Liquid Analysis of Radioactive Materials Using In Situ ToF-SIMS

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Motivation and Objective

IAEA R&D Needs
- Enhance sensitivity, reliability, and timeliness in particle analysis (T.2.R6)
- Provide new chemical and physical attributes for strengthening safeguards verification using nuclear materials with reduction in sample size (T.2.R1)

Innovated Solutions
- Use ToF-SIMS, an imaging MS technique, to generate full spectral chemical speciation with submicron lateral resolution and high mass resolution
- Analyze samples in both liquid and solid states
- Specifically, using SALVI, a unique PNNL invention as a vacuum compatible microfluidic device, to study nuclear materials

Objectives
- Liquid analysis of ICP-MS standards containing U to demonstrate sensitive analysis of nuclear materials in liquid
- Provide a more efficient approach for simple sample preparation and enhanced analysis for the IAEA nuclear safeguards mission
Comparison of existing DA techniques

Table 1. Comparison of existing DA techniques in analysis

<table>
<thead>
<tr>
<th>Measured Properties</th>
<th>SEM</th>
<th>ToF-SIMS</th>
<th>LG-SIMS</th>
<th>ICP-MS</th>
<th>XPS</th>
<th>TIMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental composition</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Molecular composition</td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isotopic comp./ratio</td>
<td></td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>2D/3D spatial mapping</td>
<td></td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Size, shape, morphology</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical state, bonding</td>
<td></td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Solid sample*</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Liquid sample*</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

*The sample state required for measurements

- ToF-SIMS has not been used as much as LG-SIMS or nanoSIMS as DA techniques in IAEA sample analysis
- Due to the SALVI invention, ToF-SIMS and SEM can handle both liquid and solid samples
System for Analysis at the Liquid Vacuum Interface

SALVI

- Use microfluidic channel to provide the liquid surface for direct probing;
- Use surface tension to hold the liquid within the aperture;
- Reduce concentration change, beam damage and memory effect by flowing the liquid.
What is ToF-SIMS?

- A vacuum surface technique;
- An imaging MS, each pixel has a m/z spectrum;
- High mass resolution (m/Dm > 10,000);
- High lateral resolution (< 100 nm);
- Permits depth profiling and 3D chemical maps;
- Monitors negative and/or positive emitted ions;
- Sensitivity is typically in a range of 0.1 to 10 ppm (part per million).

Yu et al., Microfluidics Nanofluidics, 2013, 15, 725.
SALVI: A Unique Vacuum Compatible Microfluidic Module

XIAO-YING YU, LI YANG, ZIHUA ZHU, MARTINE IEDEMA, AND JAMES COWIN
Fabrication and comparison

**TEM**
- e\(^{-}\) Beam
- Liquid flow

**SEM/X-ray fluorescence**
- e\(^{-}\) Beam, X-Ray
- X-Ray out

**Ours**
- Secondary Ions, photo-electrons
- Primary Ion Beam /X-ray

**Spin coat**
- pretreated substrate

**Exposure**
- negative photoresist

**Develop**
- UV

**Template**
- photomask

**Cast**
- PDMS

**Bonding**
- Si Wafer

**SiN Window**
- Liquid flow

**Microchannel**
- microchip

**Yang et al.,** *JVSTA,* 2011, 29 (6), article no. 061101.

Optical photos of the SiN window

Validation by SEM and EDX

A 2 µm hole is drilled by FIB, and water is filled in the channel.

Pressure < $1 \times 10^{-6}$ mbar

(1) Vacuum compatibility is fine.

(2) Water can be safely confined in the aperture.

(3) We saw aqueous surface.

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Analytical Capability Illustrations

ZIHUA ZHU, LI YANG, GENE RODEK, AND XIAO-YING YU*

Richland, WA
Analytical stability and reproducibility

IONTOF-V ToF-SIMS, 25 keV Bi\(^{+}\), \(5 \times 10^{-7}\) mbar

<table>
<thead>
<tr>
<th>t=0</th>
<th>t=1 hour</th>
<th>t=2 hours</th>
<th>t=3 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^{-})</td>
<td>C(^{-})</td>
<td>OH(^{-})</td>
<td>Si(^{-})</td>
</tr>
</tbody>
</table>

A 0.5% glutamic acid solution

Molecular ion signals from aqueous solutions

**10×10 µm² images**

- **1% formic acid**
  - ![H⁻][HCOO⁻]
  - ![H⁻][HCOO⁻]
  - ![H⁻][C₃H₇O₃⁻]
  - ![H⁻][C₃H₇O₃⁻]

- **0.5% glycerol**
  - ![H⁻][[C₃H₇O₃⁻]]
  - ![H⁻][[C₃H₇O₃⁻]]

- **0.5% glutamic acid**
  - ![H⁻][[C₅H₈NO₄⁻]]
  - ![H⁻][[C₅H₈NO₄⁻]]

**CH₂O₂**

**C₃H₈O₃**

**C₅H₉NO₄**

Molecular recognition is feasible using our SALVI!
Potential application in separation.

Detection limit estimation

Detection limit \( \approx \) three times background

- **1% formic acid**: 0.04%
- **0.5% glycerol**: 0.008%
- **0.5% glutamic acid**: 0.002%

We invented SALVI to enable in situ liquid SIMS.

Illustrated in situ SIMS to analyze ICP-MS standards consisting of U.

Demonstrated cheminformatics type of approach (SIMS spectral PCA) can be used to determine the source of radioactive materials using several certified ICP-MS standards.

Provided confidence in the novel in situ liquid SIMS analysis capability in isotopic and signature identification in IAEA safeguards missions.
In Situ Liquid SIMS

During the probing, the liquid was well maintained within the drilled hole.

Chamber pressure was maintained at $10^{-7}$ mbar during the entire measurement.

Yu, et al., RCM, 2017
Zhou, et al., JASMS, 2016
Yang, et al., JVSTA, 2011
Yang, et al., Lab on a Chip, 2011
Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

Mechanism of ToF-SIMS

Primary Ion Beam Bi$_3^+$

Before SiN punch through

During SiN punch-through

After SiN punch-through

Yu et al., Microfluidics Nanofluidics, 2013, 15, 725; Zhou et al., JAMS, 2016; Yao et al., PCCP, 2017
The LOD $^{238}\text{UO}_2^+$ in liquid SIMS is estimated to be $\sim$ 5 ppm U.
Spectral PCA of Liquid ICP-MS Standards

PC 1 Score plot clearly distinguishes samples with different U concentrations in the range from 2.5 to 20 ppm.

PC 1 loading plot explains the key peaks contributing to the differences among samples—m/z+ 270 (238UO2+).
First in situ ToF-SIMS analysis of liquids containing U in HNO₃ solution (i.e., 2.5 to 20 ppm)

Obtained a reasonable LOD of U to be ~5 ppm using µL of aliquot

Demonstrated the feasibility of SALVI enabled liquid SIMS in identifying U in liquid without complicated sample preparation and with much reduced sample volume

Provide a new solution using state-of-art in situ chemical imaging to measure physical and chemical attributes of nuclear materials for strengthening the safeguards missions
Acknowledgements

Contact:
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Email: xiaoying.yu@pnnl.gov
People Who Make This Happen

Biology & Microbiology

Spectroscopy & Microscopy

Catalysis

IP

SALVI

SIMS

SWILS

Pacific Northwest
NATIONAL LABORATORY
## Sample Matrix for In Situ Liquid SIMS

<table>
<thead>
<tr>
<th>No.</th>
<th>Solution</th>
<th>Uranium Concentration (µg/ml)</th>
<th>SIMS Analysis Method</th>
<th>SIMS Data Status</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20 ppm U030A in 3.5% HNO3</td>
<td>20</td>
<td>Four valid positive data points (mass spectra) were collected.</td>
<td>Mass spectra+PCA</td>
<td>03/07/18</td>
</tr>
<tr>
<td>2</td>
<td>10 ppm U030A in 3.5% HNO3</td>
<td>10</td>
<td>Four valid positive data points (mass spectra) were collected from two devices.</td>
<td>Mass spectra+PCA</td>
<td>03/07/18</td>
</tr>
<tr>
<td>3</td>
<td>5 ppm U030A in 3.5% HNO3</td>
<td>5</td>
<td>Six positive data points (mass spectra) were collected from two devices with no noticeable leaking during measurement.</td>
<td>Mass spectra+PCA</td>
<td>03/16/18</td>
</tr>
<tr>
<td>4</td>
<td>2.5 ppm U030A in 3.5% HNO3</td>
<td>2.5</td>
<td>Five positive data points (mass spectra) were collected with no leaking during measurement.</td>
<td>Mass spectra+PCA</td>
<td>03/16/18</td>
</tr>
<tr>
<td>5</td>
<td>3.5% HNO3</td>
<td>0</td>
<td>Five positive data points (mass spectra) were collected with minor leaks.</td>
<td>Mass spectra+PCA</td>
<td>03/02/18</td>
</tr>
</tbody>
</table>
Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

- A mass spectrometry technique that probes the chemistry and structure of the material outer surface
- Analyze the secondary ions emitted from the surface
- Traditionally, it is used to analyze the solid samples
Technical challenge and our approach

- Direct molecular beam study of a liquid surface is challenging
  - Interference from the equilibrium vapor above the surface
  - Vacuum based modern atomic probes (photons, electrons, ions and neutral atoms and molecules) are not widely used to study liquid surfaces

- Our new concept
  - Use microfluidic channel to provide the liquid surface for direct probing
  - Use surface tension to hold the liquid within the aperture
  - Reduce concentration change, beam damage and memory effect by flowing the liquid

A microfluidic Interface

A versatile portable device
Design considerations

- Mean free path
- Aperture/Reservoir gas load
- Flowing or static
- Concentration changes
- Beam damage
- Temperature drop

(a) PDMS microfluidics block; (b) Electroosmotic pump; (c) Battery; (d) PTFE tubings; (e) UHV compatible fiberglass sleeving; (f) Viton tee containing the short capillary; (g) 500 × 500 microns silicon nitride window at the center of a ~10mm × 10mm silicon wafer

Yang, L. et al., JVSTA, 2011, 29(6), art. no. 061101,
Chemical imaging at the interface

- **ToF-SIMS**: Time-of-flight secondary ion mass spectrometry
- **XPS**: X-ray photoelectron spectrometry
- **SEM**: scanning electron microscopy

Surface analysis tools
Vacuum instruments
Normally used for characterization of solid sample surfaces

<table>
<thead>
<tr>
<th></th>
<th>XPS</th>
<th>SEM</th>
<th>ToF-SIMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>elemental</td>
<td>√</td>
<td>√ (EDX)</td>
<td>√</td>
</tr>
<tr>
<td>chemical state</td>
<td>√</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Molecular</td>
<td>×</td>
<td>×</td>
<td>√</td>
</tr>
<tr>
<td>Detection limit</td>
<td>1-0.1%</td>
<td>1-0.1%</td>
<td>0.01-0.0001%</td>
</tr>
<tr>
<td>topography</td>
<td>×</td>
<td>√</td>
<td>×</td>
</tr>
<tr>
<td>Lateral resolution</td>
<td>5 - 10 µm</td>
<td>5 - 10 nm</td>
<td>0.1 - 0.2 µm</td>
</tr>
</tbody>
</table>
SEM/EDX Comparisons among Dry, Wet Samples, and Liquid Flow Cell Observations

In both the wet and dry samples, the Au signal intensity is very weak. That is, Au nanoparticles are barely seen. Much higher Au peak and lower Si and N signals inside the aperture are observed. This demonstrates the presence of Au nanoparticles while flowing through the aperture in our device.

Anti-mouse Ig G 5 nm gold nanoparticle solution

Characterizing nanoparticles on liquid surface

- The m/z spectra further illustrates possible fragments of the IgG and the buffer solution.
- The signature of gold particles is observed using the novel vacuum portable device.

Depth profile and ToF-SIMS imaging of nanoparticles on liquid surface

As the aperture is drilled through, water (H⁻, O⁻) is clearly discernible.

Au peak indicates the observation of gold particles suspended in the solution via the windowless portion of our device by ToF-SIMS.

CN⁻ is probably from the buffer or IgG fragment.

This indicates that our technique can be used to observe nanoparticles in liquid for biological analysis.
ToF-SIMS images around the aperture

IONTOF-V ToF-SIMS, 25 keV Bi⁺, $5 \times 10^{-7}$ mbar

ToF-SIMS images support our observation in SEM:
(1) Vacuum compatibility is fine.
(2) Water can be safely confined in the aperture.
(3) Water surface can be analyzed using ToF-SIMS.
Both secondary electron (SE) and back scattered electron (BSE) imaging in the low vacuum mode possible in the liquid phase; SE and BSE imaging in high vacuum mode can be done using liquid SEM; Observation of particle morphology and EDX possible using SALVI enabled liquid SEM.
System for Analysis at the Liquid Vacuum Interface (SALVI): From Molecular Imaging to a New Analytical Tool

**BES Basic Science**

Direct molecular beam study of liquid in vacuum enabled by microfluidics

A portable module for any finely focused (<1 μm) analytical tools

A new versatile multimodal mesoscale imaging tool

**Applied R&D**

Extended SALVI to applications such as material sciences, energy storage, and systems biology.

Dynamic probing of the solid-electrolyte interface

Correlative imaging

Single-cell molecular mapping using ToF-SIMS, SIM, and light microscopy

Chemical imaging of complex systems

Molecular imaging of live biofilms in the hydrated state

**Manufacturing/Commercialization**

SPI licensed the SEM and ToF-SIMS rights exclusively on May 23, 2014, and is manufacturing a commercial version.

More companies are exploring SALVI imaging (e.g., TEM) and spectroscopy applications on other instruments.

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Lab Chip, 2011, 11, 2481.
Microfluidics Nanofluidics, 2013, 15, 725.

Lab Chip, 2014, 14, 855.

Analyst, 2014, 139, 1565.