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Chapter 3.46

Multiple-sample approaches: standard downstream reference-sample calibration and multiple active samples

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This short chapter discusses the importance of having multiple samples for independent measurement and basic approaches for the geometric arrangement of the experiment.

Keywords: X-ray absorption spectroscopy; X-ray fluorescence; systematics; accuracy; uncertainty.

The use of standards is discussed in Chantler (2024*a*). A secondary sample can be as simple as a reference sample of the relevant metal foil to calibrate the edge energy of interest for X-ray absorption near-edge structure (XANES) or pre-edge structure or the X-ray absorption fine structure (XAFS), or to calibrate the structure of an unknown with respect to a foil. As such, ideally this should be in the same location as the sample, so that the divergence, beam size, bandwidth and harmonics are consistent for the reference and the sample of interest (de Jonge *et al.*, 2004; Bridges & Booth, 2024). Hence, this argues for a sample stage which can translate between the sample and reference either at each energy or in a scan before or after the primary measurement. Multiple samples are a key approach to calibration and diagnostics (Diaz-Moreno, 2024). Sayers (2000) recommended:

> If possible, representative samples should be measured at two different thicknesses. This is a good overall test for a range of thickness related effects, including sample non-uniformity, harmonic content of the beam, and leakage . . . '

A contrary position queries the additional time needed for such a measurement compared with placing a reference foil, usually downstream of the sample and with a third ion chamber in transmission, so that the pair of measurements are not in the same location but are in parallel and simultaneous. However, the fluorescence and other scattering from such a sample or reference will backscatter to the detector upstream and scatter to the detector downstream, so that the signals will interfere and overlap, especially near the edge and in the XANES region (Chantler, 2024*b*,*c*), and especially since they are chosen to have the same active K edge.

It can be necessary, with a cryostat, to have a reference foil at room temperature upstream or downstream, but preferably measured in parallel and not simultaneously, to avoid cross-talk.

Within the sample environment, the form of the sample can dictate the measurement of the X-ray absorption spectrum. All samples should be characterized before the experiment. For a metal foil or other well-defined solid sample, the measurement of mass and area can define an average thickness or integrated column density. A full foil mapping in the X-ray beam can then define the absolute calibration of a

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transmission measurement. For such well-defined samples, having three or more thicknesses as samples both allows optimal attenuation across the range from pre-edge through XAFS and permits the characterization of beam, sample roughness and other issues affecting the magnitude of XAS oscillations and structure.

For less well defined samples, including crystals or glasses, multiple thicknesses and samples can still be used to investigate numerous systematics in the measurement. Many samples will be liquid or in solution. In such cases, different concentrations or sample depths can serve the same principle and be used to investigate numerous systematics. For dilute systems, the structure and phase of the active system may change with concentration and indeed the study might be a reaction. Nonetheless, a well defined reference sample will confirm the stability of the beam and sample.

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