Real-time, on-line monitoring for quantification of U and Pu radionuclides in complex processing streams


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Abstract

Real-time quantification of radionuclides in recycling of used nuclear fuel is necessary for process control and safeguards analysis. This talk demonstrates the practical application of optical spectroscopy coupled with regression analysis to provide fast, non-destructive quantification of chemical species in complex processing streams. The approach is anticipated to be applicable to other areas of the nuclear processing field such as processing of legacy tank waste for disposal. The application employed Raman, near-infrared, and UV-Vis spectroscopy in multiple streams including aqueous and organic mixtures. It is demonstrated that accurate quantitation is achievable despite matrix effects, the presence of interfering species, or signal attenuation from competing solution species. As a result, real-time process control and enabling efficient processing of nuclear materials using the CoDCon process to produce a product stream containing a target ratio of uranium (U) and plutonium (Pu) becomes viable.
The need for nuclear energy

• Key piece of a diverse energy portfolio

• Of the green options, uniquely suited to meet baseload needs

• US currently utilizes an open fuel cycle
  – Roughly 95% U unreacted in used fuel!
  – Recycling used fuel can enhance efficiency and reduce radioactive waste volumes and lifetimes
Fuel recycle capabilities

- The chemistry and engineering are well developed
- Tremendous benefits in application can be realized with the addition of on-line monitoring
  - Real-time process control
  - Immediate safeguards and accounting of nuclear material
  - Potential for process optimization and enhanced understanding of process chemistry

Spectroscopic Investigations of Radiation Damage in Glasses Used for Immobilization of Radioactive Waste
https://www.researchgate.net/figure/A-schematic-diagram-of-closed-nuclear-fuel-cycle_fig1_265737133

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The CoDCon project

• Testing nuclear fuel recycling processes on lab scale
• Involves dissolving fuel (or simulant) and running liquid:liquid extractions to isolate U and Pu
• Goal:
  – Produce a product stream that is 30% Pu and 70% U
  – Determine if this can be controlled in real-time from on-line monitoring
  – Determine level of variability to process output

Bank of centrifugal contactors in radiological glove box where separation are completed
On-line monitoring of CoDCon

• Utilize optical spectroscopy
  – UV-vis
  – NIR
  – Raman

• … and chemometrics modeling
  – Accurately quantify in complex conditions
  – Can be applied in real-time


Project Goal

- The objective is to quantify
  - U4, U6, Pu3, Pu4, Pu6, Np4, Np5, Np6
  - in aqueous and organic phases
    - HNO$_3$ in aqueous

- using UVVis, NIR and Raman
  - although signal may be present from all / most analytes in all sensing systems some sensors are better than others for specific analytes
    - opportunity for sensor fusion
Challenges

• Analytes are radioactive and toxic
• Analytes are reactive and chemically active
  – convert from one cation to another in the presence of each other and HNO₃
• Target signal is often weak compared to other sources of signal
• Many interferences and non-linear responses
• Difficult to get concentration references in the process environment
  – must use laboratory measurements
• Difficult to obtain spectral reference measurements in the process environment
  – may be able to minimize the need w/ model
  – able to update the model easily if reference available
Modeling Strategy

• Modeling uses as much of what is known about the analytes and the process

• Model is based on classical least squares (CLS)
  – factor based model that is interpretable
  – easy to update
    • using references and accounting for new interferences
  – handle much of the non-linearity with linear factors
  – can easily be ‘lagged’ to utilize time-series to best advantage
CLS

\[ O(c_i) = (x_i - Sc_i)^T W^{-1} (x_i - Sc_i) \]
\[ \hat{c}_i = (S^T W^{-1} S)^{-1} S^T W^{-1} x_i \]

\( c_i \) = concentration at time \( i \)
\( x_i \) = measured spectrum at time \( i \)
\( S \) = analyte and interference spectra
\( W \) = clutter covariance

Classical least squares (CLS) and generalized least squares (GLS) models.

\( W \) can be used to account for “clutter” signal in the data using GLS.

Impose non-negativity.

\( W = I \) is CLS
\( W \neq I \) is GLS
Q Residuals for the Calibration Data

Calibration data consists of measurements of “pure” analytes in different concentrations of HNO₃.
Small batch of test data for mixture of Pu3+U4 (Samples 1081 to 1320)
signal - linear with concentration per unit concentration

interferences - typically not linear w/ conc

Pu3

Pu4

U4iB, U4iC

U6iB, U6iC, U6iD

U6

U4

Pu3

Pu4

U6

U4

U6iB, U6iC, U6iD
signal - linear with concentration per unit concentration

interferences - typically not linear w/ conc

Scores on Comp 1 (40.19%)

Scores on Comp 2 (0.74%)

Scores on Comp 3 (45.26%)

Class 0.5
Class 1
Class 2
Class 3
Class 4
Loci 1 and 2 on the panel show a linear and non-linear signal, respectively. The scores on Comp 1 and Comp 2 are shown for different concentrations of 0.5 M HNO₃ to 4.0 M HNO₃.

Mathematically, the expression is:

\[ \hat{c}_{U6} = \begin{bmatrix} t_1 & t_2 \end{bmatrix} \times b_{U6} \]
U4 and Pu3 for Test Data

The performance on the test data “looks poor,” especially for U4. Dig deeper….
slightly non-zero for reference
Validation Data

• Acquired several months prior to the new calibration data
• Expect different source ($I_0$)
• … and a potential interference due to
  – oops, a dissolved thermocouple
• Opportunity to show an advantage of CLS
  – easy to update
Model Performance on Validation

residuals are high!
New Interferences

Two new factors added to the model: one looks like change in the source and second looks like an unknown analyte (thermocouple?).

...but w/ CLS this is easy
Model Performance on Validation: accounting for interferences

U4 predictions are slightly higher and Pu3 predictions are slightly lower than previous model…

… and residuals are well within limits.
CLS with Lagging

\[ O(c_i) = (x_i - Sc_i)^T W^{-1} (x_i - Sc_i) + (\hat{c}_{i-1} - c_i)^T A_1 (\hat{c}_{i-1} - c_i) \]

\[ \hat{c}_i = \left( S^T W^{-1} S + A_1 \right)^{-1} \left( S^T W^{-1} x_i + A_1 \hat{c}_{i-1} \right) \]

- \( c_i \) = concentration at time \( i \)
- \( x_i \) = measured spectrum at time \( i \)
- \( S \) = analyte and interference spectra
- \( W \) = clutter covariance
- \( A_j \) = weighting at lag time \( j \) : \( A_1 = a_1 S^T S \)

With CLS it is easy to impose “contribution-based” constraints.
What about High Residuals?

\[ q_i = (x_i - Sc_i)^T W^{-1} (x_i - Sc_i) \]
\[ A_j \Rightarrow f(q_i, q_{CL}) A_j \]

reduce the lagging for measurements with high residuals

\[ f(q_i, q_{CL}) = \frac{2 \exp\left(\frac{-z}{\alpha}\right)}{1 + \exp\left(\frac{-z}{\alpha}\right)} \]

\[ \alpha = 10 \quad \alpha = 5 \]

~99% CL
Predictions for U4 with lagging

With CLS it is easy to impose “contribution-based” constraints – there are lot’s to choose from.
Conclusions

• The objective is to quantify multiple radionuclides in multiple fuel reprocessing streams and shows and example with UVVis

• Classical least squares is proving useful for this task:
  – interpretable, easy to update, can tease out small signal, can employ what we know (e.g., imposing zero constraints and non-negativity), add contribution-based constraints such as lagging