Using XANES mapping to examine the speciation of metal debris in tissue

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For many years, scanning and full field X-ray transmission microscopes have been used to map at multiple energies to produce stacks of XANES spectra. However collecting such stacks of energy maps by fluorescence has only become prevalent in the last few years on hard X-ray micro/nano probes. In studies of metals in biological tissue, there are often advantages in full XANES mapping over spot XANES. Particles and ions can leach away from metallic implants in the body and interact with tissue causing adverse reactions [1]. XRF and XAS is an excellent way to understand the chemistry of these systems.

Data were collected on ex-vivo tissues that had been extracted next to a bone-anchored hearing aid, failed metal-on-metal hip replacement and primary cell model of polymorphonuclear leukocytes exposed to titanium dioxide nanoparticles. They were obtained on the Diamond I14 and I18 beamlines using a Rayspec 4-element SDD (I14), two Vortex ME-4 detectors (I18) and Xspress-3 data processing back-ends from tissue sections and cells mounted on silicon nitride membranes (I14) and high purity silica slides (I18). Collection times per point varied between 50 and 400 ms. Map areas were several thousand μm^2 on I18 and several hundred μm^2 on I14. The data was stacked using a python routine and aligned and analyzed in the Mantis program[2].

Cluster analysis produced cumulative XANES spectra representative of regions of similar metal speciation in the tissue, showing evidence of both metallic and oxidized titanium and metallic cobalt. The data provides evidence of the number of metal forms in the sample, in a more robust manner than sampling some individual XANES points.

Selecting a XANES map region from a larger XRF map removes the issue of picking representative pixels to undertake point XANES on the sample. Full XANES mapping allows a larger set of spectra to be obtained whilst PCA can be used to assess differences in the speciation within the tissue sections. Furthermore when interrogating very small features with a larger probe XANES data can be poor as the beam position and intensity profile is not necessarily the same at each energy. The full XANES mapping method allows post-analytical realignment of the data-stack to cope with any beam drift, yielding higher quality data sets.

[1] Billi et al. *SAS J.* 2009, **3**, 133-142.
[2] Lerotic et al. *J. Synchrotron Rad.* 2014, **5,** 1206–1212.