Joint Research Centre (JRC)

Challenges for development and provision of metrological Quality Control tools in nuclear safeguards, nuclear forensics and nuclear security

Y. Aregbe - ESARDA WGDA chair

IRMM - Institute for Reference Materials and Measurements
The mission of the IRMM is to promote a common and reliable European measurement system in support of EU policies.

Confidence in Measurements®

http://www.irmm.jrc.be
<table>
<thead>
<tr>
<th>Action</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Action 15012</td>
<td>“RM Biotech” Specific knowledge on current issues and measurement problems in the field of biotechnology</td>
</tr>
<tr>
<td>Action 111102</td>
<td>“Europe RM” Specific knowledge on current issues and measurement problems for industrial applications</td>
</tr>
<tr>
<td>Action 22206</td>
<td>“ENV RM” Specific knowledge on current issues and measurement problems in the field of environment</td>
</tr>
<tr>
<td>Action 33303</td>
<td>“Food RM” Specific knowledge on current issues and measurement problems in the field of food and microbiology</td>
</tr>
<tr>
<td>Action 53102</td>
<td>“Metro” Specific knowledge on current issues and measurement problems in the field of nuclear safeguards</td>
</tr>
<tr>
<td>Common, generic knowledge</td>
<td>on the production of CRMs (general principles, study set-up, evaluation).</td>
</tr>
<tr>
<td>Common quality management</td>
<td>system and procedures; accredited to ISO Guide 34, ISO 17025, 17043</td>
</tr>
<tr>
<td>Common processing</td>
<td>facilities (mixing, grinding, sieving, bottling)</td>
</tr>
<tr>
<td>Common laboratory</td>
<td>facilities for testing of samples</td>
</tr>
<tr>
<td>Common storage and distribution</td>
<td></td>
</tr>
</tbody>
</table>
The three pillars of the NPT
  • non-proliferation, disarmament and peaceful uses of nuclear energy

The three “pillars” of nuclear security
  • prevention, detection and response
    – Nuclear security in the broad sense includes countering nuclear illicit trafficking, proliferation resistance and physical protection

The triple concept SSS (Safeguards, Security, and Safety)
  • nuclear safety and security can be seen as two sides of the same coin
    – converging more and more towards the idea of internationally binding security and safety standards

Herman van Rompuy – Nuclear Security Summit 2010
‘the EU, with its large multinational nuclear industry, has a particular interest in ensuring that the peaceful uses of nuclear energy take place with the highest standards of nuclear safety, security and non proliferation’
Quality Control

- Method validation and instrument calibration
- Traceability and comparability of measurement results
- Uncertainty of measurement results
- External performance evaluation
- Document and material standards
- Deployment of a quality system
• Support nuclear safeguards and fissile material control by providing metrological tools for bulk and particle analysis

Certified Reference Materials CRMs
• CRMs to the highest standard of uranium and plutonium
• CRMs establish traceability of a measured value (i.e. the analytical result) to a primary unit of measurement as defined in the SI system

Reference Measurements
• Only measurement results traceable to the respective SI unit can be regarded as truly comparable.
• Reliable measurement results of high quality to safeguards authorities and for environmental applications in bulk and particle analysis

Interlaboratory Comparisons
• External evaluation of measurement performance
Development of reference methods and reference materials
Determination of nuclear signatures

- **Modified Total Evaporation (MTE)**
  - New tool for TIMS for measurements of U-minors in nuclear safeguards; forensics; geo-and cosmo-chemistry;
  - Unprecedented level of accuracy for isotope ratio measurements;
  - Joint advancement in measurement sciences of international reference and safeguards laboratories (IRMM, ITU, DOE-NBL, IAEA-SGAS)

*Journal of Analytical Atomic Spectrometry, 2011, 26, 550*
Pu CRMs for “age dating”

In nuclear forensics

“Age” defined as the “Time that has passed since the last chemical separation of the mother and daughter isotopes”

“clocks” – pairs of mother-daughter isotopes:

$^{241}\text{Pu}/^{241}\text{Am}$ (alpha, gamma and IDMS-TIMS using $^{243}\text{Am}$-spike)

$^{238}\text{Pu}/^{234}\text{U}, ^{239}\text{Pu}/^{235}\text{U}, ^{240}\text{Pu}/^{236}\text{U}$ (and $^{242}\text{Pu}/^{238}\text{U}$) – IDMS-TIMS

Co-operation with JRC - ITU Karlsruhe – feasibility study on several samples of NBS Pu(SO$_4$)$_2$.4H$_2$O and IRMM PuO$_2$
Age in years of NBS SRM 946 (calculated for 17 October 2010) for the "clocks" $^{238}\text{Pu}/^{234}\text{U}$, $^{239}\text{Pu}/^{235}\text{U}$ and $^{240}\text{Pu}/^{236}\text{U}$ with expanded uncertainties ($k=2$). Their average of $40.43 \pm 0.13$ a ($k=2$) is indicated by a dashed black line while the uncertainty of this value is depicted in dashed grey lines.

Spin off: additional results on isotope ratios for NBS 946, NBS 947, NBS 948 – action sheet NBL-IRMM
Pu – “fingerprints” in environmental samples

Isotopic plutonium "fingerprint" using TIMS

• Reactor-grade $^{240}\text{Pu}/^{239}\text{Pu} \sim 0.4$ or higher

Environmental samples from Chernobyl:
K2-K6 core soil sampled 2, 3, 5 and 6 cm from the top
Oko13 moss sample same sampling site
Oko20 moss sample 1-2 km distance from the nuclear power plant


• Global fallout $^{240}\text{Pu}/^{239}\text{Pu} \sim 0.18$

Isotopic plutonium "fingerprint" using TIMS

• Weapons-grade $^{240}\text{Pu}/^{239}\text{Pu} \sim 0.03-0.07$

IAEA 368 collected at Moruroa Atoll, the former nuclear weapon testing site.
Activity concentration 31 Bq/kg ($^{239+240}\text{Pu}$)
Isotopic “fingerprinting” U-particles

- Detection of any undeclared nuclear material or activities
- Attribution of intercepted materials
- Response to theft, illegal transfer of nuclear materials
- Cooperation with ITU, CEA/DAM and DOE-LLNL (action sheet)

**Age determination**
• Single particle measurement by TIMS

1. Deposition of an individual particle on a carburized single Re filament

NUSIMEP-6 sample
High-quality isotopic data on single U-reference particles were obtained using an improved method based on in situ SEM micromanipulation, filament carburization and MIC detection.

The improved method has been successfully applied for detection of U-signatures in real-life particles collected at a nuclear facility:


**Objective:** production of U-oxide reference particles certified for isotopic abundances and U amount content per particle to be used for evaluating sensitivity in MS techniques (SIMS, TIMS, LA-ICP-MS).

**Method:** Loading of a fixed number (1–6) of monodispersed U-oxide particles (aerosol generator, ITU) on carburized Re-filaments and analysis by ID-TIMS using a $^{233}$U spike isotopic IRMM-058 CRM.

**First results:**

- Set 1: particle(s) + spike
- Set 2: particle(s) + spike + additional HNO$_3$ 8 M

- Estimated U-density (slope of the regression line) = 4.54 g cm$^{-3}$
  Material density is 5.35 g cm$^{-3}$ if assumed stoichiometry for particles is U$_3$O$_8$ and 5.46 g cm$^{-3}$ if assumed stoichiometry is UO$_3$.
- Particles are probably composed of microspheres of highly defected material with a lower density than that expected for a crystalline U-oxide form (8.38 g cm$^{-3}$ for U$_3$O$_8$ and 7.0 g cm$^{-3}$ for UO$_3$).
Interlaboratory Comparisons

- External control tool for measurements of nuclear fuel cycle materials and environmental samples
- Evaluation of measurement performance
- Comparability of analytical measurement results
- Demonstration of measurement capabilities on all levels of the international measurement infrastructure from normal field laboratories to network laboratories to reference laboratories to national metrology institutes involved in measurements for nuclear safeguards
- Demonstration of competence on a high quality level to accreditation, authorisation, and inspection bodies as well as to safeguards authorities
REIMEP - Regular European Interlaboratory Measurement Evaluation Programme

- REIMEP was started by IRMM in 1982 for carrying out external control of the quality of the measurements of the nuclear fuel cycle materials
- REIMEP samples are matching materials analysed routinely in the nuclear industry and controlled by safeguards authorities (UF6, synthetic input solution, synthetic MOX fuel solution, U and Pu nitrate)

NUSIMEP - Nuclear Signatures Interlaboratory Measurement Evaluation Programme

- The Nuclear Signatures Interlaboratory Measurement Evaluation Programme (NUSIMEP) was established in 1996 to support the growing need to trace and measure the isotopic abundances of elements characteristic for the nuclear fuel cycle present in trace amounts in the environment

http://irmm.jrc.ec.europa.eu/interlaboratory_comparisons
NUSIMEP-6

- IAEA recommended participation (Technical Meeting on Particle Analysis of Environmental Samples for Safeguards 2007)
- 20 participants from 15 institutes:
  - IAEA-SAL, 7 NWAL, 2 JRC, research institutes & universities
  - All nuclear weapons states were represented
- Graphite planchet
- Measurement of $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$
- Routine measurement procedure

\[
\frac{n(235\text{U})}{n(238\text{U})} = 0.007 \pm 0.00035 \quad (k=2)
\]
\[
\frac{n(238\text{U})}{n(235\text{U})} = 0.348 \pm 0.0075 \quad (k=2)
\]

This graph displays all measurement results and their associated uncertainties. These uncertainties are shown as reported, with various coverage factors and levels of confidence. The grey band represents the reference interval ($X_{ref} \pm 2u_{ref}$).
TWO GRAPHITE DISKS:
-WITH SINGLE DEPOSITION
-WITH DOUBLE DEPOSITION

TASK: ISOTOPIC COMPOSITION
-10 PARTICLES OF SINGLE DEPOSITION
-20 PARTICLES OF DOUBLE DEPOSITION

DOUBLE DEPOSITION PREPARED IN OUR AEROSOL CHAMBER

PARTICLE DENSITY VERIFIED BY SEM
ISOTOPIC COMPOSITION VERIFIED BY SIMS
NUSIMEP-7

61 single depositions
7 selected

14 double depositions
7 selected
Double deposition: average results

NUSIMEP-7: Uranium isotope amount ratios in uranium particles

Certified value for \( \frac{n(^{235}\text{U})}{n(^{238}\text{U})} \) enrichment 1 : 0.009 072 6 ± 0.000 004 5 \( [U=k \cdot u_c (k=2)] \)

This graph displays all measurement results and their associated uncertainties.
These uncertainties are shown as reported, with various coverage factors and levels of confidence.
The grey band represents the reference interval (\( X_{ref} \pm 2u_{ref} \)).

- Laboratory value > 10% reported by labs 7107 (LA-ICP-MS), 7092 (LA-ICP-MS) and 7104 (Alpha Spectrometry)

\( \pm 1\% \pm 2\% \)
Double deposition: average results

NUSIMEP-7: Uranium isotope amount ratios in uranium particles

Certified value for \( n(^{235}U)/n(^{238}U) \) enrichment 2: 0.034 148 ± 0.000 017 \( [U=k \cdot u_c (k=2)] \)

This graph displays all measurement results and their associated uncertainties. These uncertainties are shown as reported, with various coverage factors and levels of confidence. The grey band represents the reference interval \( (X_{ref} ± 2u_{ref}) \).
Double deposition: average results

NUSIMEP-7: Uranium isotope amount ratios in uranium particles
Certified value for $n(^{234}\text{U})/n(^{238}\text{U})$ enrichment 1 : 0.000 074 365 ± 0.000 000 060  

$U = k \cdot u_c (k=2)$

This graph displays all measurement results and their associated uncertainties. These uncertainties are shown as reported, with various coverage factors and levels of confidence. The grey band represents the reference interval ($X_{ref} \pm 2u_{ref}$).

$\pm 5\%$
$\pm 10\%$

This graph displays all measurement results and their associated uncertainties. These uncertainties are shown as reported, with various coverage factors and levels of confidence. The grey band represents the reference interval ($X_{ref} \pm 2u_{ref}$).
Double deposition: average results

NUSIMEP-7: Uranium isotope amount ratios in uranium particles

Certified value for $n(^{234}\text{U})/n(^{238}\text{U})$ enrichment $2 : 0.00034514 \pm 0.0000024 \ [U=k\cdot u_c (k=2)]$

This graph displays all measurement results and their associated uncertainties. These uncertainties are shown as reported, with various coverage factors and levels of confidence. The grey band represents the reference interval $(X_{ref} \pm 2u_{ref})$.

±5% ±10%

value > 20% reported by lab 7104 (Alpha Spectrometry) and 7109 (LA-ICP-MS)
NUSIMEP-7: Uranium isotope amount ratios in uranium particles

Certified value for $n(^{236}\text{U})/n(^{238}\text{U})$ enrichment 1 : 0.000 008 020 5 ± 0.000 000 007 1

This graph displays all measurement results and their associated uncertainties. These uncertainties are shown as reported, with various coverage factors and levels of confidence. The grey band represents the reference interval ($X_{\text{ref}} ± 2u_{\text{ref}}$).

$\pm 100\%$

value > 100% reported by labs 7099 (SEM-TIMS) and 7104 (Alpha Spectrometry)
Double deposition: average results

**NUSIMEP-7: Uranium isotope amount ratios in uranium particles**

Certified value for $n^{(236)U}/n^{(238)U}$ enrichment $2 : 0.000\ 103\ 268 \pm 0.000\ 000\ 070 \ \ [U=k\cdot u_c (k=2)]$

This graph displays all measurement results and their associated uncertainties. These uncertainties are shown as reported, with various coverage factors and levels of confidence. The grey band represents the reference interval ($X_{ref} \pm 2u_{ref}$).

- **LG-SIMS E2**
- **SEM-TIMS E2**
- **LA-ICP-MS E2**
- **SIMS E2**

$\pm 100\%$

*value > 100%* reported by labs 7109 (LA-ICP-MS) and 7104 (Alpha Spectrometry)
Further Development in U-particle QC tools

- Cooperation with IAEA SGAS and ITU on SIMS analysis (LG-SIMS)
- Cooperation (action sheet) with LLNL and PNNL on the Study of Chemical Changes in Uranium Oxyfluoride Particles (nano-SIMS, \(\mu\)-Raman)
- Cooperation with CEA on characterisation of uranium reference particles
- Further development of the aerosol deposition
- Production of QC samples dust with few particles of different uranium enrichments (optical microscope)
- Production and certification of monodispersed particles in cooperation with ITU
- NUSIMEP-9
U/Pu synthetic input solution prepared from dissolved MOX fuel with addition of NU (U:Pu = 100:1)

REIMEP-17 samples will be prepared and distributed by ITU
REIMEP-17 samples will be certified by IRMM: IRMM provides the reference values for U and Pu amount contents and isotopic compositions

3 different concentrations for nuclear laboratories:

a) high – (Pu in mg range) addition of inactive fission products - spiking is possible with IRMM-1027 LSD spike
b) medium – (Pu in μg range)
c) low - (Pu in ng range) for environmental labs – NUSIMEP-8

Start foreseen: beginning of 2012!
Consultant / expert group meetings

- Exchange of expertise using the ESARDA platform
- Exchange of expertise using the INMM annual meetings (NBL-SME, ACS N15)
- Exchange of expertise using the CETAMA WGs
- IAEA Technical Meetings
  - Particle Analysis of Environmental Samples for Safeguards
  - Bulk Analysis of Environmental Samples for Safeguards
  - Nuclear Reference Materials for Safeguards Verification Measurements by Destructive Analysis (DA)

- Technical advice to DG DEVCO and EEAS for ECAS via EC-SP
Scientific/technical advice via EC-SP

- Support to ECAS (IAEA)
  - EU contribution to new Nuclear Material Laboratory from IfS

H. Nackaerts IAEA Deputy Director General, Head of the Department of Safeguards, Y. Amano IAEA Director General, Y. Aregebe EC-JRC-IRMM and G. Voigt Director IAEA-SGAS at the groundbreaking ceremony for the new IAEA Nuclear Material Laboratory, Seibersdorf, 7 Sept. 2011.
Exchange beyond the safeguards community on dedicated technical topics relevant to nuclear safeguards, forensics and security
Dedicated ESARDA WG DA workshops

- Measurements of Minor Isotopes in Uranium – hosted by IRMM
  - ESARDA BULLETIN, No. 40, December 2008

- Measurements of Impurities in Uranium – hosted by ITU
  - ESARDA BULLETIN, No. 43, December 2009

- Direct analysis of solid samples using LA-ICP-MS – hosted by HAEA
  - ESARDA BULLETIN, No. 46, December 2011

- Workshop on Uncertainties in Nuclear Measurements
  - 8-9 Nov. 2011 – will be hosted by the IAEA-SGAS
    - Compare and discuss the different approaches in uncertainty estimation
    - Consistency of measurements carried out by nuclear laboratories and by operators with the GUM approach (ITV2010)

- WGDA technical sheets on QC, RMs, Masspec, COMPUCEA, titration, colourmetry via:
  http://esarda2.jrc.it/references/Technical_sheets
Recommendations

- Quality control must be extend also to the minor isotopes
- Composition- & Matrix-matched reference materials
- Internal and external quality control
- Uranium particle reference materials with certified amount of 1-2 pg per particle with different isotopic compositions mixed with interfering elements (Pb, …)
- Reference U, Pu particles mixed with dust
- Particles of different sizes: 0.1-10 μm
- “Trace Elements in Yellowcake” reference material
- Trace elements in uranium dioxide
- Isotopic reference materials (Pb, S, Nd) in uranium-containing matrices
- Interlaboratory comparisons for minor isotope, impurity and particle analysis
- Interlaboratory comparison on “age-dating”
Supporting ESARDA’s educational role in reaching the general public
Training & Education

- Chapter I of the EURATOM treaty concerning the promotion of research
- European Council conclusion on the need for skills in the nuclear field

- ENEN training courses on safeguards
  - ESARDA academic course on Nuclear Safeguards and Non-Proliferation (IRMM, ITU, DGENER, IAEA, DOE, ...)
  - BNEN advanced course on safeguards in Belgium (SCK, IRMM)

- Use of Reference Materials and the Estimation of Measurement Uncertainty (IRMM)

- Nuclear forensics training (ITU)

- EUSECTRA - European nuclear security training centre (ITU)
### Conclusions

#### Technical convergence of nuclear safeguards, nuclear forensics and nuclear security

**Scientific Disciplines:** Chemistry, Physics, Material science

<table>
<thead>
<tr>
<th>Analytical and technical tools</th>
<th>Nuclear material analysis</th>
<th>Environmental sample analysis</th>
<th>Seized/collection material analysis</th>
<th>Metrological quality control tools</th>
<th>Other sources of information</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Verification of non-diversion</td>
<td>Detection of undeclared activities</td>
<td>Consistency, Coherence, Conformity of information, materials and processes</td>
<td>Certified Reference Materials (CRMs) Interlaboratory Comparisons (ILCs)</td>
<td>Close cooperation with data analysts, police, governments,…</td>
</tr>
<tr>
<td>Amount content, isotopes</td>
<td>Bulk and particle analysis; isotopic fingerprint</td>
<td>Bulk and particle analysis; isotopic fingerprint; anionic and metallic impurities, microstructure, “age” – last separation date</td>
<td>Metrological quality control tools</td>
<td>Method development, method validation, QC/QA</td>
<td></td>
</tr>
</tbody>
</table>

**Nuclear Safeguards**
- Complete, correct and comprehensive picture of a State’s nuclear activities

**Nuclear Forensics**
- Identifying origin and intended use using information inherent to the (nuclear) material

**Nuclear Security**
- Prevention/Detection/Response of theft, sabotage, unauthorized access, illegal transfer of nuclear/radioactive materials and associated facilities
Conclusions

- In contrast to the relevant differences of political and legal nature similarities between nuclear safeguards, forensics and security in advancement and applicability of analytical techniques.

- Confidence in comparability and reliability of measurement results in nuclear material and environmental sample analysis are established via certified reference materials (CRMs), reference measurements, and interlaboratory comparisons.

- The organisation of dedicated workshops and active participation in training courses on topics relevant to these three fields create a public awareness of the synergies beyond the safeguards community and opens possibilities for cooperation in research and development.

- Within the WG DA, ESARDA is currently keeping abreast of methodologies applicable in the fields of nuclear safeguards, security and forensics.
Acknowledgement

- Magnus Hedberg, K Mayer and colleagues from JRC-ITU
- Jane Poths, S Balsley and colleagues from IAEA-SGAS
- F Pointurier and colleagues from CEA/DAM
- A Ruas and colleagues from CEA/DEN
- R Kips and colleagues from US DOE LLNL
- P Mason and colleagues from US DOE NBL
- ESARDA WG DA vice-chair and all members
- Invited experts and participants in ESARDA WG DA Workshops
- JRC colleagues