Anomalous Rayleigh scatter of transition metals contained in amorphous systems

This most recent allocations of beamtime add to a growing body of published data referring to the utility of low-angle scattering and XRF methods in the detection and characterisation of disease including recent (2004) publications reporting on measurements performed at XMAS [1-3] and at SRS (Daresbury, UK) [4-6].

The recent beamtime reported here looked specifically at anomalous scattering in aqueous Zn and Zn-bearing tumorific tissue utilising an improved detector configuration design. The utility of the method was considered in the examination of a second solute, sol-gel method silica glass dilutely doped with various elements.

The improved method utilises the high degree of polarisation on XMAS, to obtain a virtually scatter free signal reaching the detector placed at 90 degrees in the plane of the beam. The close correspondence of the variation in the predominantly fluorescence signal with energy from this detector compared to the extracted K-alpha peak from the germanium detector positioned at a forward angle is observed.

This report focuses on the strong anomalous signals that are theoretically predicted and observed in Zn, Cu and Er doped glasses close to atomic edges and the distribution of concentrations of Zn in wax-mounted benign and malignant breast tissue samples using micro-XRF. Further results were obtained including the acquisition of anomalous x-ray scattering (AXS) data for the Zn aqueous system via angle scans at specific energies, full EXAFS spectra recorded in the glasses and 2D diffraction data for tissue samples and glasses.

Figures 1 and 2 show anomalous elastic scattering and near-edge EXAFS for Zn, Ge and Er doped sol-gel glasses. The K-edges Zn and Ge and the L II edge of Er were examined. A sharp at-edge minimum is observed in all cases occurring at the maximum point of inflection in the fluorescence data corresponding therefore with the definition of the quoted edge in neutral atoms and theoretical predictions of the elastic scattering minimum. The positions of the minima are in good agreement with the calculated adjustment to the edge position due to chemical shift of the ionic dopant. Figure 1-ii shows similar edge related features in aqueous Zn as previously reported. The scale associated with the scattering signal is approximately 5th-10th of that of the fluorescence due to the relatively high angle used to avoid diffraction effects but is predicted in the independent atom approximation to be of comparable magnitude at low angles.

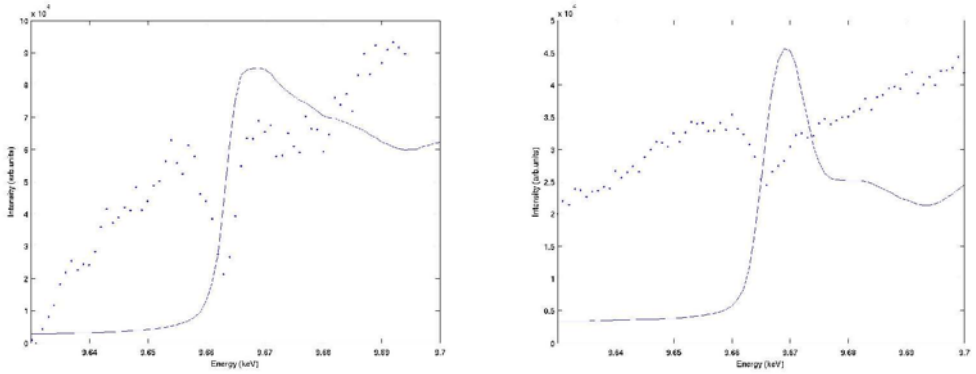

Figure 1. Elastic scattering (points) and fluorescence (lines) at the K-edge of Zn for i) Zn doped glass (1% by wt) and ii) an aqueous solution of $ZnNO_3$ (0.1 mol/l)

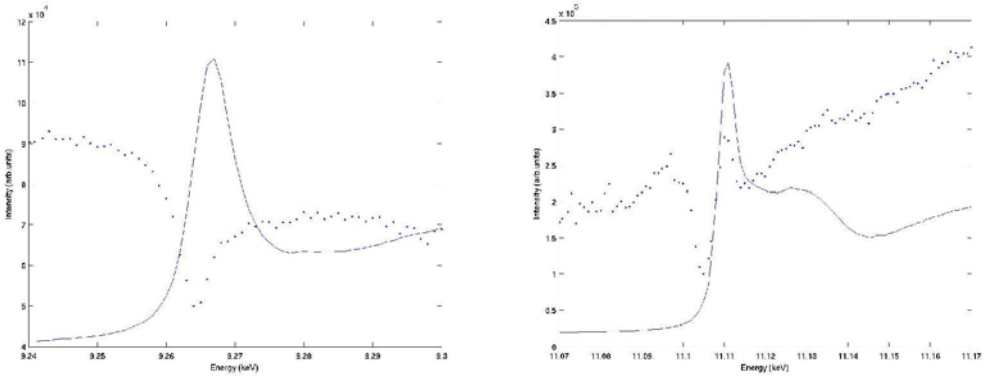

Figure 2. Elastic scattering and fluorescence at the i) K-edge of Ge in Ge doped glass (1% by wt) and L-II edge of Er doped glass (0.5% by wt)

Figure 3 shows summed data of the fluorescence yield near-edge observed in one tissue and an apparent spatial variation in concentration of Zn measured using a micro-XRF dimension beam (166 x 200 microns) for a wax mounted tissue samples. Of note is a chemical shift in the position of the K-edge for tissue compared with that of aqueous Zn suggesting a covalent nature to the Zn similar to that of Zn in silicate. The rapid variation in concentration in regions corresponds to the interface between tumour tissues to fat, as identified by a pathologist, supporting its identification as Zn bearing MMP-2 known to be associated with the manifold of metastatic disease infiltration.

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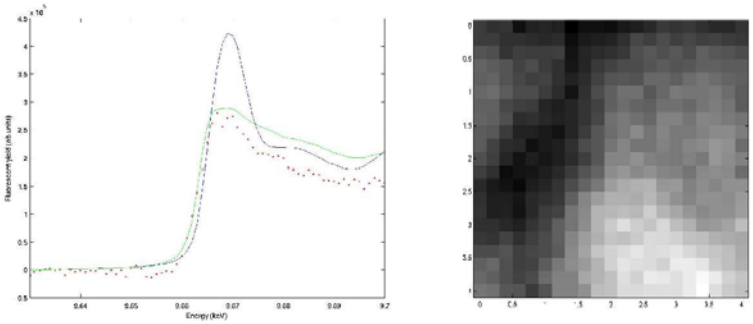

Figure 3. i) NEXAFS spectra of diseased tissue versus aqueous Zn and Zn doped glass and ii) micro-XRF distribution in a 4 mm × 4 mm section of wax mounted malignant tumour

Anomalous scattering offers new information at the atomic edges. These direct measurements confirm predictions of the position of the near-edge minimum in the elastic scattering cross-section enabling the optimization of an anomalous x-ray scattering (AXS) diffraction technique to within a few eV of the optimum energy choice not offered with conventional data determined for neutral atoms. These results provide support for further investigation of an anomalous elastic scattering imaging modality. AXS gives radial density information that is atom specific yielding, in the case of metalloprotein bound metals, a signature scattering pattern.

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