



	Experiment title: Combined micro-XRF, tomography and XANES- imaging: quantitative development and application to various materials	Experiment number: CH-474
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Names and affiliations of applicants (* indicates experimental&s):

K. Janssens*, University of Antwerp, Belgium

A. Rindby*, Chalmers University of Technology, Goteborg, Sweden

Report:

The conventional measurement scheme employed during micro-XRF experiments yields information on the two-dimensional distribution of chemical elements at or just below the surface of the investigated material (elemental mapping). The aim of this experiment was to extend this capability to the level of oxidation state-specific mapping, to demonstrate the possibility of determining for example the distribution of Mn in the 2+ and 4+ states inside a material.

For the experiments, an X-ray microbeam of $3 \times 10 \mu\text{m}^2$ was employed as produced by an Au zone plate. The primary radiation originated from a high-beta undulator and the 5th harmonic was employed to yield a **beam** of ca. 10^9 ph/s. Monochromatization of the beam was performed by means of a Si<111> crystal mounted into a fixed-exit monochromator. In order to determine the local oxidation state of Mn-species in a material by means of its XANES profile, the primary beam energy was varied between 6.520 and 6.580 keV. Before impinging on the sample, the primary beam passed through an ionisation chamber and a 15 μm diameter pinhole. The transmitted X-ray beam was recorded by beams of a PIN-diode positioned behind the sample. Fluorescent radiation emitted by the samples was collected by means of a collimated Si(Li) detector (10mm^2 effective area) positioned at ca. 3 cm from the sample. Samples were observed with a high-quality optical microscope equipped with a long-working distance lens.

- First, the position, size and intensity of the primary beam were determined at different energy values within this energy-interval by scanning a thin Cr-strip through the beam. Within the investigated energy-range the beam size varied from 2.9 to 3.3 μm ; the center of the beam did not move more than 1 μm . When only the monochromator angle was scanned (while the undulator characteristics were left unchanged), a maximal intensity variation of about a factor of two was observed which could readily be compensated for by normalisation to the primary beam intensity as measured by the ionisation chamber.
- From thin films or small grains of various reference compounds such as Mn-metal, MnSO_4 , MnO_2 and KMnO_4 , transmission and fluorescent XANES profiles were recorded around the Mn edge in order to obtain the edge-shift for the Mn^{2+} , Mn^{4+} and Mn^{7+} species relative to Mn^0 and record the characteristic shape of the near-edge region. Relative to Mn^0 (assumed to be at 5.548 keV), the Mn^{2+} XANES profile featured an edge shift of ca. 8 eV while the white line of the MnO_2 profile was present at approx. 5.653 keV. As could be expected, the profile recorded from a grain of KMnO_4 featured a strong pre-edge peak at ca. 6.645 keV.
- The capability of ID22 to obtain information on the chemical state of a specific element was used to determine the local oxidation state of Mn inside a sample of corroded Roman glass. During a period of ca. 1900 years, immediately below the surface of this material, a hemi-spherically shaped corrosion body developed consisting of multiple layers of sub-micron thickness. Relative to the original glass, the corrosion body is depleted in a number of elements (mostly cations such as Na^+ , K^+ , Ca^{++} . . .) which are replaced by protons. The brown colour of the corroded glass is related to the increased Mn and Fe content of the corroded glass.
- In general, no specific knowledge of the oxidation state of these elements inside and in between the various layers that constitute the corrosion body is available, although the brown colour suggest the presence of MnO_2 . In order to evaluate and optimise strategies for restauration of glass objects from the Roman period, a detailed knowledge on the distribution of the various species throughout the different parts of the corroded layer is required. By positioning the microbeam at different locations inside the corrosion body and its surroundings (superficial corrosion crust, original glass around the corroded area) it was straightforward to establish that within specific areas of the corrosion body predominantly Mn^{4+} was present; these areas featured a dark brown colour under the optical microscope; also inside the superficial crust, a Mn^{4+} pattern was obtained. In the original glass as well as in the other areas of the corrosion body, a mixture of Mn^{2+} and Mn^{3+} was observed.
- In order to demonstrate the oxidation-state specific mapping capability of the setup, XRF maps of a $300 \times 300 \mu\text{m}^2$ area inside the corrosion body were recorded at primary energies 6.550 keV (only Mn^{2+} excitation) and 6.564 keV (crest-energy of Mn^{4+}). By subtracting both images from each other after appropriate scaling, an image of the distribution of Mn^{4+} throughout the scanned area was obtained, indicating that inside the leached-out glass Mn is only present as MnO_2 -precipitates in between the thin glass layers forming the corrosion body while *inside* the glass itself, Mn either has the 2+ or 3+ state.

