CRM: 3 new CETAMA standards in 2016
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CRM : 3 new CETAMA standards in 2016

CEA/DEN/DRCP/SERA/LAMM : C. Rivier
CETAMA MAIN OBJECTIVES IN THE NUCLEAR FIELD

CETAMA (The Commission for establishment of analytical methods) is a unit of CEA (the French Alternative Energies and Atomic Energy Commission) in charge of improving the quality of analytical results in the nuclear field

- Based on a network of experts and analytical labs
- 13 Working Groups under activity

Catalog of certified reference materials for nuclear fuel cycle needs, regularly updated
High purity standards and solutions (U, Pu and Np),
High chemical purity Pu metal MP2 renewing: MP4 PuO₂ pellets

U matrix CRMs
- MINx & Gems series (Uranate)
- MP2-MP4 MIRF
- ²⁴²Pu
- ²³⁷Np
- HDBP

Isotopic composition (U, Pu)
- ²⁴³Am spike (IRMM collab)

Solution standards:
- Chemical purification
- High yield separation process
- Radiolysis risk management

Solid standards:
- Homogeneity (powder< pellet…)
- Improvement of uncertainty assessment in the certification process

Necessity to enhance collaborations in the nuclear chemical metrology field
34 Reference material catalog of CETAMA: recent and on going CRM

High purity standards and solutions (U, Pu and Np),

High chemical purity Pu metal MP4

Matrix CRMs & impurities
- Feldspath UOC
- Nuclear 25 oxides glass
- Floralies

MINx & Gems series (Uranate)

Isotopic composition (U, Pu)
- $^{243}$Am spike (IRMM collab)

$^{242}$Pu, $^{237}$Np, HDBP

Homogenized real samples in support to method characterisation by ILC
2. Reference sample characteristics assessment: Possible use as RM

RM “matrix” and impurities lead to complex developments
- A lot of matrix: mud, concrete, resin, metals
- With stable interfering, coming from the matrix itself, and radioactive ones
IAEA specifies several target values for measurement uncertainties for the control of nuclear materials. For example, relative uncertainty for Pu analysis by ID-TIMS is 0.18%.

Destructive analysis: mainly relative techniques

Achieving these target values requires:

- to have a well structured metrological scheme based on chemical and isotopic certified reference materials
- Characteristics of the method: trueness and precision
- To participate in interlaboratory comparison
Use of reference materials (ISO Guide 33)

**Material for instrument calibration**
- High chemical purity RM
- Standard solutions
- Sources

**Material for method trueness and precision assessment**
- RM « matrix »
- Isotopic spikes

**Calibration curve setting on**

**Calibration QC**

**Initial characterisation of analytical method**

**QC material (global measurement process)**
UOC Feldspath new « matrix » CRM
Front end of fuel cycle
Safeguards and forensic
Collaboration with
IAEA/NML & NWAL expert laboratories
AREVA and CEA laboratories

More details in:
C. Rigaux et al. CETAMA TM  Sept 2015
C. Rigaux et al. IAEA TM  Feb 2016
**UOC FELDSPATH NEW « MATRIX » CRM**

- **UOC: FELDSPATH**
  - Matrix: ammonium uranate
  - Certification
    - date: 1989
    - impurities: Fe, PO$_4$, SO$_4$

- Enlarged certification to other impurity contents:
  - U, Ca, Fe, Mg, Mo, V, Zr, REE pattern

- Identification of the origin of the ore samples

- Uncertainty improvement

- **ASTM C967-08**
  - Specification for ore concentrates

- **Both certification and PTS ILC**

- **Excess variance approach**
  - to take into account the spread of the results and the uncertainties of the laboratories
**METHODOLOGY AND DATA PROCESSING**

\[
x_{CRM} = x_{char} + \delta x_{hom} + \delta x_{stab}
\]

\[
u_{CRM} = \sqrt{u_{char}^2 + u_{hom}^2 + u_{stab}^2}
\]

- Data processing of analysis results:
  - Potentiometry analysis of U content
  - Mainly ICP MS methods for impurities
  - Weighted mean (GUM)
  - Robust statistics
  - Weighted mean+Excess variance

- Homogeneity /stability:
  - stratified random sampling on 10 bottles
  - ANOVA statistical processing on 1 factor
  - ISO guide 35
  - Normalized deviation test (between 1989 and 2015)

<table>
<thead>
<tr>
<th>element</th>
<th>Fe</th>
<th>Ca</th>
<th>Mg</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td>U inter</td>
<td>13.6093</td>
<td>10.6019</td>
<td>0.17267</td>
<td>0.296685</td>
</tr>
<tr>
<td>U intra</td>
<td>8.0233</td>
<td>4.8233</td>
<td>0.0428</td>
<td>0.133967</td>
</tr>
<tr>
<td>U hom</td>
<td>0.9649</td>
<td>0.9814</td>
<td>0.1471</td>
<td>0.1647</td>
</tr>
<tr>
<td>U relatif (%)</td>
<td>3.03</td>
<td>0.92</td>
<td>0.78</td>
<td>0.22</td>
</tr>
</tbody>
</table>
CONCENTRATION OF THE MAJOR IMPURITY CERTIFIED VALUE

**U**

**Mo**

**Zr**

**Fe**

**Ca**

**Mg**
• Based on 4-6 laboratory results
• ICP MS and QMS
• Excess variance approach
• Homogeneity component : 3%
<table>
<thead>
<tr>
<th>Eléments Terres Rares</th>
<th>Teneur REE (mg/kg U)</th>
<th>U MRC relatif à k=2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0,0083</td>
<td>56,6%</td>
</tr>
<tr>
<td>Ce</td>
<td>0,0178</td>
<td>36,5%</td>
</tr>
<tr>
<td>Sm</td>
<td>0,0041</td>
<td>29,3%</td>
</tr>
<tr>
<td>Eu</td>
<td>0,00068</td>
<td>47,1%</td>
</tr>
<tr>
<td>Gd</td>
<td>0,0045</td>
<td>51,1%</td>
</tr>
<tr>
<td>Tb</td>
<td>0,00054</td>
<td>33,3%</td>
</tr>
<tr>
<td>Dy</td>
<td>0,00262</td>
<td>25,2%</td>
</tr>
<tr>
<td>Ho</td>
<td>0,00049</td>
<td>24,5%</td>
</tr>
<tr>
<td>Er</td>
<td>0,00129</td>
<td>30,2%</td>
</tr>
<tr>
<td>Yb</td>
<td>0,00126</td>
<td>42,1%</td>
</tr>
<tr>
<td>Lu</td>
<td>0,00020</td>
<td>55,0%</td>
</tr>
</tbody>
</table>
UOx 25 glass new matrix CRM

- Specific HLW real matrix

Collaboration

AREVA and CEA

More details in

M. Crozet et al. CAC2016 (Barcelona, June)
M. Crozet et al. ASTM workshop 2016 (Vienna, June)
First step: fabrication (CEA/DEN/DTCD–LCV)
- Precursors: SiO$_2$, B$_2$O$_3$, Na$_2$O, Al$_2$O$_3$, CaO, Nd$_2$O$_3$, Fe$_2$O$_3$, ZrO$_2$, ZnO, MoO$_3$, Li$_2$O, La$_2$O$_3$, Cs$_2$O, Ce$_2$O$_3$, BaO, Pr$_2$O$_3$, MnO$_2$, SrO, TeO$_2$, P$_2$O$_5$, NiO, Cr$_2$O$_3$, SnO$_2$, RuO$_2$, Pd
- Grinding
- Homogeneity

Second step: certification (CETAMA)

\[
X_{CRM} = X_{char} + \delta X_{hom} + \delta X_{stab}
\]

\[
\frac{m_{ox,glass}}{m_{glass}} = m_{\text{B precursor}} - m_{\text{B lost}} + m_{\text{glass (precursors)}} + m_{\text{impurities}} - m_{\text{lost glass}}
\]

\[
\frac{X_{CRM}}{2} = u_{\text{char}}^2 + u_{\text{hom}}^2 + u_{\text{stab}}^2
\]

\[
u_{\text{hom}} = \sqrt{u_{\text{between}}^2 + u_{\text{within}}^2}
\]

- Stratified random sampling
- ANOVA 1 factor
Third step: verification (CETAMA)

- Confirmation by ILC
- XRF Q and SQ
- ICP OES and MS
CRM UOx Glass: 25 components

- 22 certified mass contents
- 3 indicative mass contents

<table>
<thead>
<tr>
<th>Component</th>
<th>% w/w</th>
<th>U CRM k=2 % w/w</th>
<th>U CRM rel k=2 % of % w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>44.52</td>
<td>0.67</td>
<td>1.5%</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>13.38</td>
<td>0.28</td>
<td>2.1%</td>
</tr>
<tr>
<td>Na₂O</td>
<td>9.23</td>
<td>0.19</td>
<td>2.0%</td>
</tr>
<tr>
<td>CaO</td>
<td>3.66</td>
<td>0.19</td>
<td>5.0%</td>
</tr>
<tr>
<td>Nd₂O₃</td>
<td>3.512</td>
<td>0.042</td>
<td>1.2%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.921</td>
<td>0.040</td>
<td>1.3%</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>2.771</td>
<td>0.035</td>
<td>1.3%</td>
</tr>
<tr>
<td>ZnO</td>
<td>2.383</td>
<td>0.032</td>
<td>1.3%</td>
</tr>
<tr>
<td>MoO₃</td>
<td>2.221</td>
<td>0.030</td>
<td>1.3%</td>
</tr>
<tr>
<td>Li₂O</td>
<td>1.951</td>
<td>0.034</td>
<td>1.7%</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>1.521</td>
<td>0.034</td>
<td>2.2%</td>
</tr>
<tr>
<td>Cs₂O</td>
<td>1.361</td>
<td>0.019</td>
<td>1.3%</td>
</tr>
<tr>
<td>BaO</td>
<td>0.865</td>
<td>0.029</td>
<td>3.4%</td>
</tr>
<tr>
<td>Ru₂O₇</td>
<td>0.853</td>
<td>0.016</td>
<td>1.9%</td>
</tr>
<tr>
<td>Pd</td>
<td>0.776</td>
<td>0.022</td>
<td>2.9%</td>
</tr>
<tr>
<td>Pr₂O₃</td>
<td>0.660</td>
<td>0.021</td>
<td>3.2%</td>
</tr>
<tr>
<td>MnO₂</td>
<td>0.470</td>
<td>0.016</td>
<td>3.5%</td>
</tr>
<tr>
<td>SrO</td>
<td>0.402</td>
<td>0.013</td>
<td>3.3%</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.220</td>
<td>0.011</td>
<td>4.8%</td>
</tr>
<tr>
<td>NiO</td>
<td>0.080</td>
<td>0.010</td>
<td>13%</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.0501</td>
<td>0.0063</td>
<td>13%</td>
</tr>
<tr>
<td>SnO₂</td>
<td>0.0300</td>
<td>0.0038</td>
<td>13%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>% w/w</th>
<th>U k = 2 % w/w</th>
<th>U rel k = 2 % of % w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>TeO₂</td>
<td>0.205</td>
<td>0.017</td>
<td>8.5%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.183</td>
<td>0.072</td>
<td>1.7%</td>
</tr>
<tr>
<td>Ce₂O₃</td>
<td>1.221</td>
<td>0.021</td>
<td>1.7%</td>
</tr>
</tbody>
</table>
U metal Floralies serie

- Impurity in uranium matrix
- Complementary of “Champignon” series ($\text{U}_3\text{O}_8$)
- Renewing of old CETAMA CRM
Cutting of U metal stored in oil
Isotopic composition of natural uranium
Devoted to the calibration for SQ impurity analysis:
  - mainly metal and alkali metal
  - Different range of concentrations
Certification by ILC
  - ICP AES and molecular or atomic spectrophotometry measurement
  - Without uncertainty value assessment nor confidence interval?

Improvement of the certified composition assessment?
<table>
<thead>
<tr>
<th>Ref. SAMPLE</th>
<th>ELEMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ag</td>
</tr>
<tr>
<td>Bleuet</td>
<td>&lt;0,5</td>
</tr>
<tr>
<td>Capucine</td>
<td>0,5</td>
</tr>
<tr>
<td>Dahlia</td>
<td>0,6</td>
</tr>
<tr>
<td>Eglantine</td>
<td>1,2</td>
</tr>
<tr>
<td>Fuschia</td>
<td>1,3</td>
</tr>
<tr>
<td>Géranium</td>
<td>10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ref. SAMPLE</th>
<th>ELEMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>Verveine</td>
<td>1020</td>
</tr>
</tbody>
</table>

- Unit : mg.Kg⁻¹</sup>⁻¹
- Homogeneity >2 g samples
“Matrix” and impurities RM lead to complex developments but are of paramount importance for safeguards and D&D analysis.

The fabrication of homogenised real samples well characterised thanks to ILC data processing approaches is a suitable solution:

- from synthetic doped sample to real sample

- Future European project proposal devoted to D&D waste analysis
- 4 main topics and challenges
  - Sampling methodology extension to HA and MA waste
  - NDA / in situ current techniques performance assessment, new development
  - DA adaptation in laboratory – performance assessment
  - Matrix CRM

Call for partners: danielle.roudil@cea.fr or cetama@cea.fr
Thank you for your attention
Nuclear Reference Materials producers

- **CETAMA**

- **LNHB**

- **Institute for Reference Materials and Measurements**

- **NIST**

- **CERCA-LEA (Activity standards lab)**

- **NUCLITEC**

- **New Brunswick Laboratory**
  U.S. Department of Energy