheets

Acknowledgements

- US DOE Nuclear Energy Advanced Fuel Cycle Initiative (AFCI), Separations Campaign
- US NNSA Office of Nonproliferation and International Security (NA-24)
- PNNL's Sustainable Nuclear Power Initiative (SNPI): Centrifugal contactor instrumentation