Developments in Nuclear Forensics at LLNL

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Requirements for Nuclear Forensics

• Validated Analytical Methods
  – RIMS
• Well Characterized & Meaningful Signatures
  – Radiochronometry
  – Stable Isotopes
• Knowledge & Experience to Enable Interpretation of Forensic Results
  – Comparative Methods
  – Interpretive Methods
• Demonstrated Competencies
LLNL LION (Finished October 2015)

TOF-MS optimized for accuracy, precision, and versatility
Resonance Ionization Mass Spectrometry

Elementally selective ionization followed by mass analysis

1) **Desorption**

*Pulsed desorption event removes atoms and molecules from a solid*

2) **Ionization**

One element is ionized by the resonant photons

3) **Mass Analysis**

Photo-ions are accelerated to mass analyzer

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**Sensitivity - Selectivity - Speed - Spatially Resolved**
Measurement of Cs, U, & Pu isotopes from UO$_2$ fuel

Cs isotope ratios measured as SIMS before U and Pu are removed from the sample, preserving them to be measured next.

Cs signal is two orders of magnitude greater than Pu signal during this measurement.
Isotope ratios reported by RIMS in UO$_2$ fuel

U, Pu, and Cs isotope ratios reported by RIMS

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Measured (1σ)</th>
<th>RSD (1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{234}$U/$^{238}$U</td>
<td>0.00060(3)</td>
<td>7%</td>
</tr>
<tr>
<td>$^{235}$U/$^{238}$U</td>
<td>0.07025(54)</td>
<td>0.8%</td>
</tr>
<tr>
<td>$^{236}$U/$^{238}$U</td>
<td>0.00501(22)</td>
<td>6.1%</td>
</tr>
<tr>
<td>$^{240}$Pu/$^{239}$Pu</td>
<td>0.1319(20)</td>
<td>1.4%</td>
</tr>
<tr>
<td>$^{242}$Pu/$^{239}$Pu</td>
<td>0.00344(27)</td>
<td>7.8%</td>
</tr>
<tr>
<td>$^{137}$Cs/$^{135}$Cs</td>
<td>0.630(3)</td>
<td>0.46%</td>
</tr>
</tbody>
</table>

Comparing three neighboring cube samples near the rod center

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{240}$Pu/$^{239}$Pu</th>
<th>RSD (2σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LANL - Ca</td>
<td>0.1335(35)</td>
<td>2.6%</td>
</tr>
<tr>
<td>RIMS - C</td>
<td>0.1319(40)</td>
<td>2.8%</td>
</tr>
<tr>
<td>LANL - Cb</td>
<td>0.1312(29)</td>
<td>2.2%</td>
</tr>
</tbody>
</table>

RIMS measurements are consistent with LANL chemistry results
Uranium Oxide: Useful Yield

Pre-sputtering raises uranium useful yield in uranium oxide from \( \sim 0.6\% \) to 6.5\% depending on the type of primary ion and impact energy.

- Virgin \( \text{UO}_2 \): 0.6\%
- \( \text{He}^+ \) dosed \( \text{UO}_2 \): 4.1\%
- \( \text{Ar}^+ \) dosed \( \text{UO}_2 \): 6.5\%
- 2-color RIS: 38\%
- 3-color RIS: 24\%
- 1-color RIS: 23\%

*Ranebo et al., 2009*
Radiochronometry

• The model age of nuclear material is a powerful signature for nuclear forensics

• *Comparative signature:* no assumptions are required about sample purification or production history

• *Predictive signature:* model sample history is assumed
  – sample was completely purified from decay products at some time in the past
  – sample has remained a closed system since that time
Concordant and discordant radiochronometers

- **Concordant model ages** from two or more radiochronometers provide a high degree of confidence that the model age represents the actual purification age of the sample.
  - May help to identify the process.
- **Discordant model ages** provide information on the relative fractionation between daughter isotopes and parent during sample production.
  - Regardless of concordance or discordance, if the system remains closed, the model dates are constant, high-value signatures.

Kayzar and Williams (2016) JRNC 307:2061-2068
What if **none** of the simple model assumptions are valid?

0) This sample probably formed over a relatively long time period (continuously or discontinuously?)
1) Both parent and daughter are incorporated during formation
2) The system was not closed

The expression for a radioactive grand-daughter:

\[
N_3 = \frac{\lambda_2 \lambda_1}{(\lambda_2 - \lambda_1)} N_1(0) \left[ \frac{(e^{-\lambda_1 t} - e^{-\lambda_3 t})}{(\lambda_3 - \lambda_1)} - \frac{(e^{-\lambda_2 t} - e^{-\lambda_3 t})}{(\lambda_3 - \lambda_2)} \right] \\
+ \frac{\lambda_2 N_2(0)(e^{-\lambda_2 t} - e^{-\lambda_3 t})}{(\lambda_3 - \lambda_2)} + N_3(0)e^{-\lambda_3 t}
\]
Just as the simpler closed-system chronometers assume no fractionation between the parent and daughter, the straight-forward application of these open-system methods requires the assumption of no fractionation between the daughter and granddaughter.

Note that these methods, shown here graphically, cannot give a unique age for the sample until more is known about the potential sequestration (fractionation) of daughter products from uranium during production. For unknown samples, they will give the minimum and maximum age of the material.
Blind:  12.5 yrs < Time Since Filling <  27 yrs
True Age = 17.7 yrs
Oxygen isotopes signatures record geolocation and process.

**Known**
- Global $^{18}$O/$^{16}$O variations in H$_2$O

**Unknown**
- Global variations in water $^{18}$O/$^{16}$O are well-documented.
- There is temperature-dependent fractionation of $^{18}$O/$^{16}$O when water is used to produce nuclear materials.
- Process-specific fractionation must be measured to extract geolocation information.

**Oxygen isotope signature**

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Our previous work has shown that oxygen isotope values in UO₂ fuel pellets from different production facilities.

\[
\delta^{18}O = \frac{\left(\frac{^{18}O}{^{16}O}\right)_{\text{sample}} - \left(\frac{^{18}O}{^{16}O}\right)_{\text{reference std}}}{\left(\frac{^{18}O}{^{16}O}\right)_{\text{reference std}}} \times 1000 \text{ per mil = 0.1 %}
\]
Point-to-Population Comparison: When There is Not an Exact Match

- Most common situation, i.e. no exact match available
- Used to tie forensic samples to historic data (e.g. production measurements)
- Statistical methods can evaluate similarities using one or many characteristics

**Limitation:**
conclusions are limited by availability of comparative data
Alameda County Swap Meet
Sample: Initial Analyses

Major Phase: Uranium Ammine Oxide Hydrate

U concentration: 73 wt% U

$^{87}\text{Sr} / ^{86}\text{Sr}: 0.712004$

$^{235}\text{U} / ^{238}\text{U}: 0.0072591$

$^{234}\text{U} / ^{238}\text{U}: 0.00005259$
Alameda County Swap Meet Sample: Multivariate Approach

PCA Helps Guide Interpretation
- Used to establish consistency with a known population
  - Inclusion/exclusion
- Unknown is consistent with US material in PCA space.

iDAVE – automated multivariate statistical package
- iDAVE queries can provide a “predicted source”
- Assumes unknown source is represented in the database
- Queries generate leads, but do not unequivocally identify unknown samples

Multivariate statistical techniques allow for simultaneous comparison of many variables.
Subject matter expertise and judgement must be applied to determine similarity between samples or compliance with a threshold value.

Agreement or disagreement between a single metric (or even class of metrics) may not be indicative of the relationship between samples.

– Example: the presence of certain trace elements from may be related to processing after production (i.e. crushing in a ball mill) that would make two similar samples look unrelated, at least based on trace elements.
Summary

• Resonance Ionization Mass Spectrometry shows great promise for applications in nuclear forensics due to its sensitivity, specificity, and spatial resolution
• Model age is a powerful signature for nuclear forensics
  – comparative: establish or eliminate genetic link
  – predictive: assume sample history
• Most of our attention in nuclear forensics has been focused on the actinides, but stable elements can carry information as well.
• Our ability to analyze samples far outstrips our ability to interpret our analytical results – improvements in both comparative and predictive approaches are needed.