

## Chapter 3.48

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# Other calibration and diagnostic tools

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While for most X-ray absorption experiments a linear correction of the energy scale is sufficient to calibrate the spectra, in this section the limitations of this approach are discussed, in particular for the case where data are collected over an extended energy range. A selection of options that can be adopted to enhance the accuracy of the energy scale for spectral data are reviewed. The need for a database of reference metal foil spectra collected with high energy accuracy is highlighted. Such a database allows a multi-energy calibration of experimental data for experiments where a linear correction extrapolated from a single energy point is not sufficient. A section is devoted to discussion of energy calibration for data collected using a dispersive spectrometer, and also addresses some of the difficulties that the lower resolution of dispersive-mode data introduces into the task of accurate energy calibration.

### 1. Introduction

X-ray absorption spectroscopy (XAS) is a powerful technique that provides structural information on the local environment of an absorbing atom in a broad variety of systems (Bunker, 2010). By studying the variation of the absorption coefficient of the absorbing atom with the energy of the incident photon, information about the electronic state of the absorbing atomic centre and the spatial and geometrical arrangement of the neighbouring atoms can be extracted. The experimental data are collected by measuring the intensity of the radiation before and after the sample as a function of the incident energy, and if the experiment is performed in transmission mode then the function to be analysed is obtained by taking the natural logarithm of the ratio of these values. In cases where transmission mode cannot be used because, for example, the absorbing atom is at a very low concentration or is embedded in a very heavy absorbing matrix, or the sample does not transmit X-rays, the intensity of the characteristic fluorescence line emitted by the absorbing atom can be measured as an alternative probe of the absorption coefficient, as its ratio to the intensity of the incident radiation is proportional to the absorption process.

Following from the above, in order to collect reliable data two conditions need to be fulfilled. First of all, the energy of the radiation impinging on the sample needs to be known and, secondly, the intensity of the radiation has to be determined in an accurate manner, free from any spurious effects that can affect the data quality.

This section will focus on determination of the energy scale of the incident radiation, and a review of the different methods that are generally used to achieve a reliable energy calibration will be provided. A special mention will be given to the challenges in energy calibration of data collected in dispersive mode.

#### Related chapters

Volume I: 2.25, 3.4, 3.5,  
3.7, 3.11, 3.14, 3.43, 3.45,  
3.46, 4.6, 4.7, 7.2

## 2. Energy calibration for X-ray absorption data collected in scanning mode

As mentioned above, XAS techniques require accurate energy calibration. Together with the intensity and the shape of the features in the absorption spectrum, the absolute energy positions of these features contain very valuable information that is useful for determination of the electronic state of the absorbing atom type under study and the geometrical structure of its local environment. In addition, a precise energy scale is essential for determining accurate interatomic distances from the spectral frequency components manifest in the extended-range absorption spectrum.

At modern synchrotron-radiation sources, most XAS beamlines use double-crystal monochromators to select the energy of the radiation impinging on the sample. They consist of two single crystals of a pure material such as silicon or diamond set in a nondispersive configuration and cut to appropriately orient a defined crystal plane to the incident X-ray beam. The orientation of the crystal pair is then scanned over an angular range to facilitate the transmission of a series of energies through the device. For any specific crystal orientation, the energy of the radiation diffracted by the crystals can easily be calculated by applying Bragg's law if the  $d$ -spacing of the diffracting crystal planes and the angle of incidence of the X-rays to these planes are known. However, due to mechanical and thermal issues these two variables are not easy to determine with sufficiently high accuracy for precise spectroscopic measurements. To achieve the required performance to facilitate quantitative spectroscopic work, the normal procedure is to calibrate the energy of the radiation transmitted through the monochromator by the measurement of the absorption spectrum of a metal foil as a known standard. The positions of the sharp spectral absorption-edge features of the foil spectrum collected as the reference are then compared with tabulated energy values, and the monochromator energy is assigned to these positions. The quality of the calibration clearly depends strongly on the accuracy of the tabulated reference data (Bearden & Burr, 1967; Kraft *et al.*, 1996), as they are used to calculate the incident angle of the radiation on the monochromator crystal.

Once the angle of the monochromator has been determined for a given energy point, angular increments away from this point as the crystals are reoriented during a scan are typically calculated by counting steps of the axis drive motor of the monochromator or, in more modern devices, by using angular encoders.

Once calibration of the monochromator has been achieved, the reproducibility of the energy scale has to be ensured. It is common during an XAFS experiment to compare the absorption spectra of different samples, where changes in the positions of spectral features and the absorption edge itself are usually interpreted as changes in the chemical state of the absorbing atom or changes in its local structure. There are several factors that affect the reproducibility of the energy scale achieved by the monochromator. Some of them are related to the mechanics of the monochromator, although this

is less of an issue nowadays due to the modern technology implemented in most devices. Others are related to the stability of the optical components upstream of the monochromator, such as mirrors. Angular movements of the source can also affect the reproducibility of the energy scale, as well as changes in the  $d$ -spacing of the monochromator crystal due to variations in heat load. In addition, the energy resolution of the spectrometer can have an effect on the measured position of sharp spectral features such as the absorption edge and pre-edge features, so it is important to keep this constant during the experiment if reliable comparative studies are to be performed.

Although at modern sources extra care is taken to minimize all of the factors affecting the reproducibility of the energy scale, it is still recommended to use *in situ* energy calibration when taking spectroscopy measurements. There are three main methods to achieve this.

The first method was developed in a quantitative manner by Arthur (1989). It consists of using secondary reflections or glitches that appear in the absorption spectrum at specific energies to calibrate the energy scale of the sample under study. Arthur extended the work performed by Rek *et al.* (1984), and in addition to prediction of the angle and the energy for monochromator glitches he predicted the shape and magnitude of the multiple reflections using dynamical diffraction theory. He pointed out the need to use the central glitches originated by a double-crystal monochromator to calibrate the monochromator energy, as the energy and shape of the central glitches are independent of the azimuthal angle of the crystal, the magnitude of which is seldom known with sufficient precision.

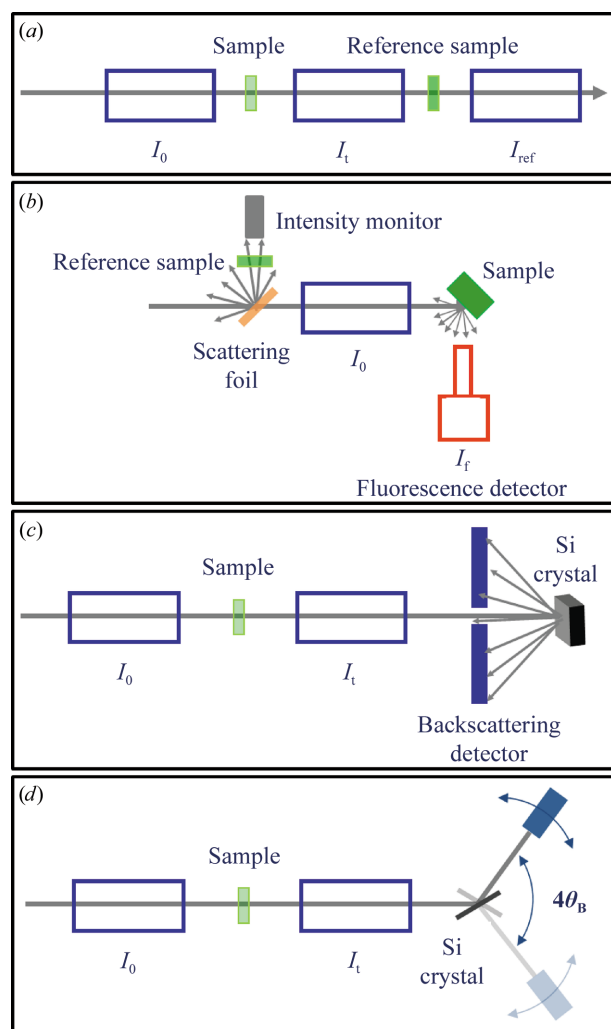
Unfortunately, implementation of this method is not always convenient, as it is possible that these parasitic features appear at energy values that are far away from the energy range scanned during the experiment.

The second method consists of recording an absorption spectrum of a reference foil simultaneously with collection of the spectrum of the sample under study (Goodin *et al.*, 1979), as shown in Fig. 1(a). A reference sample containing the same absorption element, usually as a foil if available, is placed downstream of the sample in the path of the X-rays and after the transmitted intensity monitor,  $I_t$ . An additional intensity monitor is then placed after the reference sample,  $I_{\text{ref}}$ , and the absorption spectrum is directly obtained by taking the natural logarithm of the ratio of  $I_t$  and  $I_{\text{ref}}$ . As the reference-sample energy scale should not change with time due to the inherent stability of the metal foil, the energy positions of known features in the spectrum are used as a simultaneous calibration for the experiment. This method is the most commonly used, although it cannot be applied if there is no intensity transmitted by the sample, such as when the samples under study are very absorbing and the detection method used is fluorescence, or when the experimental setup blocks the path of the transmitted X-ray beam.

In these cases, the method used for internal calibration consists of inserting a thin scattering foil just before the incident intensity monitor (Cross & Frenkel, 1999). The scattered radiation is then allowed to pass through a reference sample,

and an intensity monitor, usually a pin diode, is used to measure the radiation absorbed by the sample (Fig. 1*b*). The sharp decrease in detected X-ray intensity due to the absorption edge of the reference sample can be observed using this method and the energy of the feature can be used as a calibration point for the experiment.

In both of the cases mentioned above, a linear correction of the experimental data collected following the edge position of the reference sample is usually sufficient to achieve an accurate energy scale. However, if the shift is significant then this correction can introduce distortions in the energy scale, as the angle of the monochromator and the energy selected do not follow a linear relationship. As has been shown by Diaz-Moreno (2012), a linear correction of 10 eV at the edge position for an iron foil, corresponding to an angular misalignment of  $0.0233^\circ$ , translates into a 4 eV distortion in the energy scale 1000 eV above the edge. This distortion gives rise to differences of 0.01–0.02 Å in the peak positions shown in the corresponding Fourier transforms.



**Figure 1**  
Schematic of the most common experimental setups used for internal energy calibration during absorption scan collection (see the text for details).

In order to address this, some authors have proposed alternative methods that can provide the energy calibration of an XAFS spectrum using more than one point in the scan. Pettifer & Hermes (1985) built a device that collects the Laue diffraction pattern from a perfect silicon crystal as the absorption scan is measured. A scheme of this setup is shown in Fig. 1(*c*). In the cases of Acrivos *et al.* (1982) and Stümpel *et al.* (1991), a Bond diffractometer was utilized (Bond, 1960; Fig. 1*d*). In both cases, the collection time of the absorption spectrum increased considerably. More recently, Tantau *et al.* (2014) used a powder sample (LaB<sub>6</sub> SRM 660a) to accurately calibrate the beam energy from a monochromator over a broad range of energies. This method has been applied to the collection of XAS data with an accurate energy calibration (Chantler, 2010).

An alternative and very comprehensive calibration method would be to calibrate a reference-sample absorption spectrum that is collected simultaneously with the sample using a foil measured with a very highly accurate energy scale, as is the case in measurements that have been performed by Kraft *et al.* (1996). Once the calibration parameters have been found, they can be applied to the real sample, so not only a linear correction is performed, *i.e.* the calibration is performed at every single point.

It is important to highlight that in most cases the collection of the absorption spectrum of a reference sample at the same time as measurement of the sample signal and application of a linear correction is generally sufficient to extract the information that is sought in the experiment. All that this requires is the availability of tabulated edge energies for metal foils. However, the availability of a database of reference foil absorption spectra collected with very high energy accuracy is advisable. If this were performed, and if it is necessary for the experiment, a multipoint energy-scale calibration can be performed and not just a linear correction extrapolated from a single fixed point. This database would also be very useful for the calibration of absorption spectra collected using energy-dispersive spectrometers (Ferrero *et al.*, 1997; Ruffoni & Pettifer, 2006).

### 3. Energy calibration for X-ray absorption data collected in dispersive mode

Dispersive XAS beamlines utilize a single crystal that is elliptically bent in the horizontal plane to polychromatize a divergent incident white beam of X-ray photons to produce a wavelength-dispersed diffracted beam covering a moderate bandpass of energies. This beam is spread into a broad horizontal fan on the polychromator crystal face, which due to the curvature of the polychromator crystal then converges to a focus where the sample is placed. Thus, the sample is illuminated by all of the wavelengths selected by the crystal simultaneously. The range of energies impinging on the sample depends heavily on the spectrometer, but typically falls into the range 700–2000 eV depending on the choice of the central energy selected by the primary orientation of the polychromator crystal lattice. After the sample, the beam diverges again and its intensity is measured using a position-

sensitive detector. Each pixel in the detector consequently measures the intensity of X-rays with different energies. As there is no need to scan any component in the beam, the measurements are very fast and, detector permitting, can be made in milliseconds or even microseconds if such speed is desired. An additional benefit of this class of spectrometer with no moving parts is that femtometre accuracy in bond lengths can be achieved using the differential method, as shown by Pettifer *et al.* (2005).

As a result of the measurement, the collected data correspond to an uncalibrated absorption spectrum. Due to the geometry of the dispersive configuration, the range of energies of the beam that are collected in each pixel depends on the design of the spectrometer: the distance from the X-ray source to the polychromator crystal, the size of the illuminated region of the crystal, the curvature of the crystal, the distance from the polychromator to the sample, the distance from the focal point (sample position) to the detector, the size of the detector *etc.* As such, it is extremely difficult to calibrate the absorption spectrum before the measurements, and the accepted methodology for placing the measured spectrum onto a known energy scale is to perform the conversion from pixels to energy once the spectrum has been measured.

Three main methods have been developed for calibration of absorption spectra measured in a dispersive configuration.

The first method was described by Gaur *et al.* (2011) and consists of measuring the absorption spectra of two known standard samples with absorption-edge energies that have been well established and that are in the range that is measured for the sample spectrum that needs to be calibrated. The pixel number corresponding to the absorption edge is then transformed into energy by following the tabulated values. The dispersion of energies across the position-sensitive detector is then given by dividing the difference in energy of the two edges by the difference in channel numbers. This allows the channel numbers (pixel positions) to be assigned to corresponding energy values, assuming a uniform and linear distribution of energies between the two fixed points.

This implementation of this method is not always convenient, as it is not always the case that the absorption edges of two well known and calibrated samples can be found in the energy range under study. However, the main limitation of the method described by Gaur is the linear correction to the energy scale that is applied. In the dispersive geometry, the polychromator is bent to take the shape of an ellipse to focus the X-ray beam at the sample position with a large dispersion of energies. This means that the dispersion of energies is not linear in space and a higher order correction is needed.

The second method consists of comparing the absorption spectrum of a known sample taken in the dispersive configuration with the spectrum collected from the same sample using a calibrated conventional scanning spectrometer. By comparing the two spectra across the full measured range, one can calculate a set of parameters that are necessary to transform the pixel-number scale into an energy scale. The required parameters are the coefficients of a polynomial of an order which is generally higher than one, of the form

$$x(E) = a_0 + a_1x(\text{pixel}) + a_2x_2(\text{pixel}) + \dots + a_nx_n(\text{pixel}), \quad (1)$$

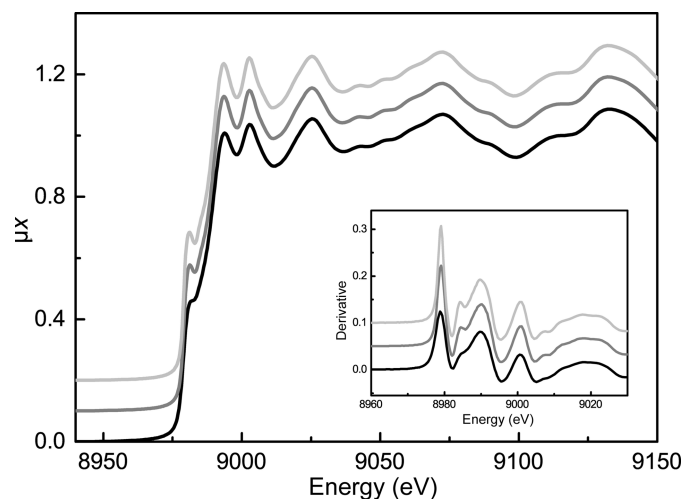
where  $x(\text{pixel})$  is the coordinate in pixel number and  $x(E)$  is the transformed coordinate.

The  $a_0$  term provides the underlying energy translation of the spectrum and  $a_1$  stretches the spectrum in a linear manner, while the higher order terms account for the nonlinearity of the energy scale. Most of the time, the use of a polynomial of order two is sufficient to reproduce the reference spectrum to an acceptable standard. This methodology is used in many of the computer codes that are available for the calibration of data measured in dispersive configuration, such as the *XAID* module (Sánchez del Río, 1997) in the *XOP* package (Dejus & Sánchez del Río, 1996; Sánchez del Río & Dejus, 2004) and *WinXAS* (Ressler, 1997).

This methodology works well if the instrument-response functions of the dispersive and scanning beamlines are identical. However, it was pointed out by Ruffoni & Pettifer (2006) that this is not always the case, and very often the instrument resolution achieved by a dispersive spectrometer is significantly poorer than the resolution achieved by the spectrometer used to measure the reference spectrum. Two main corrections need to be applied before calibration. One is related to the differences in the tails of the instrument function between the reference monochromator (normally using two or four reflections) and the dispersive polychromator (one reflection only). The second arises from the differences in X-ray penetration into the monochromator crystal of the scanning beamline and the polychromator of the dispersive beamline. This last factor is more significant at high energies and when the polychromator is operating in a Bragg reflection configuration. The resolution achieved by a typical dispersive spectrometer at the Cu *K* edge (8979 eV) using a Si(111) crystal in Bragg geometry is illustrated in Fig. 2. This is compared with the resolution achieved using a Si(111) double-crystal monochromator operating in scanning QEXAFS mode and with a Si(111) scanning four-bounce monochromator (Diaz-Moreno *et al.*, 2009).

Hagelstein *et al.* (1992) proposed use of the multiple beam diffraction produced by the polychromator crystal as a method for the calibration of the energy scale of data measured in a dispersive configuration. This method is similar to the technique proposed by Arthur (1989) for the calibration of data measured in scanning mode and relies on knowledge of the orientation of the crystal. Ferrero *et al.* (1997) implemented this methodology within the *CALISPE* code.

Although this method is not widely used for the calibration of the absolute energy scale, the use of multiple beam diffraction to monitor the changes in the calibration polynomial due to small drifts of the optical elements is the most reliable approach that is available. This is mainly due to the impossibility of collecting a reference spectrum simultaneously with the XAS data when using a dispersive spectrometer, where the measurements need to be performed consecutively. Thus, the reference spectrum is taken at the beginning and the end of a time-resolved series and, if a shift is observed, a linear interpolation is generally made and applied



**Figure 2**

Comparison of the resolutions achieved by three different spectrometers at the Cu *K* edge using a Si(111) crystal. Black line: the resolution achieved by a typical dispersive spectrometer working in Bragg geometry (I20-EDE beamline, Diamond Light Source). Dark grey line: the resolution achieved using a double-crystal monochromator operating in scanning QEXAFS mode (B18 beamline, Diamond Light Source). Light grey line: the resolution obtained using a scanning four-bounce monochromator (I20-Scanning beamline, Diamond Light Source). The inset figure shows the first derivatives of the absorption spectra.

to the sequence of spectra collected from the sample in the intervening period. This assumption is not always correct and can result in erroneous interpretation of the changes in a time-resolved series.

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