Elemental Imaging of Actinides in Human Tissues Using LA-ICP-MS and SR Micro-XRF

Eva VERGUCHT[1*], Andrei IZMER[1], Björn DE SAMBER[1,2], Bart VEKEMANS[1], Karen APPEL[2], Sergei TOLMACHEV[3], Laszlo VINCZE[1] and Frank VANHAECKE[1]

1. Department of Analytical Chemistry, Ghent University, Krijgslaan 281 (S12), B-9000 Ghent, Belgium
2. HASYLAB at DESY, Notkestraβe 85, D-22607 Hamburg, Germany
3. United States Transuranium & Uranium Registries, College of Pharmacy, Washington State University, 1845 Terminal Dr, Ste 201, Richland, WA-99354, USA

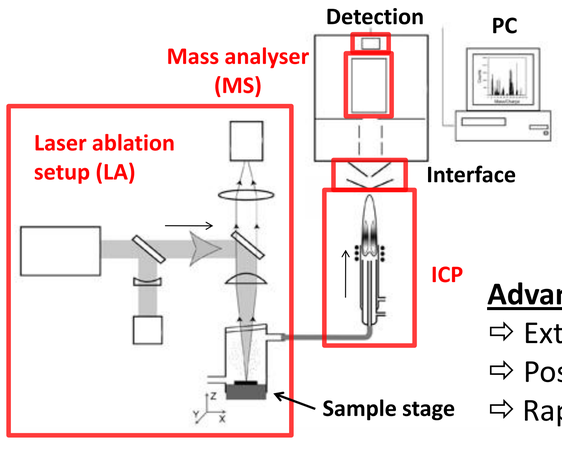
Introduction

The aim of this study was to evaluate the capabilities and limitations of two state-of-the-art highly sensitive analytical techniques for elemental imaging of the distribution of actinides in human tissues, in both a qualitative and a semi-quantitative manner: Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and Synchrotron Radiation (SR) micro X-Ray Fluorescence (micro-XRF) spectrometry.

The United States Transuranium & Uranium Registries (USTUR) studies the uptake, the translocation and the biokinetics of actinides in humans [1]. Human tissue sections from two USTUR cases (Registrants), which were occupationally exposed to certain actinides (U, Pu, Am), were investigated in this work. Both registrants passed away in 2008, *i.e.* a long time after the exposure. Prior to analysis, the samples were embedded in paraffin and cut in thin slices using a microtome.

LA-ICP-MS Instrumentation

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is based on the detection of positively charged ions generated via a high temperature plasma discharge. For these experiments, a New Wave Research UP193HE ArF* laser ablation unit or a GeoLas 200M 193 nm ArF* ablation unit coupled to an ELEMENT XR SF-ICP-MS instrument was applied.



Experimental conditions

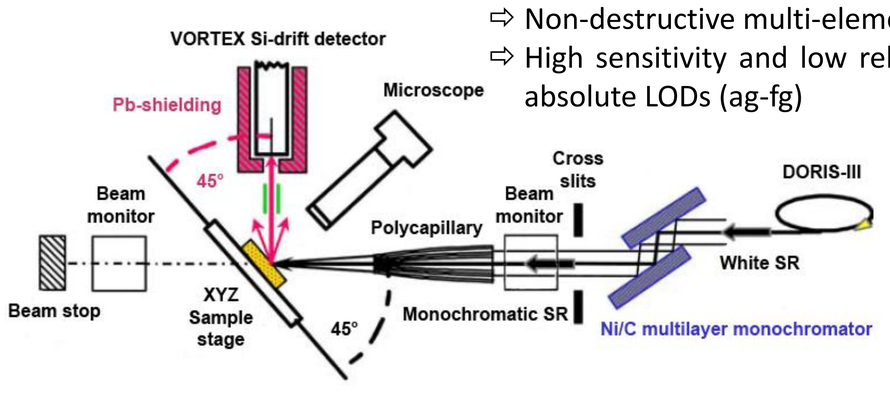
- ⇨ RF power: 852 W
- ⇨ Flow rates He: 0.5 l/min, Ar: 0.7 l/min

Advantages of LA-ICP-MS

- ⇨ Extreme sensitivity and detection limits (ppb-ppt)
- ⇨ Possibility to measure isotopes and isotope ratios
- ⇨ Rapid bulk/micro-analysis of a wide variety of samples

SR Micro-XRF Instrumentation

Synchrotron micro-XRF experiments were performed at Beamline L of the Hamburger Synchrotronstrahlungslabor (HASYLAB), part of the Deutsches Elektronen-Synchrotron (DESY) located in Hamburg, Germany.



Advantages of SR micro-XRF

- ⇨ Non-destructive multi-element microscopic analysis
- ⇨ High sensitivity and low relative LODs (sub-ppm) & absolute LODs (ag-fg)

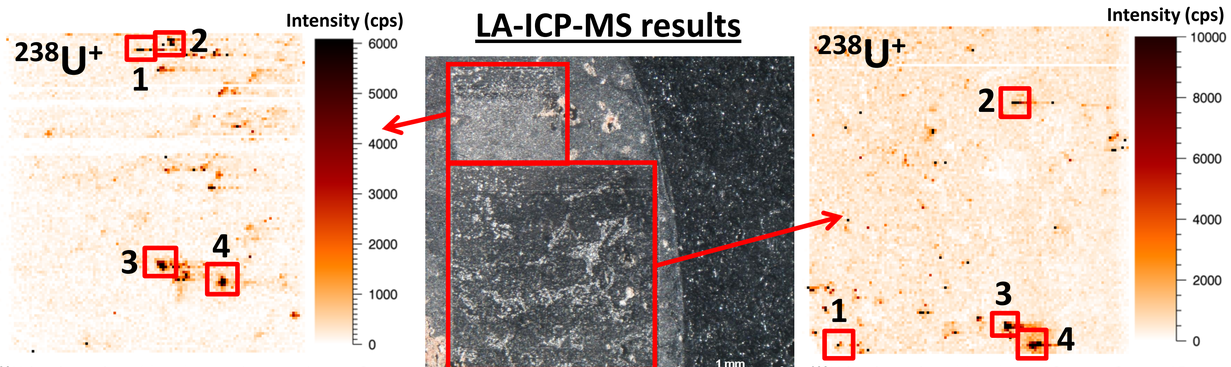
Experimental conditions

- ⇨ Energy: 19.5 keV
- ⇨ Spot size: ≈ 17 µm
- ⇨ Ambient air sample environment

Results: Case 1060

- ⇨ Several times exposed to uranium: a parabronchial lymph tissue (chest)

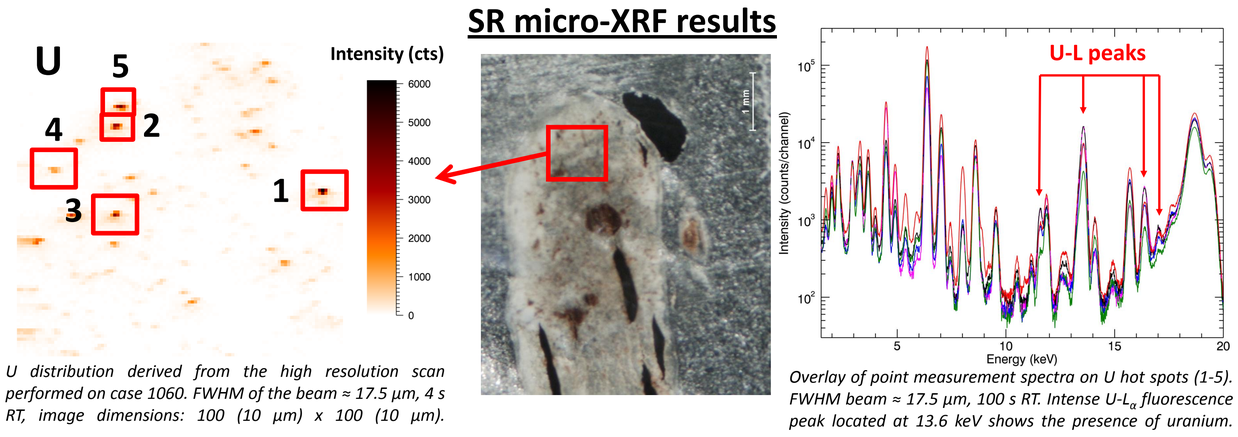
LA-ICP-MS results



^{238}U ion intensity, ablated area: 1 mm x 1 mm, 8 µm laser beam diameter, 10 Hz laser repetition rate, 0.70 J/cm² energy density, 8 µm lateral scanning speed.

^{238}U ion intensity, ablated area: 2 mm x 2 mm, 15 µm laser beam diameter, 10 Hz laser repetition rate, 0.70 J/cm² energy density, 15 µm lateral scanning speed.

SR micro-XRF results



U distribution derived from the high resolution scan performed on case 1060. FWHM of the beam ≈ 17.5 µm, 4 s RT, image dimensions: 100 (10 µm) x 100 (10 µm).

Overlay of point measurement spectra on U hot spots (1-5). FWHM beam ≈ 17.5 µm, 100 s RT. Intense U-L_α fluorescence peak located at 13.6 keV shows the presence of uranium.

Semi-quantitative results

LA-ICP-MS results		
Hotspot	^{238}U concentration (µg/g)	^{238}U concentration (µg/g)
1	9.6 ± 0.5	26.7 ± 1.5
2	0.85 ± 0.04	0.32 ± 0.02
3	1.35 ± 0.06	1.37 ± 0.08
4	0.89 ± 0.04	3.0 ± 0.2

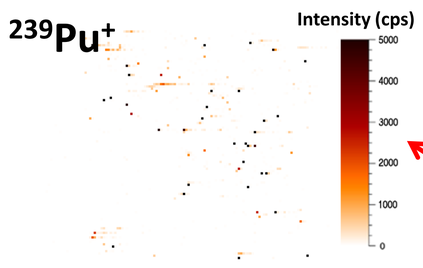
Semi-quantitative results were obtained using a series of standards (HAP and dried gelatine droplets) spiked with U.

SR micro-XRF results	
U concentration (µg/g)	Hotspot
30.38 ± 0.33	1
17.81 ± 0.31	2
31.26 ± 0.34	3
8.37 ± 0.29	4
19.34 ± 0.31	5

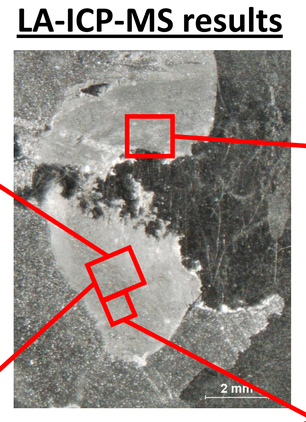
Results: Case 0407

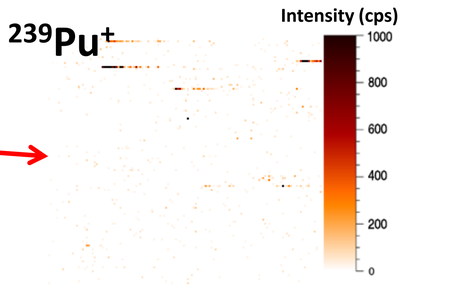
- ⇨ Exposure to plutonium and americium: a paratracheal lymph tissue (throat)

LA-ICP-MS results



^{239}Pu ion intensity, ablated area: 1 mm x 1 mm, 10 µm laser beam diameter, 10 Hz laser repetition rate, 0.64 J/cm² energy density, 10 µm lateral scanning speed.

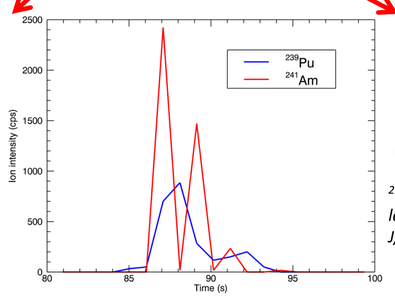


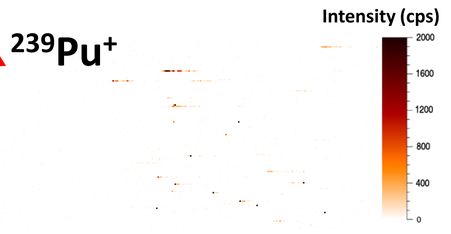


^{239}Pu ion intensity, ablated area: 2 mm x 2 mm, 15 µm laser beam diameter, 10 Hz laser repetition rate, 0.66 J/cm² energy density, 15 µm lateral scanning speed.

⇨ Graph: plot of the $^{239}Pu^+$ and $^{241}Am^+$ ion signal intensities versus time.

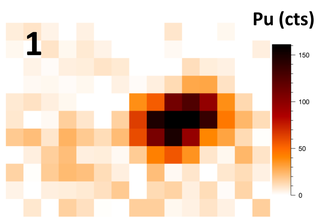
⇨ The americium signal does not come from extensive peak tailing of the plutonium signal, since the latter is much lower in intensity. This thereby confirms the presence of Am within the investigated area.



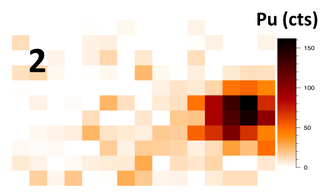


^{239}Pu ion intensity, ablated area: 0.5 mm x 0.4 mm, 10 µm laser beam diameter, 10 Hz laser repetition rate, 0.70 J/cm² energy density, 10 µm lateral scanning speed.

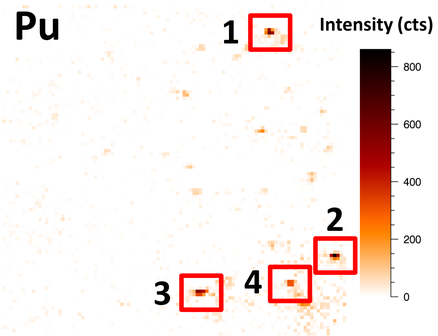
SR micro-XRF results



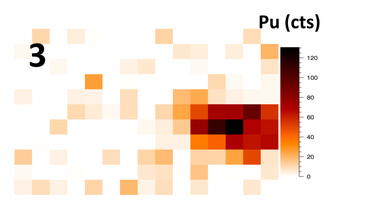
Plutonium map at the position of hot spot 1. FWHM beam ≈ 17.5 µm, 1 s RT, 5 µm step size.



Plutonium map at the position of hot spot 2. FWHM beam ≈ 17.5 µm, 1 s RT, 5 µm step size.



Pu distribution derived from the high resolution scan performed on case 0407. FWHM of the beam ≈ 17.5 µm, 5 s RT, image dimensions: 101 (10 µm) x 105 (10 µm).



Plutonium map at the position of hot spot 3. FWHM beam ≈ 17.5 µm, 1 s RT, 5 µm step size.

Plutonium map at the position of hot spot 4. FWHM beam ≈ 17.5 µm, 10 s RT, 5 µm step size.

Conclusions

Both advanced methodologies are able to visualise the heterogeneous distributions of U and Pu on the microscopic level. The microscopic hot spots of U and Pu can be easily revealed on the trace element level. Only the LA-ICP-MS measurements could show the presence of Am in case 0407. Besides the actinides of interest also Zr microparticles and aggregates can be reported (not shown here).

References

[1] United States Transuranium and Uranium Registries. Available from: http://www.ustur.wsu.edu/AboutUs/overview.html (Last access: 7 June 2012)

Corresponding Author

* Eva Vergucht, X-ray Microspectroscopy and Imaging Group, Department of Analytical Chemistry, Ghent University, Eva.Vergucht@UGent.be