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Use of reference standards

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X-ray absorption spectroscopy (XAS) uses standards in many contexts, especially in (i) reference metal foil determinations and calibrations of the monochromator energy and the energy on the sample, (ii) definitions or measurements of the edge energy for the extraction of χ, (iii) measurements of chemical shifts of the edge and pre-edge features, whether for fingerprinting or for principal component analysis, and (iv) measurements of a normalizable absorption coefficient. This chapter summarizes common approaches and some recommendations for XAS.

Almost all synchrotron beamlines calibrate their monochromator, tuning, detuning, harmonic rejection mirrors and optics with a reference foil for a given experiment. This relates to the general topic of calibration and diagnostics (Diaz-Moreno, 2024). Typically, the K edge of the relevant key metal is used to define a local, time-dependent offset, given all of the experimental conditions used in setting up the experiment. Very often, a standard set of metal foils is used (Wong, 1999) and a key reference determination of an edge energy is given from a standard reference database (Kraft *et al.*, 1996; Thompson *et al.*, 2009). A standard set of these foils are also very often set up as a standard filter bank at the beamline, whether upstream or downstream of the sample location, and ‘the key’ foil is set up downstream of the sample, in series with the active measurement, so that three ion chambers are used, with the sample attenuation defined by I_1/I_0 and the reference-foil attenuation defined by I_2/I_1 (Diaz-Moreno, 2012). The activity to control, that is to measure and correct for, dark current, dead time and energy calibration was called for in the original Q2XAFS conclusion summary (Ascone *et al.*, 2012). One key recommendation here is to provide energy and amplitude calibration in a beamline-portable manner, since the definition of an edge energy is resolution-dependent.

As opposed to convention, however, we should ask how to define energies and standards. In the X-ray regime, from about 1 keV through 100 keV, the key marker for an energy, when measured under controlled conditions, is the characteristic fluorescence $K\alpha_{1,2}$ spectrum, especially for transition-metal foils. These can and should be used for X-ray emission spectroscopy standards, for fluorescence detector calibration and for more complex experimental geometries such as resonant inelastic X-ray scattering (RIXS) and high-energy resolution fluorescence detection (HERFD). The most accurate determinations, with their provenance, are presented in Chantler *et al.* (2024). Even today, this is a sparse set of energies and is certainly not continuous. Nonetheless, the best current characterizations can and should be used as the best energy markers and the most platform-portable energy calibrations available.

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Older work provided a ‘peak energy’. Given the asymmetry of all X-ray emission spectroscopy (XES) characteristic profiles, this can be strongly dependent upon experimental resolution and bandpass. In principle, the peak energy can vary from an ideal ‘perfect resolution’, or for example a HERFD peak energy, to the centre of mass of the spectrum contained within the region of interest (RoI) of the detector. The difference, and hence the error, can be as much as half of the spectral full width at half maximum or more. Hence, this inaccuracy can be several electronvolts or more.

Most crystallographic work understands that the excitation energy for such a standard should be ‘much’ higher than the absorption-edge energy, and an heuristic is that it should be 2–3 times the edge energy. Increasingly, we realize that failure to observe this can result in a similar scale of errors of imputed calibration energy. Secondly, the standard should be a ‘Standard’: a well defined (transition-metal) foil of suitable, defined purity, roughness, profile, thickness *etc*. These are very rare. Many beamlines use a standard thickness foil set (Wong, 1999). Many have used the same individual foil for decades, neglecting impurities, damage or profile characterization. For absolute work and normalization, this has a large impact; for relative energy shifts and characterization, the chosen nominal thickness often belies corrections for roughness, scattering and other effects. Nonetheless, these (foils and reference analyses) are great resources.

A better approach is to use a calibrated empirical sum of Lorentzians for portability with additional instrumental broadening. This has been used successfully for a range of detection resolutions (Dean *et al.*, 2019, 2020; Melia *et al.*, 2019; Chantler *et al.*, 2024). Recently, theoretical approaches have begun to permit more portable characterization and hence a more accurate energy standard, including a spectral standard (Nguyen *et al.*, 2022; Dean *et al.*, 2022). In principle, these can be accurate to 2 parts per million (~0.02 eV). In the context of a synchrotron beamline, these (XES characteristic spectral calibrations) are often awkward to implement, but developments are permitting a suitable characterization for many beamlines.

Far more commonly, the reference foil sits in a filter bank, upstream or downstream of the sample, and the XAS absorption-edge energy is used to calibrate the X-ray energy of the optic, especially for transmission measurement. In this case (absorption-edge energy calibration), the set of reliable edge measurements is even more sparse (Chantler *et al.*, 2024) and is perhaps dominated by the excellent work of Kraft *et al.* (1996), which is now some years old. Please see the caveats on the reference use of an edge energy defined not by theory but by the experimental peak of the first-derivative spectrum (the point of steepest slope of the edge; Chantler & Bourke, 2024; Chantler, 2024*a*; Chantler *et al.*, 2024). Especially note that the definition of the edge position is then dependent upon the beamline optic resolution, the bandwidth and the sample nanoroughness, and that the energy can vary by almost half the width of the edge.

Both of these sets of X-ray energy standards (characteristic *K* or *L* spectra and absorption *K* or *L* edges) are temperature-dependent and can depend upon bandwidth, beamline optics and harmonics within their definitions. Most reference characterization to date has been at ‘room temperature’, although this may have significant variability.

Again, a better definition is to characterize the whole XAS (pre-edge, edge, white line, XANES) and use the spectrum to define a resolution-resistant portable definition. Such determinations or characterization do exist (de Jonge *et al.*, 2005, 2007; Glover *et al.*, 2008, 2010; Tantau *et al.*, 2015; Sier *et al.*, 2020; Ekanayake *et al.*, 2021; John *et al.*, 2023), but have not generally been used for this purpose to date. Typical accuracies are better than 1 eV. A convenient selected summary of data sets is presented in this volume (Chantler, 2024*b*).

Normal operational use for a standard experiment is to check and calibrate the offset of a monochromator system at the specific *K*-edge energy of the targeted transition metal, and then to assume that the rest of the monochromation setup will vary smoothly with the same offset for all energies. This is not true in general because of the tuning or detuning functional with energy, the harmonic mirror rejection functional with energy, the variable heat load on the first crystal of the (double-crystal) monochromator and its time-dependence and functional with energy, and any geometric offset or misalignment with the second monochromator crystal or coupling. Hence, it is better and recommended to have at least two edge-energy calibrations for each experiment and to investigate whether indeed they can be represented as a constant energy offset, a constant angular offset or a more complex functional (Ekanayake *et al.*, 2021; John *et al.*, 2023). In past work on second- and third-generation sources, a functional error of up to 100 eV has been observed, measured and corrected for down to a level of 1 eV or so, which is not a constant offset and is not linear with energy or angle (Chantler *et al.*, 2001; de Jonge *et al.*, 2005, 2007; Glover *et al.*, 2008). Then again, a constant or linear offset may be a perfectly good estimate and approximation of energy calibration on some well supported well characterized beamlines.

Energy calibration is one of the important initial steps for an accurate measurement of XAFS on the absolute energy grid. Differences in the energy resolution of beamline optics can add to the confusion regarding the definition of edge reference energies, near-edge profiles and pre-edge features. For example, the XANES literature suffers from this problem. Some of the practical ways to improve the energy resolution of the beamline for energy-calibration purposes include having nondivergent beam optics and having a small opening of the vertical y slits to reduce off-axis energy shifts. This can then simplify the comparison with reference standards and reference publications. Sometimes a requirement for higher flux necessitates a broader beam in height or width or a focusing optic on the sample for measuring unknown samples. Smaller energy steps (0.2 eV as opposed to 0.5 eV) for low-energy edges (for example the Mn *K* edge) can help to map the edge profile more clearly and define the energy offset and reference position more unambiguously.

Another very common practice for energy calibration, spectral calibration and reference is to have a reference foil in series and downstream of the sample(s). Chantler (2024*c*) gives more details of these arrangements. A filter bank, daisy wheel (Chantler, 2024*d*) or multiple active samples can be used to characterize some of these concerns using multiple reference edges or multiple thicknesses depending upon which key systematic might be of interest. Some beamlines have proposed and implemented *ad hoc* backscattering crystals or foils or detectors to give a point offset characterization, but we are not aware of any definitive literature reference for these. In part, they fall under the important reference energy calibration using powder or single-crystal diffraction standards, as discussed in detail in Chantler (2024*e*). In general, there is much exciting and original work in this space, and much to work on and learn for all beamline optics, and this is an area of future development and refinement which should become more reliable, more beamline-portable and more fully implemented.

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