



# Imaging of the distribution of actinides in human tissues using LA-ICP-MS and SR micro-XRF

Thesis submitted in fulfilment of the requirements  
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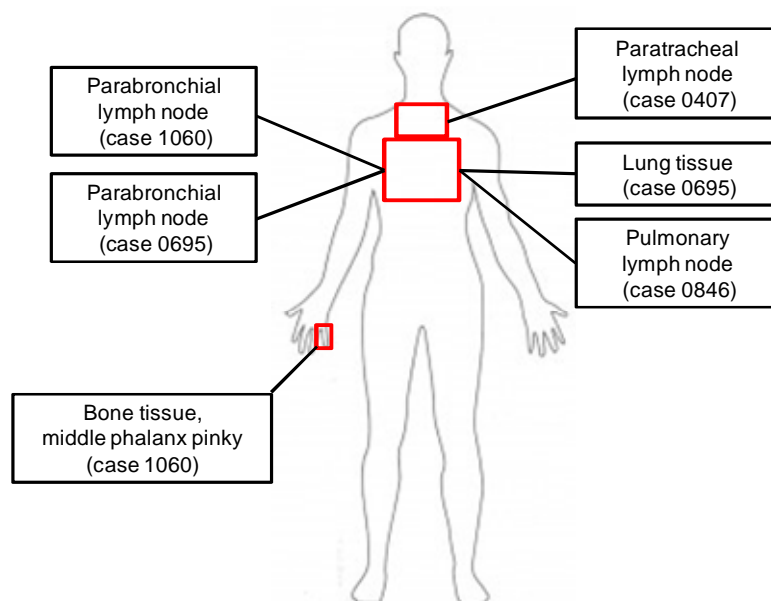
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## **Imaging of the distribution of actinides in human tissues using LA-ICP-MS and SR micro-XRF**

The aim of this study was to evaluate the capabilities and limitations of several approaches for elemental imaging of actinides in human tissues provided by the United States Transuranium and Uranium registries (USTUR, Washington State University). Tissue sections from four different registrant cases were investigated, which were acute or chronically exposed to actinides (U, Pu, Am) or beryllium. Detailed information concerning the exposure and working environment was provided by USTUR for each case. Below, the four cases are summed up together with the corresponding samples and the major elements of interest for each case. The locations of the different tissues in the human body are schematically shown in Figure 1.

- Case 1060: parabrachial lymph tissue and bone tissue - uranium.
- Case 0407: paratracheal lymph tissue - plutonium and americium.
- Case 0695: parabrachial lymph tissue and lung tissue - beryllium, plutonium and americium.
- Case 0846: pulmonary lymph tissue - beryllium and americium.



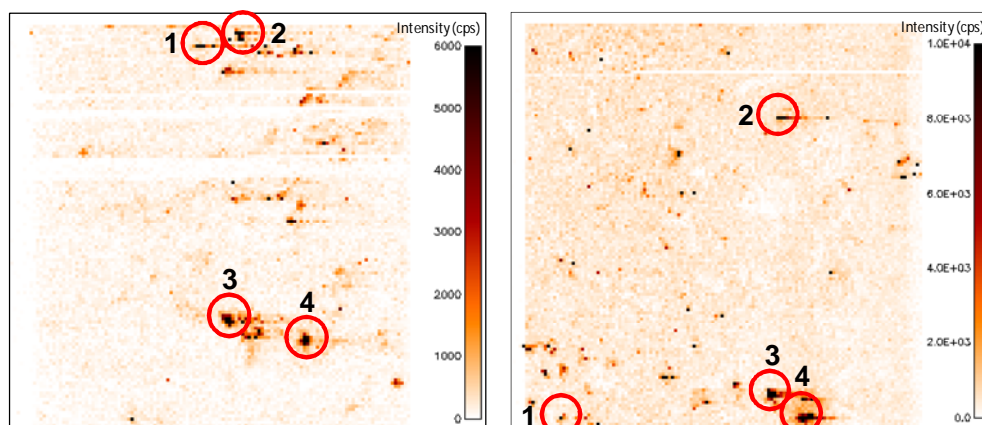
**Figure 1. Locations of the tissues in the human body.**

Two highly sensitive techniques were applied to investigate the human tissues: laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and laboratory/synchrotron radiation based microscopic X-ray fluorescence (SR micro-XRF). For the LA-ICP-MS experiments, the New wave Research UP193HE ArF\* excimer-based laser ablation system coupled to the ELEMENT XR SF-ICP-MS instrument was mainly applied. For the micro-XRF

experiments, a laboratory EDAX Eagle III instrument was used, as well as the synchrotron radiation based hard X-ray microprobe beamline L at DESY, HASYLAB (Hamburg, Germany). Since both LA-ICP-MS and micro-XRF were used to investigate the tissues, attempts could be made to compare both approaches in terms of sensitivity and efficiency for this specific study.

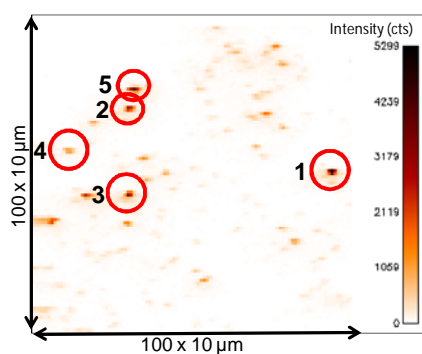
All samples investigated were originally frozen and then fixed in formalin before sending to Ghent. For analysis, the samples were later embedded in paraffin and cut in thin slices with a microtome. The samples were then mounted on glass slides for LA-ICP-MS analysis or mounted free-standing for (SR) micro-XRF analysis. It should be taken into account that the sample preparation could induce a redistribution/leaching of the elements during the sample treatment steps. Several elements of interest possibly could have been redistributed, partially or even totally removed. In future actinide research studies, other sample preparation methods should therefore be explored.

For case 1060, the major element of interest was uranium. Both a parabranchial lymph node embedded in paraffin and a bone sample embedded in epoxy resin were available for analysis. The lymph node sections were subjected to LA-ICP-MS and SR micro-XRF experiments. For the LA-ICP-MS study, two areas were investigated within the sample, which both showed the presence of uranium under the form of hot spots (Figure 2).

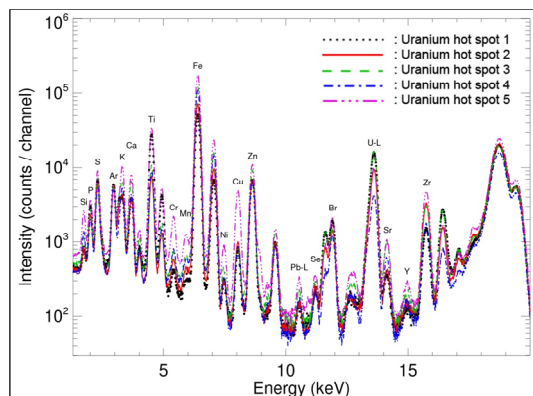


**Figure 2.**  $^{238}\text{U}$  distribution in area 1 (left, max 6000 cps) and area 2 (right, max 10000 cps) on a parabranchial lymph node from case 1060. The red circles indicate multiple hot spots which were subjected to a semi-quantitative study.

Similar results were obtained from the SR micro-XRF experiments at beamline L. Figure 3 shows the uranium distribution derived from the high resolution scan performed on the XRF-sample from case 1060. Five hot spots are indicated by red circles which were subjected to point measurements. The overlay spectrum of the point measurements on the uranium hot spots is shown in Figure 4, revealing an intense  $\text{U-L}_\alpha$  fluorescence peak at 13.6 keV.



**Figure 3. Uranium distribution derived from the high resolution scan on case 1060.**



**Figure 4. Spectra of the point measurements performed on the uranium hot spots (case 1060).**

A semi-quantitative study of the LA-ICP-MS and SR micro-XRF elemental maps using a calibration curve constructed on the basis of a series of dried gelatine droplet standards (doped with appropriate amounts of U) and pressed pellets of hydroxyapatite (HAP, spiked with U), revealed that the concentration of the uranium hot spots is within a similar range (up to  $\approx 30 \mu\text{g/g}$ ). The results of the semi-quantitative study are shown in Table 1.

	$^{238}\text{U}$ Concentration ( $\mu\text{g/g}$ )	$^{235}\text{U}$ Concentration ( $\mu\text{g/g}$ )	U Concentration ( $\mu\text{g/g}$ )
Hot spot 1	$9.6 \pm 0.5$	$26.7 \pm 1.5$	$30.38 \pm 0.33$
Hot spot 2	$0.85 \pm 0.04$	$0.32 \pm 0.02$	$17.81 \pm 0.31$
Hot spot 3	$1.35 \pm 0.06$	$1.37 \pm 0.08$	$31.26 \pm 0.34$
Hot spot 4	$0.89 \pm 0.04$	$3.0 \pm 0.2$	$8.37 \pm 0.29$
Hot spot 5	/	/	$19.34 \pm 0.31$

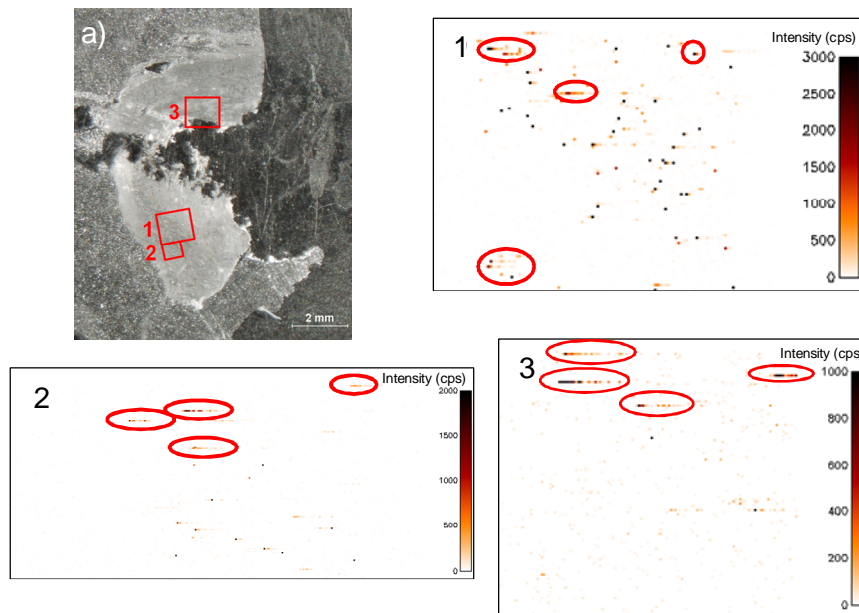
**Table 1. Concentration levels of the hot spots found within the areas investigated on the parabrachial lymph nodes originating from case 1060.**

Interestingly, also significant amounts of zirconium were found within the areas investigated on the parabrachial lymph node, which were also present under the form of hot spots. The presence of this element can possibly be explained by the use of zirconium cladding as a covering material for fuel rods in nuclear reactors.

The bone sample, embedded in epoxy resin, originating from case 1060 was studied using LA-ICP-MS only. Unfortunately, the presence of uranium hot spots could not be confirmed.

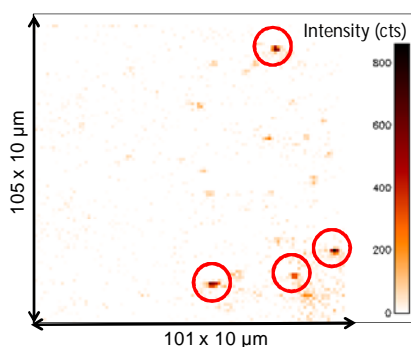
For case 0407, a paratracheal lymph node embedded in paraffin was analysed. Within this sample slice, the presence of plutonium and americium was examined. The lymph node section was subjected to both LA-ICP-MS and SR micro-XRF experiments. For the LA-ICP-MS study, three areas were investigated, which all revealed the presence of plutonium under

the form of hot spots (Figure 5). In addition, possibly one ablated area demonstrated the presence of americium.

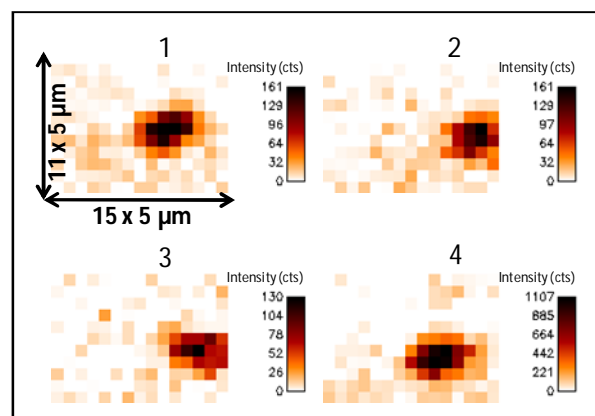


**Figure 5. Microscopic image of the LA-ICP-MS sample originating from case 0407 (a),  $^{239}\text{Pu}$  distribution in area 1 (max 3000 cps), area 2 (max 2000 cps) and area 3 (max 1000 cps). The red circles indicate plutonium hot spots.**

The SR micro-XRF experiments confirmed that plutonium is present under the form of hot spots (Figure 6). Small high resolution maps were made at the position of four plutonium hot spots, enabling a more accurate determination of the particle composition (Figure 7). In addition, also significant amounts of zirconium and uranium were found which were again distributed under the form of hot spots. Unfortunately semi-quantitative studies could not be carried out, given the potential danger and limited availability of plutonium and americium standard material.



**Figure 6. Plutonium distribution map derived from high resolution mapping performed on the XRF-sample originating from case 0407.**



**Figure 7. Plutonium maps derived from high resolution scans at the position of plutonium hot spot 1, 2, 3 and 4.**

The target elements for case 0695 (parabronchial lymph node/lung tissue) and case 0846 (pulmonary lymph node) were beryllium, plutonium and americium. The sections were subjected to LA-ICP-MS and micro-XRF experiments. None of the experiments performed (LA-ICP-MS/micro-XRF) on the sections could reveal the presence of the target elements within the areas investigated. Interestingly, the micro-XRF measurements showed the presence of significant amounts of titanium and zirconium. The detection of beryllium is not possible when using micro-XRF as an analytical technique. This is due to the low fluorescence yield for the low atomic number elements, the presence of a beryllium window in front of the detector and a large absorbing air path between sample and detector.

On all previously mentioned cases, also laboratory micro-XRF measurements were performed. Additional interesting information concerning the elemental distributions of elements such as P, S, Ca and K could be obtained with increased sensitivity due to the in-vacuum environment. However, no actinides could be detected due to the inherent higher detection limits of laboratory based micro-XRF compared to synchrotron radiation based micro-XRF.

From the experiments performed in this study, it can be confirmed that both LA-ICP-MS and SR micro-XRF are very useful techniques to study the trace level metal distribution of actinides in (human) tissue sections. LA-ICP-MS however, causes serious damage to the sample investigated, precluding a second measurement to be performed on the same sample area, which is not the case for (SR) micro-XRF experiments. As a consequence, several new mappings and long point measurements could be made at the position of actinide hot spots. Although the accessibility and availability of measurement time at a synchrotron radiation facility hard X-ray microprobe is limited, a large quantity of reliable results can be obtained within a limited amount of beamtime. Due to the tremendous developments in X-ray optics, synchrotron radiation beams with nanometer spot sizes are already available, enabling future studies of the actinide distribution within single particles. By using LA-ICP-MS, information concerning the isotope ratios of the target elements can be obtained, enabling also information to be obtained on the possible enrichment or depletion of e.g., uranium particles.