Nuclear material characterization: CEA/DAM Ile de France capacities. Focus on SIMS analysis

Anne-Laure FAURÉ, Fabien POINTURIER, Olivier MARIE, Amélie HUBERT, Anne-Claire POTTIN, Maxime BRIDOUX

CEA, DAM, DIF, F-91297 Arpajon, France

NKS-B Seminar on Nuclear Forensics in Nordic Countries
5th – 6th October 2015
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  - Organic compound characterization
  - Particle analysis

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- Some applications of SIMS in the field of nuclear material characterization:
  - Presentation of the results obtained for the CMX-4 exercise organized by NF-ITWG
  - Measurement of fluorine in micrometric uranium particles
  - Geolocation of uranium via oxygen measurement in micrometric uranium particles?

- Links between CEA and nordic countries

- Conclusion
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Conclusion
Some history about CEA/DAM Ile de France

Environment Survey of Nuclear test Sites

1996

Environment Monitoring of French CEA military division centers

2001

IAEA NWAL for environment samples for bulk and particle analysis

2010

Analysis of higher amounts of NM (> 100 mg)

Specificity of the laboratories: capability to perform trace analysis in environmental samples → adaptation of this expertise in the nuclear material characterization when low amounts of material is available.
Bulk analysis: precise isotopic ratios and quantification of U and Pu at trace level

**Chemical treatment:**
- Total dissolution of the sample by acid digestion,
- Addition of tracers ($^{233}$U and $^{244}$Pu) for isotopic dilution,
- Separation, concentration and purification of U and Pu by ion exchange chromatography.
- Great care to protect samples from contaminations (cross contamination, atmosphere, glassware...)

**Uranium and Plutonium measurements by MC-ICP-MS (Neptune Plus, Thermo):**
- High sensitivity: >1.2 V/ppb
- Measurement of $^{236}$U/$^{38}$U isotopic ratio below $10^{-7}$ for a 1ppb solution,
- Detection limit for Pu below 0.5 fg ($1\text{ fg} = 10^{-15}\text{ g}$).
Decay chain of the $^{238}\text{U}$

- $^{238}\text{U}$ 4.5x$10^9$ y
- $^{234}\text{Th}$ 24.1 d
- $^{234}\text{U}$ 2.45x$10^5$ y
- $^{230}\text{Th}$ 7.5x$10^4$ y
- $^{226}\text{Ra}$ 1599 y
- $^{206}\text{Pb}$ stable

Uranium extraction and refining

During chemical purification, daughter isotopes are discarded

Starting of the chronometer

Results of REIMEP 22 interlaboratory comparison on the age determination of a young uranium material (below 2 years)

- Varga et al, Applied radiation and Isotopes, 2015, 102, 81-86
Each uranium ore type gets a specific REE pattern (depending on the geological origin). The REE patterns remain unaltered from uranium ores to uranium ore concentrates (UOC).

REE measurements on a quadrupole ICP-MS (“X Series”, Thermo)
- Need for an internal spike to obtain precise concentrations (no need if only REE pattern is requested)
- LD < ppb (1 ng/g U)


Chemical treatments on chromatography resins
1) to remove uranium
2) to concentrate REE

~ 100 mg UOC dissolution in PFA pre-cleaned vials
Organic compound analysis: detection of trace polymer residues, solvents or explosives

- Uranium processing may include solvent extraction using a variety of organic solvents. Uranium can also be associated with explosive materials (nuclear weapon), fiber reinforced materials.
- The identification of these products provides useful information about the production process and/or origin of the nuclear material.

Direct analysis by Orbitrap

Extraction by Twister™ followed by Gas Chromatography

- Bridoux et al, Analytica Chimica Acta, 2015, 869, 1-10
Fundamentals on Particle Analysis

A way to detect proliferation without having access to the nuclear material

- Micrometric particles coming from a nuclear facility have an uranium isotopic composition characteristic of the industrial process.

Need of sensitive techniques 1) to detect uranium particles and 2) to measure isotopic ratios on individual uranium particles.
Detection of Uranium bearing particle among thousands of other particles, mainly dust particles

- **Scanning electron microscope (SEM)**: Use of an automated particle detection software, “Gun Shot Residue” to identify U particles thanks to EDX analysis. No information on the U isotopic composition.

- **Fission Track (FT)**: Irradiation of samples under well thermalized neutron flux to induce U/Pu fission. Information on the size of the particle or $^{235}$U abundance.
Detection of Uranium bearing particle among thousands of other particles, mainly dust particles

**Secondary Ion Mass Spectrometry (SIMS)**: Use of an automated particle detection software, Automated Particle Measurement. Estimation of the $^{235}$U abundance. *(See after)*

CAMECA IMS 7F
(Gennevilliers, France)
Precise isotopic composition measurement

- **Thermal Ionization Mass Spectrometry (TIMS)**

- **Secondary Ion Mass Spectrometry (SIMS)**

Thermo Triton
(Bremen, Germany)

![TIMS filament](image)

![Graph Showing Isotopic Ratios](image)

- Natural Uranium
- Low Enriched Uranium
- High Enriched Uranium
- 235U/238U
- 234U/238U
- 0.001 0.01 0.1 1 10

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Identification of U chemical phases

- Measurement on individual particle with μ-Raman after SEM localization
- Possible coupling with a SEM for micrometric particles analysis (≥ 2 μm).

Main uranium compounds encountered during the different steps of the fuel cycle

- UO₂, UF₄
- UF₆, UO₂F₂
- Uranium Ore concentrates
- U, UO₂
- U₃O₈

Pointurier and Marie, Journal of Raman Spectroscopy, 2013, 44, 12, 1753-1759
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- Links between CEA and Nordic countries
Principle: Bombardment of a sample surface with primary ions followed by mass spectrometry measurement of the emitted secondary ions.

Some information on basics and instrumentation can be found on the following links:
- SIMS Theory Tutorial from Evan Analytical Group (www.eag.com)
- SIMS Tutorials from the School of Geosciences, University of Edinburgh (www.geos.ed.ac.uk)

High vacuum: \(10^{-8}-10^{-10}\) mbar
Principle and Instrumentation

Cesium source:
light elements (C, N, O, F…)

Duoplasmatron source:
U, Th, Pu

Electron gun:
analysis of insulated sample

Chamber

Detection block:
Electron multiplier, Faraday cup, channelplate

Magnetic sector
Sample treatment for particle analysis

Particle extraction by sucking up (Vacuum impactor)

Swipe sample containing particles

Particle extraction by means of a plastic tip

Particle extraction is performed inside a laminar flow box (in a disposable glove bag when using the vacuum impactor technique)
SIMS particle analysis process

1. Particle localization using APM software (duration ~ 12h)

   - Principle: acquisition of ionic images of $^{235}$U and $^{238}$U
   - Data treatment to set the particle boundaries
   - Achievement of the coordinates of the particles and the distribution of the $^{235}$U abundances

2. Selection of particles of interest for precise microbeam measurements

   - Is@238 per field (cps)
   - Is@238 per pixel (cps)

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Focus on particle selection from APM result

What are the aims of APM? 2 cases:
1) The sample contains just a few uranium particles: APM helps to find these particles and to get their coordinates
2) In some samples, thousands of uranium particles can be detected. APM helps to select particles among the main isotopic composition and the extrema.

Characterization of some of these particles to determine precisely the $^{235}$U main abundance

Characterization of these particles to determine precisely the $^{235}$U minimum abundance
Microbeam measurement

Sample: NBS 100
Data file: D:\Cameca IMS Data\Analyses\Standard\NBS U100 NZ\2015\21-09-2015\NBS100-21092015# Recipe: No_name_2.rdp
Duo+ 1e: 1000eV Ip: 2.39e-01/2.30e-01nA Raster: 0um DT: Off Gate: 100%
P: 3.3e-10mbar SpleHV: +5000V MR: 400 FA: 1800um CD: 400um DeltaE: 75eV
Comments:

Achievement of all precise isotopic compositions of U particles
### Advantages

<table>
<thead>
<tr>
<th>Advantage</th>
<th>Drawback</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space resolution of a few µm, down to 50 nm (NanoSIMS)</td>
<td>Isobaric interferences</td>
</tr>
<tr>
<td>Low detection limits down to ppb level (1µg/kg)</td>
<td>Matrix effect</td>
</tr>
<tr>
<td>In situ analysis</td>
<td>Low roughness (&lt; a few microns)</td>
</tr>
<tr>
<td>Very low sample consumption (may be less than 1 µm³)</td>
<td>Planeity</td>
</tr>
<tr>
<td>Large panel of analysis: Isotopic and elemental measurements, ion images, depth profiling</td>
<td>Samples must be compatible with high vacuum</td>
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</tbody>
</table>
SIMS particle analysis: new generation of instruments

- **The LG-SIMS (or IMS 1280)**: new generation of SIMS instrument enabling
  - Simultaneous detection of all uranium isotopes (ion multi-collection)
  - Removal of most of the isobaric interferences (high mass resolution)

- **The NanoSIMS**: state of the art of ionic images with a lateral resolution of 50 nm.

Left SEM images of UO$_2$ particles. Right nanoSIMS ion image of $^{16}$O in UO$_2$ particles. From Lawrence Livermore National Laboratory, USA
The place of SIMS in the analytical procedure of nuclear material

- **Need of very low amount of material:**
  - Sampling can be performed at the beginning of the characterization
  - For bulk material, particle sampling by wiping the surface or loading of some fragments of the material.
  - For powder material, sampling with a plastic tip.

- **SIMS can be used as a “screening technique”**

- Be careful with the tools used for sampling because it can lead to interferences for further analysis
  - Metallic tools can leave metallic particles that can be detected for instance by SEM or by ICP-MS after chemical treatment.
  - Plastic tools can leave organic particles than can be detected for instance by organic mass spectrometric techniques.

- More generally, it is recommended to use very high quality reactants and inert recipients (like PTFE vials) to minimize the risk of contamination and to have a quite well-established analytical procedure before any sample manipulation.
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Presentation of the CMX-4 exercise

- Fourth exercise organized by the Nuclear Forensics International Technical Working Group (NF-ITWG)
  - Objective of ITWG: ITWG is a working group of experts including scientists, law enforcement officers, first responders and nuclear regulators. Their aims are to provide assistance and technical solutions on the field of nuclear forensics to national or international authorities.
  - 4th Comparative Material Exercise (CMX-4): 3 uranium samples were provided to participating laboratories. The 16 labs were asked to provide information related to the 3 samples based on an exercise scenario.

- Description of the samples: two pellets and one powder sample

Particles were extracted by means of a tip (ES1) or by wiping the surface of the pellets with a cotton cloth (ES2 and ES3). Particles were loaded onto carbon planchet with the vacuum impactor technique.
First results: Distribution of the $^{235}$U abundances given by APM

Cluster A

Cluster B

Cluster C

ES1

ES2

ES3
**What information does APM brings?**

- “Bell-shape” distributions which **centers are in good agreement with the analysis of macroscopic amounts of materials** (“bulk” measurements carried out by ICP-MS).

- **Possibility to compare the main $^{235}$U abundances**: Average $^{235}$U abundances of ES1 and ES3 are very close and largely different from the average $^{235}$U abundance of ES2.

- **What more?** Detection of depleted uranium in two samples, detection of low enriched uranium up to 4% $^{235}$U in all samples. APM analysis is a mean to detect a large range of isotopic composition at particle level.

**APM results:**

<table>
<thead>
<tr>
<th></th>
<th>ES1</th>
<th>ES2</th>
<th>ES3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximal $^{235}$U abundance (%)</td>
<td>4.73 ± 0.29</td>
<td>3.77 ± 0.41</td>
<td>4.26 ± 0.25</td>
</tr>
<tr>
<td>Minimal $^{235}$U abundance (%)</td>
<td>0.89 ± 0.09</td>
<td>0.41 ± 0.13</td>
<td>0.49 ± 0.08</td>
</tr>
<tr>
<td>Average $^{235}$U abundance (atomic %)</td>
<td>2.70 ± 0.30</td>
<td>1.83 ± 0.35</td>
<td>2.55 ± 0.35</td>
</tr>
<tr>
<td>Number of particles</td>
<td>4 596</td>
<td>910</td>
<td>915</td>
</tr>
</tbody>
</table>
Second results: precise isotopic abundances of particles coming directly from the samples (about 40 particles per sample)

What additional information do we obtain with minor isotope measurements ($^{234}\text{U}$, $^{236}\text{U}$)?

- From $^{234}\text{U}/^{238}\text{U}$ vs $^{235}\text{U}/^{238}\text{U}$: alignment of all ratios, forming « enrichment lines ».
  This lines depend on the « feed »: NU, DU, RU

- Detection of $^{236}\text{U}$ in some particles means that uranium was irradiated.
Last results: analysis of particles coming from the outside of the ultimate bag of the nuclear material samples

Description of the sample packaging:

Particles coming from the outside of the ultimate bag were extracted by wiping the surface of the bag with a cotton cloth. Particles were loaded onto a carbon disk with the vacuum impactor technique.
Last results: Comparison of the isotopic composition of the particles coming from the samples and the outside of the ultimate bag

What does SIMS analysis reveal?

- General agreement between the isotopic composition of particles coming from the samples and the ultimate bags: The isotopic composition of the three samples can be estimated without opening the ultimate bag.

- Only one particle coming from the ultimate bag of ES2 has an isotopic composition which is not consistent with the ones of the three materials. Samples were packed in another facility? In case of « real » material seized, these analyses can help to identify the places where the material was stored or handled, from its origin to the place where it was seized.
Detection of fluorine in micrometric uranium particles: a way to detect a conversion activity

Detection of fluorine → signature of a conversion and/or enrichment activity

Uranium isotopic measurement + fluorine detection → discrimination between natural uranium (ore or yellow cake), converted uranium and enriched uranium

Detection of fluorine in micrometric uranium particles: a way to detect a conversion activity

- **Fluorine is easily detectable at the mass corresponding to $^{238}\text{U}^{19}\text{F}$ with the DUO source.**
  - Advantage of detecting fluorine at $^{238}\text{U}^{19}\text{F}$ mass instead of $^{19}\text{F}$ mass: 1) more confidence that fluorine is chemically linked to uranium, 2) UF$^+$ sensitivity is better than F$^+$.

- **Development of a database** by measuring the relative amount of fluorine in particles from Uranium Ore Concentrate materials (CETAMA, France), conversion plant workshop, UF$_4$ material (CRM 17B, NBL, USA).
Use of the database to compare the relative amount of fluorine measured in real-life particles coming from inspected nuclear facilities.

When a natural uranium composition is measured, the relative fluorine amount measurement provides additional information on the industrial origin of the nuclear material.

<table>
<thead>
<tr>
<th>swipe sample</th>
<th>CP 2</th>
<th>CP 1</th>
</tr>
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What can be concluded? Uranium was converted at one point before the sampling but was not enriched.

Fluorine measurements are routinely done for IAEA samples since 2014.
Environmental samples coming from outside of the conversion plant buildings (CP1 and CP2):

What can be concluded? High level of fluorine was detected in particles collected outside of the building of the conversion facility even if 4 years elapsed between the sampling date and the analysis.
Natural isotopic fractionning

(http://serc.carleton.edu/microbelife/research)

\[ \delta^{18}O = \left( \frac{^{18}O/^{16}O}_{\text{sample}} / \frac{^{18}O/^{16}O}_{\text{standard}} \right) - 1 \times 1000 \]

(GNIP AIEA/WMO 2006)

Rain water → Groundwater → Process water ↔ Uranium oxide

Need for high precision methods to distinguish close geographic areas

- Oxygen isotopic ratio is easily measurable by SIMS using Cs primary ions with an external precision of ~ 0.1%.
- So in theory, SIMS is suitable for these analysis but…
Before any geolocation attempt, the first question to answer is “where does the oxygen in uranium oxyde come from?”

**Source of oxygen: Water, Air, Acid…**

Crushing, chemical purification, liquid extraction, washing, precipitation, drying…

**Best way to answer the first question:** sampling an industrial process at every step.

While waiting for such samples, measurement of the oxygen composition of UOC sample after different treatments inspired by the production of one CRM sample called Morille from CETAMA.

**Morille (UOC CRM, Cetama) production process**

- Agaric (UOC)
- Granulometry
- Acid impregnation
- Homogenization
- Grinding
- Roasting
- Drying Calcination
- Morille

Particle sampling after each treatment
Preliminary results: Each treatment affects the isotopic ratios, mainly thermal treatment at high temperatures.

Conclusion of Jonathan Plaue, University of Nevada, in his thesis “Forensics signatures of chemical process history in uranium oxyde: “[…] Oxygen isotope ratios in the real-world samples neither directly correlate with the oxygen isotope ratios of local meteoric water nor support a consistent alternative fractionation. […] the real-world variability in particle sizes and time at temperature profiles is sufficient to complicate interpretation oxygen isotope ratios in U$_3$O$_8$ samples as a reliable geolocation signature. […]”

Post conversion U compounds may be more suitable for geolocation via oxygen isotopic composition.
Links between CEA/DAM Ile de France and Nordic countries regarding nuclear material and environmental sample analyses

- **2012**: Training of a young scientist from VTT, Finland on ICP-MS

- **2012**: Collaboration on the characterization of PuO₂ particles produced by VTT in the framework of an IAEA support action for Safeguards purposes.
  - Participation of CEA/DAM Ile de France and the VTT Technical Research Center of Finland

- **2015**: Following the CMX-4 exercise, redaction of a paper on the use of μ-Raman spectrometry and DRX for the chemical phase identification.
  - Participation of CEA/DAM Ile de France and CEA Valduc, the Swedish Defence Research Agency (FOI), the Australian Nuclear Science and Technology Organization (ANSTO) and the South African Nuclear Energy Corporation (NESCA)
Conclusions

CEA/DAM Ile de France developed/is developing a large panel of methodologies to characterize nuclear material:
- From **milligrams amounts** down to the **micrometric particle scale**
- Both qualitative (U chemical form, …) and quantitative (Pu amounts, …)

**SIMS** is a technique that is particularly suited for to the characterization of **nuclear material**:
- Possibility to measure almost of all the elements of the periodic table
- **High sensitivity** : analysis of individual micrometric particles
- Very low sample consumption : **almost non destructive**
- Capability to characterize particles of nuclear material collected on the packaging
- Capability to characterize irradiated nuclear material in shielded instrument (CEA Cadarache)

To conclude on **SIMS**, it has its place in the **analytical techniques to implement in a lab that needs to characterize nuclear material**.

To further increase the knowledge on nuclear material characterization:
- **Collaborations** between countries, institutes, **round robin exercises** are essential for scientific exchanges.
- Development of **reference material** is also required to develop and validate new methodologies. *In 2015, a new UOC CRM “Feldspath” (CETAMA, France) has been qualified (REE, impurities).*