Analysis of nuclear materials for safeguards and forensics

Séminaire CETAMA «L'analyse: du nano au macro ...»
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Nuclear analytical measurements play a key role for
• the development of nuclear technology and for
• the assurance of its peaceful use

Contents:

1/ Analysis of uranium/plutonium at high concentrations (reprocessing)
   – the role of modelling

2/ Nuclear forensics
   – age determination
How to safeguard a reprocessing facility?

The verifications performed are based upon flows into and out of the main processing areas of a 3-area-structure:

1. *Pond and dissolution area:* ....

2. *Process and product area:*
   chemical process area (separation, purification,...) from the input accountancy tank to the storage entrance;
   - *(Non-)* destructive assay of feed input into the plant and samples from the separation process

   Target accuracies must be below 1% ("bias defect")

3. *Storage areas for final products:* ....
The main technique:
**Hybrid K-edge/XRF Densitometer (HKED)**

**XRF:**
- U/Pu atom ratio

**K-edge densitometer:**
- In U & Pu solutions the actinide with the highest concentration ↔ U atom concentration

**U & Pu atom concentration**
**XRF**

**U/Pu ratio**

**Hybrid K-edge Densitometry (HKED)** used extensively in Safeguards e.g. to determine U and Pu concentration in dissolved spent fuel (or dissolved MOX product)

**K-edge densitometry: U conc.**

**XRF: U/Pu ratio**

requires a multi-point instrument calibration → expensive & time consuming

*Feasible if the matrix does not change*

► Alternative for variable matrices, e.g. pyrochemistry:

single-point calibration involving a physical sample, supplemented by the modelling of correction coefficients by MCNP modelling
Computed corrections for input samples to the PUREX process

U Kα₁ X-rays are more attenuated by concentrated samples than the higher energy Pu Kα₁ X-rays → U/Pu ratio reduces with concentration

Variation of the MCNP calculated U/Pu-ratio as a function of the U concentration

\[
y = -0.0269x + 143.31 \\
R^2 = 0.993
\]

U Kα₁ / Pu Kα₁

U matrices, 14 mm container
Forced Collisions & Point Detector

U concentration (g/L)

Joint Research Centre

Kα₁ of U = 98.4 keV
Kα₁ of Pu = 103.8 keV

Corrections are really needed!
2\textsuperscript{nd} example:

Pyro-processing samples \(\rightarrow\) high Z elements (Cd, Bi) \(\rightarrow\) attenuation of X-rays

Aqueous $\text{HNO}_3$, U/Pu = 100

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>(0–300) g/L Bi + 10 gU/L</td>
</tr>
<tr>
<td>II</td>
<td>(0–300) g/L Cd + 10 gU/L</td>
</tr>
<tr>
<td>III</td>
<td>(10–300) g/L U</td>
</tr>
</tbody>
</table>
Pyro-processing of spent fuel: Matrix-dependent MCNP corrections for U/Pu ratios

Experimental point-calibration at 150 g/L, see

Matrix correction factor:

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Correction factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>1.019</td>
</tr>
<tr>
<td>U</td>
<td>1.025</td>
</tr>
<tr>
<td>Bi</td>
<td>1.046</td>
</tr>
</tbody>
</table>

Up to 8% corrections!

single point-calibration plus MCNP modelling reduces the traditional multi-point calibration effort
On 16/12/2003 ~ 3 kg of radioactive material was detected in Rotterdam Harbour, NL in a shipment from Jordan.

- Bulk samples and swipes
Results - 1

▶ U isotopes:

Gamma spectrometry:
- U-235 enrichment 0.7 %

<table>
<thead>
<tr>
<th>TIMS</th>
<th>U-234</th>
<th>U-235</th>
<th>U-236</th>
<th>U-238</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>0.0050 (± 6.8%)</td>
<td>0.712 (± 0.12%)</td>
<td>&lt;bdl</td>
<td>99.28 (± 0.012%)</td>
</tr>
<tr>
<td>Sample B</td>
<td>0.0053 (± 6.8%)</td>
<td>0.712 (± 0.12%)</td>
<td>&lt;bdl</td>
<td>99.28 (± 0.012%)</td>
</tr>
</tbody>
</table>

Thermal Ionisation MS:

Regions of spectrum: FUND25A.CNF
Results - 1

- U content from titration points at yellow cake material

- Trace elements:
  
  **ICP-MS**
  
  - Main impurities: Ca, Cr, Fe, Mo, Na, Ni, **P** (>1000 ppm)

- Ore either young or low U content: Pb isotopes ~ natural

<table>
<thead>
<tr>
<th>MC-ICP-MS</th>
<th>$^{204}\text{Pb}$</th>
<th>$^{206}\text{Pb}$</th>
<th>$^{207}\text{Pb}$</th>
<th>$^{208}\text{Pb}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case study</td>
<td>1.47 ± 0.03</td>
<td>24.83 ± 0.10</td>
<td>21.47 ± 0.09</td>
<td>52.24 ± 0.20</td>
</tr>
<tr>
<td>material</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural Pb</td>
<td>1.4</td>
<td>24.1</td>
<td>22.1</td>
<td>52.4</td>
</tr>
</tbody>
</table>
Results - 1

SEM/EDX:

- agglomerates of small crystals with an average length of 10 µm and diameter of 2 µm
- uranium with iron, nickel and chromium impurities. Al, Ca, Mg and Si in the amorphous part around.
XRD:
- complicated powder pattern with broad peak shape
- similarities with the following compounds:
  - Ca(UO$_2$)$_3$CO$_3$(OH)$_6$ · 3H$_2$O (Urancalcarite)
  - (NH$_4$)$_4$UO$_2$(CO$_3$)$_3$
    (Ammonium Uranyl Carbonate)
• intermediate product from uranium processing
  ✓ microstructure, crystal structure and the presence of CO$_3^{2-}$ points to AUC
• high P indicates phosphate based ores
  ✓ igneous rocks in e.g. Kola, South Africa, Brazil
  ✓ sedimentary rocks in e.g. North Africa, Middle East, USA
• natural Pb isotopic composition suggests a young and low U content deposit
  (e.g. in phosphorite ores U content is ~100 ppm)
Infrared Spectroscopy

- Material is AUC \cdot xH_2O (cf. literature spectrum)
- Nitrate impurity (from solvent extraction)
- Sulphate impurity (from dissolution of starting material)

IR bands from:
- uranyl,
- nitrate,
- sulfate,
- water
Rare earth element pattern (REE):
Valuable signature for determination of ore-type;
REE pattern hardly changes during hydrometallurgy

- Phosphoria formation
- Marine sedim. Tethyan phosphorite shale-like pattern (Egypt)
- Continental “old” phosphorite (Khubugsul)
- Marine sedimentary Tethyan phosphorite seawater-like pattern (Israel)
- Case study material
**87Sr/86Sr ratio:**

\[ ^{87}\text{Rb} \rightarrow ^{87}\text{Sr} \text{ (β-decay with } 4.8 \times 10^{10} \text{ a).} \]

Phosphorites have low Rb/Sr → 87Sr/86Sr low
Age Dating

- “Age” dating refers to the time of last chemical purification of material.
- Key element of nuclear forensics, makes it possible to determine origin of material.
- Based on the ingrowth of daughter nuclides separated from the parent.
Age determination:

Age from $^{234}\text{U}/^{230}\text{Th}$ ratio:

100 ± 10 years!

Thorium not completely removed during chemical processing.
Problem with $^{234}\text{U} / ^{230}\text{Th}$ age determination: result depends on the quality of the U/Th separation

Alternative: age from the $^{232}\text{Th} / ^{228}\text{Th}$ ratio:

- If separation U/Th incomplete $\rightarrow$ high amount of residual thorium, initial activity ratio $^{228}\text{Th} / ^{232}\text{Th} = 1$
- Depends upon Ra/Th separation; chemically different.
Results - 3

Alternative: age from the $^{232}$Th / $^{228}$Th ratio:

$$
\begin{align*}
^{232}\text{Th} & \rightarrow^{1.41 \times 10^{10} \text{a}}^{228}\text{Ra} \\
^{228}\text{Ra} & \rightarrow^{5.75 \text{a}}^{228}\text{Ac} \\
^{228}\text{Ac} & \rightarrow^{6.13 \text{h}}^{228}\text{Th} \\
^{228}\text{Th} & \rightarrow^{1.91 \text{a}}
\end{align*}
$$

- Initial decrease:

$^{228}$Th decay faster than build-up from $^{228}$Ra

Production date: 1988 $^{\pm 4.2, +7.7}$ years

rather than 100 years with U/Th
The U-234/Th-230 clock works with another material:

22 February 2007, Lauenförde, Germany
14 Uranium pellets found in a garden

Last chemical separation
Nov./Dec. 1990

Pellet production campaign Feb./March 1991;
Fall 1991 upgrade of physical protection at the fuel production facility
Outlook on age determination

- Investigate uranium and plutonium age dating for both mass spectrometric and radiometric methods
- Contributions to uncertainty budget from
  - Sample measurement itself
  - Calibration constants
  - Physical constants such as half-lives
- Double ratio method for Pu age determination
  - $^{238}\text{Pu}/^{234}\text{U}$, $^{239}\text{Pu}/^{235}\text{U}$ and $^{240}\text{Pu}/^{236}\text{U}$
Traditional Daughter/Parent Equation

Decay constants used in age dating calculations. Following Bateman equations:

\[
R_{dp} = \frac{N_d}{N_p} = \frac{\lambda_p}{\lambda_d - \lambda_p} \left(1 - e^{\lambda_p t - \lambda_d t}\right) + \frac{N_d^0 e^{-\lambda_d t}}{N_p^0 e^{-\lambda_p t}}
\]

\[
t = \frac{1}{\lambda_p - \lambda_d} \ln \left(1 - \frac{R_{dp}}{\frac{\lambda_d - \lambda_p}{\lambda_p}}\right)
\]

Uncertainty contributions for the age \( t \):
- measured D/P ratio \( R_{dp} \), half-lives of D and P
Uncertainty contributions for age dating of Pu materials:

- $^{238}\text{Pu}/^{234}\text{U}$, $^{239}\text{Pu}/^{235}\text{U}$ and $^{240}\text{Pu}/^{236}\text{U}$

- Half-life uncert. only significant for methods with ratio uncertainty <1%
- At very low ratio uncertainty difference between contributions of half-life between institutions
Two pairs of atom ratios can be used to calculate the age.

If both parents and both daughters are the same element then the need for IDMS is eliminated, only chemical separation.

Numerical solution is required
Preliminary, MC method

\[
\frac{R_{dp1}}{R_{dp2}} = \frac{N_{d1}N_{p2}}{N_{d2}N_{p1}} = \frac{\lambda_{p1}(\lambda_{d2} - \lambda_{p2})(1 - e^{\lambda_{p1}t - \lambda_{d1}t})}{\lambda_{p2}(\lambda_{d1} - \lambda_{p1})(1 - e^{\lambda_{p2}t - \lambda_{d2}t})}
\]

Numerical root solver to calculate "t"

Age
Infrared analysis confirms ammonium uranyl carbonate

$^{87}\text{Sr}/^{86}\text{Sr}$: low value is typical for phosphorites (Rb incompatibility)

REE pattern: flat, no Eu or Ce anomaly → previously found in certain sandstone-type and reworked phosphorite

Production date: 1988 $^{+7.7}_{-4.2}$ years (Al Qa’im was operational from 1984 to 1990)

Etc...

Any of the data is not in disagreement with the presumption that the material originates from Iraq.
Safeguards at reprocessing facilities:
the needs stimulated major improvements in accuracy/precision (from 1% to 0.1%) for U/Pu measurements.

Nuclear forensics:
interaction between various disciplines (chemistry, physics, materials science),
advances made in trace element detection for source attribution and in age determination.

Coupling between experiment and modelling becomes more important.
Summary / Outlook

A strong nuclear nonproliferation regime is vital for the application of nuclear technology to prevent

► clandestine production of fissile material
► diversion of fissile material from the civil fuel cycle

Effective safeguards and nonproliferation will continue to require cutting edge and highly sensitive detection techniques for nuclear material