Joint Research Centre (JRC)

Improvements in U particle analysis by LG-SIMS

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Fine uranium particulate material or aerosols are often released in the handling of uranium bearing materials. The normal nuclear safety monitoring cannot detect this material as the radiation is below detection limits.

The **sample kits** contain swipes, gloves, labels, a marker pen and zip bags. **Sampling** of dust at a nuclear facility. The sampling locations will differ from the type of facility that is inspected.
Typical uranium particles size is sub-micrometer. The NUSIMEP 7 particle population had a mean diameter of 0.35µm.

Sometimes small U particles are agglomerated on larger particles with a size of several tens of µm.

Particles with diameters ~ 0.1 - 0.2 µm are needed to make precise isotopic measurements of both major and minor isotopes (depends on isotopic).

The settling time in still air is long (often counted in days for 1 m settling)

Small particles make age determinations difficult.
Requirements on the analytical methods

Particle searching

1. Fast screening that also provides information on enrichment for selection of particles for isotopic measurement
2. Ability to find the smallest particles (50-100nm)

Particle isotopic measurements

1. Accurate measurements of both minor and major isotopes
2. High precision (high ion yield)

Particle distribution. (Resolution 1050x and 3500x).
IAEA network of laboratories (NWAL)
(Picture with courtesy to IAEA)

Capacity, samples per year for IAEA:
- AFTAC USA 400
- ESL IAEA 100
- LMA Russia 80
- ITU EC 30
- AWE UK 20
- CEA France 20
- JAEA Japan 20
- Total 670

New laboratories:
- KAERI Korea 20
- CAEA China 20
- UWA Australia 20

New applicant laboratories in blue
ES particle labs circled
Sample analysis by the NWAL

Two methods are currently used by the network

Fission track analysis combined with TIMS

Fission tracks from neutron activated U particles. (Courtesy to F. Esaka, JAEA).

TIMS (Triton) at ITU

SIMS analysis

SG-SIMS (CAMECA 4FE6) at ITU.
Advantages with SIMS:

• SIMS is the only method that can make both screening and isotopic measurements in one instrument

• SIMS has the best timeliness

• Sample preparation is quick and uncomplicated

• SIMS has a high sensitivity due to a high ion yield (in the percent range)

• SIMS can provide isotopic information on thousands of particles from automated screening measurements

Disadvantage:

• Interferences
Sample Preparation – Vacuum Impactor

Vacuum impactor.

- Good particle distribution.
- Quick (actual preparation takes seconds).
- The entire preparation can be done in a glove bag.

The sample work is done in a glove bag to minimize the risk of cross contamination.
Examples of samples analyzed using APM screening software:

**Safeguards sample:** 16,216 particles were found in the screening measurements. Main distribution around 10% with a few depleted and a few particles up at 20%.

**Forensic sample:** 210 particles were found in the screening measurement. Depleted to 96% enrichment.
A limitation with normal SIMS: Interferences

- **Isobaric species**: ($^{238}\text{U} - ^{238}\text{Pu}$) (Cannot be resolved by high mass resolution).
- **Hydride interference** $^{235}\text{UH} - ^{236}\text{U}$. Peak striping based on the measurement of $^{238}\text{U}/^{238}\text{U1H}$.
- **Organic materials**.
- **Molecular species**. Common interferences that require a mass resolution of about 2800 are the PbAl, PbSi interferences.

**Large Geometry – SIMS** removes almost all interferences while operating at almost full transmission.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Interference</th>
<th>MRP (M/AM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{234}\text{U}$</td>
<td>$^{208}\text{Pb}^{26}\text{Mg}$</td>
<td>2864</td>
</tr>
<tr>
<td></td>
<td>$^{207}\text{Pb}^{27}\text{Al}$</td>
<td>2802</td>
</tr>
<tr>
<td></td>
<td>$^{206}\text{Pb}^{28}\text{Si}$</td>
<td>2613</td>
</tr>
<tr>
<td>$^{235}\text{U}$</td>
<td>$^{208}\text{Pb}^{27}\text{Al}$</td>
<td>2741</td>
</tr>
<tr>
<td></td>
<td>$^{207}\text{Pb}^{28}\text{Si}$</td>
<td>2580</td>
</tr>
<tr>
<td></td>
<td>$^1\text{H}^{234}\text{U}$</td>
<td>48490</td>
</tr>
<tr>
<td>$^{236}\text{U}$</td>
<td>$^{208}\text{Pb}^{28}\text{Si}$</td>
<td>2566</td>
</tr>
<tr>
<td></td>
<td>$^{182}\text{W}^{54}\text{Fe}$</td>
<td>1496</td>
</tr>
<tr>
<td></td>
<td>$^1\text{H}^{235}\text{U}$</td>
<td>38152</td>
</tr>
<tr>
<td>$^{238}\text{U}$</td>
<td>$^{206}\text{Pb}^{16}\text{O}_2$</td>
<td>2752</td>
</tr>
<tr>
<td></td>
<td>$^{208}\text{Pb}^{30}\text{Si}$</td>
<td>2372</td>
</tr>
<tr>
<td></td>
<td>$^{182}\text{W}^{12}\text{C}_2^{16}\text{O}_2$</td>
<td>2112</td>
</tr>
<tr>
<td></td>
<td>$^{182}\text{W}^{56}\text{Fe}$</td>
<td>1419</td>
</tr>
<tr>
<td></td>
<td>$^{50}\text{Ti}^{138}\text{Ba}$</td>
<td>930</td>
</tr>
<tr>
<td>$^{238}\text{U}^1\text{H}$</td>
<td>$^{207}\text{Pb}^{16}\text{O}_2$</td>
<td>2574</td>
</tr>
<tr>
<td></td>
<td>$^{183}\text{W}^{56}\text{Fe}$</td>
<td>1378</td>
</tr>
</tbody>
</table>
ITU is currently replacing its CAMECA 4FE6 with a new CAMECA 1280 HR

Small Geometry – SIMS, r = 117 mm

Large Geometry – SIMS, r = 585 mm
The first Cameca LG-SIMS was installed at UCLA in 1992.

**Evaluating LG-SIMS for Safeguards purposes:**

A first evaluation of LG-SIMS was made at Cameca and NORDSIM-Stockholm in 2005.

An evaluation report was submitted from EC-JRC to IAEA in 2009 including the work presented in the thesis of Y. Ranebo.

**Two major technical issues that has been solved:**
1. Increase of mass dispersion to allow for uranium measurements on the multi collector.
2. Development of APM software for automated screening measurements.
Secondary Ion Mass spectrometry (SIMS) is the only technique that can both locate the U particles and make isotopic analysis within one instrument.

Small Geometry (SG) - SIMS $r = 117$ mm

Large Geometry (LG) - SIMS $r = 585$ mm
New developments; Image processing

APM software:

• **Available for 6F, 7F and 1280**
• Possible to use different settings for pre-sputter and measurements => faster
• Oxides can be used for the pre-trigger => faster
• Can record images simultaneously on the 1280 => faster
• Can be combined with automated (chain) micro beam measurements

Charles Evan’s made **Psearch** data acquisition system (2004 version).

**Only runs on older SIMS systems like 3F, 4F**
APM – image processing algorithms

**Fixed threshold method:**

- 73 particles identified
  - Threshold = 50 cts
  - Duration = 1 sec
- 22 particles identified
  - Threshold = 200 cts
  - Duration = 1 sec

The drawbacks of the fixed threshold method are clearly visible:

- **Particle agglomeration:** closely situated particles are often identified as one unless the threshold is fortuitously set in the correct range.
- When the threshold is increased to avoid this problem, smaller particles are missed
- Fast

SIMS scanning ion image of $^{235}\text{U} + ^{238}\text{U}$ sum over a 500x500µm² area.
New developments; Image processing

New image processing software with auto threshold function based on the so-called Niblack algorithm.
**APM – image processing algorithms**

**Niblack** method
Threshold $T(x,y) = m(x,y) + k \times sd(x,y)$

- **SIMS scanning ion image of $^{235}$U + $^{238}$U sum over a 500x500µm² area.**

- **129 particles identified**
  - Deviation factor $k=0.2$
  - Duration ~ 2 sec

- **132 particles identified**
  - Deviation factor $k=0.8$
  - Duration ~ 2 sec

**Niblack** method significantly improves the **particle separation**:
- an increase in deviation factor $k$ from 0.2 to 0.8 provides an improved particle separation, but defined particle areas become smaller.

**Fast**
**APM – image processing algorithms**

**Auto-threshold** method, Iterative method based on the local maxima in the image

- 120 particles identified
- Background exclusion = 5%
- Duration ~ 36 sec

- 141 particles identified
- Background exclusion = 1%
- Duration ~ 50 sec

- **Auto-threshold** method provides optimized particle separation:
  - the exclusion level is lowered
  - the threshold is optimized for each particle
  - large particle areas, which improves the precision on the enrichment computed for each particle
  - Slow

SIMS scanning ion image of $^{235}\text{U} + ^{238}\text{U}$ sum over a 500x500µm² area.
APM results on mixed NBS 100 + NBS 500 sample

- Niblack method (14279 particles)
- Fixed threshold method (7574 particles)
- Auto-threshold method (15541 particles)
ITU did not participate with the 1280HR in the NUSIMEP-7 round robin as it is not installed and validated at ITU. The NUSIMEP-7 double deposition sample was still measured at Cameca to verify the instrument performance. 22 particles were analyzed, three measurements were rejected as they were mixtures of particles with different isotopics. The uncertainties are calculated, propagating mass bias uncertainty and the uncertainty from the hydrogen correction for the 236/238 ratio.

235/238 measurement on NUSIMP-7, 2-sigma error bars

235/238 measurement NUSIMEP-7, enrichment no 1
235/238 measurement NUSIMEP-7, enrichment no 2

235/238 measurement on NUSIMP-7, 2-sigma error bars
Minor isotopes NUSIMEP-7, enrichment no 1

234/238 NUSIMEP-7, rsd = 2.36%, dev. certified = -0.07%

236/238 NUSIMEP-7, rsd = 4.88%, dev. certified = 6.88%

Minor isotopes NUSIMP-7, 2-sigma error bars
Minor isotopes NUSIMEP-7, enrichment no 2

**234/238 NUSIMEP-7, rsd = 0.87%, dev. certified = -0.5%**

- **Mean**
  - Certified +10%
  - Certified -10%

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**236/238 NUSIMEP-7, rsd = 1.35%, dev. certified = -0.36%**

- **Mean**
  - Certified +100%
  - Certified -100%

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Minor isotopes NUSIMP-7, enrichment 1, 2sigma error bars
Find 38

$^{137}$Cs was detected in all samples in trace levels.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{234}$U</th>
<th>$^{235}$U</th>
<th>$^{236}$U</th>
<th>$^{238}$U</th>
<th>Date of prod. (± 4 years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F38/1</td>
<td>0.2735 ± 0.0014</td>
<td>25.919 ± 0.010</td>
<td>0.0716 ± 0.0007</td>
<td>73.736 ± 0.028</td>
<td>January 1981</td>
</tr>
<tr>
<td>F38/2</td>
<td>0.2620 ± 0.0013</td>
<td>24.502 ± 0.010</td>
<td>0.0580 ± 0.0006</td>
<td>75.178 ± 0.029</td>
<td>July 1980</td>
</tr>
<tr>
<td>F38/3</td>
<td>0.3512 ± 0.0018</td>
<td>32.625 ± 0.012</td>
<td>0.0786 ± 0.0008</td>
<td>66.945 ± 0.025</td>
<td>April 1984</td>
</tr>
<tr>
<td>F38/4</td>
<td>0.2858 ± 0.0015</td>
<td>27.316 ± 0.010</td>
<td>0.0951 ± 0.0005</td>
<td>72.303 ± 0.027</td>
<td>July 1982</td>
</tr>
<tr>
<td>F38/5</td>
<td>0.1964 ± 0.0010</td>
<td>18.460 ± 0.010</td>
<td>0.0449 ± 0.0005</td>
<td>81.298 ± 0.032</td>
<td>January 1981</td>
</tr>
<tr>
<td>F38/6</td>
<td>0.1114 ± 0.0006</td>
<td>10.547 ± 0.006</td>
<td>0.0253 ± 0.0003</td>
<td>89.316 ± 0.036</td>
<td>August 1976</td>
</tr>
<tr>
<td>F38/7</td>
<td>0.1161 ± 0.0006</td>
<td>11.009 ± 0.006</td>
<td>0.0301 ± 0.0003</td>
<td>88.844 ± 0.036</td>
<td>March 1980</td>
</tr>
<tr>
<td>F38/8</td>
<td>0.2913 ± 0.0015</td>
<td>27.349 ± 0.016</td>
<td>0.0753 ± 0.0008</td>
<td>72.285 ± 0.029</td>
<td>September 1981</td>
</tr>
<tr>
<td>F38/9</td>
<td>0.3372 ± 0.0014</td>
<td>30.833 ± 0.018</td>
<td>0.0725 ± 0.0007</td>
<td>68.757 ± 0.027</td>
<td>November 1979</td>
</tr>
</tbody>
</table>
Find 38 all samples

Two groups of enriched U particles were found in all samples, LEU and 96% 235U.
Summary

One of the main improvements in uranium particle analysis for Safeguards purposes in the last 10 years is the implementation of LG - SIMS.

• The LG - SIMS combines highest quality with speed.

• LG-SIMS provides additional information compared to other methods (Distribution of enrichments, elemental information).

Laboratories that have purchased LG - SIMS and has particle search capabilities with APM software:

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Location</th>
<th>Roles</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESL</td>
<td>IAEA - Austria</td>
<td>Will make U particle analysis for IAEA by LG-SIMS (~250 samples per year)</td>
</tr>
<tr>
<td>UWA</td>
<td>Australia</td>
<td></td>
</tr>
<tr>
<td>LMA</td>
<td>Russia</td>
<td></td>
</tr>
<tr>
<td>ITU</td>
<td>EC – Germany</td>
<td></td>
</tr>
<tr>
<td>NIST (Gaithersburg)</td>
<td>USA</td>
<td>US labs mainly use FT/TIMS for uranium particle analysis (~400 samples per year).</td>
</tr>
<tr>
<td>LANL</td>
<td>USA</td>
<td></td>
</tr>
<tr>
<td>Schafer Vallecitos</td>
<td>USA</td>
<td></td>
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</table>