Detector-related issues

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This chapter focuses on some of the most important issues related to the use of detectors in X-ray absorption spectroscopy measurements and provides guidelines on how to correct or reduce distortions via the choice of an optimal setup and pre-processing of the experimental data.

1. Issues related to ion chambers

Ion chambers (Calvin & Nariyama, 2023) are the most widely employed detectors in transmission-mode X-ray absorption spectroscopy (XAS) and also as incident-intensity monitors in fluorescence and electron-yield detection. Normally, they should be operated under a bias voltage exceeding the recombination region, namely in the ion-chamber regime (Ahmed, 2015), near the middle of the current/voltage plateau (Knoll, 2011). Since the voltage value at which the ion-chamber regime is reached depends on the total radiation energy absorbed, issues may arise if the voltage supply and/or defects in the detector construction limit the maximum applied voltage. This is particularly dangerous for measurements of sample transmission. In fact, while the flux measured before a sample ($I_0$) is supposed to be relatively constant over time and to vary smoothly with energy, the flux measured after the sample ($I_1$) changes with its absorbance; therefore, if the gas filling the ion chamber measuring the transmitted intensity has been calculated for a strongly absorbing sample, its absorption is much higher than for the detector $I_0$. In this case, if measurements are performed on a series of strongly and weakly absorbing samples without optimizing the detector, it may be the case that the more weakly absorbing samples are measured in the recombination region and the resulting spectra are distorted. A typical symptom is noncompensation of baseline noise and monochromator glitches (Bunker, 2010) between the two detectors since $I_1$ is no longer linearly proportional to the photon flux. Solutions to the aforementioned problems are the use of sufficiently high voltages (determined by tracing $I/V$ plots; Pettifer et al., 1999), correct calibration of the absorption of all samples (Bunker, 2010) and the choice of an appropriate gas filling to keep the ion-chamber regime at a given maximum voltage.

A second possible pitfall to avoid is related to the fact that the current observed using planar ion chambers correctly operated near the saturation region may depend on the beam position in the chamber. This can be due to geometrical factors that produce large regions with a non-uniform electric field. On a typical XAS beamline, the dimensions of the plates perpendicular to the beam direction may be considered to be so large that the volume containing ion–electron pairs has a
uniform field. On the other hand, at the X-ray entrance and exit of the ion chamber the field cannot be constant and bends at the border of the plates, with the field lines being less dense. If the volume at the entrance and exit of the chamber is large with respect to the active flat region inside the plane electrodes, the ion-chamber regime is reached at a higher bias voltage and appreciable vertical position sensitivity appears (Müller et al., 2013). To reduce this effect, the length of the chamber electrodes can be made much larger than the dead volume at the extremities of the chamber, or guard electrodes may be used. A guard electrode is a portion of the electrode that is not connected to the current amplifier but directly to ground. Two guard electrodes may be installed immediately before and after the central electrode, as described by Knoll (2011). These electrodes will collect a large part of the current related to the non-uniform part of the electric field at the cost of having a larger unused detector volume.

Signal-to-noise issues in ion chambers and solutions for improvement have been reported by Pettifer et al. (1999). One of the most important and common problems is microphony. Microphony may be caused by mechanical vibrations of the cables, the ion chamber itself or through sound propagating in the gas medium. Low-noise (internally lubricated) cables must be used and the chamber construction and installation must be as rigid as possible. The detector must be isolated from the rest of the beamline mechanically and electrically and environmental noise must be reduced (typically vacuum pumps, fans and gas blowers, fast valves, active coolers or air conditioning).

While most XAS experiments are performed using high-purity gases (mostly nitrogen, helium, argon or krypton), oxygen and water impurities may be present and their large electron-attachment cross section (Kuffel, 1959) may transform fast electrons into slow negative ions; these impurities contribute to chamber nonlinearity through a reduced drift velocity. The use of sealed detectors and high-purity gases largely reduces this problem (Pettifer et al., 1999). The electrodes must be mechanically attached to the chamber body through insulators. Insulators may be a source of noise and dark current. If the insulator is exposed to ionizing radiation it will build up charges on its surface and randomly discharge through the gas or its own surface. Impurities that are present in the gas may also attach to it and worsen the performance: insulators must be protected from radiation. Dark current must be carefully measured and subtracted prior to experiments.

The quality of the signal obtained from ionization chambers will depend on the electronics employed. Low-drift and low-ripple high-voltage supplies are important (products offering 0.0001 % peak-to-peak ripple levels exist); even if the chamber is operated under or very close to saturation conditions, bias voltage oscillations are always transformed into small current oscillations. The other side of the detection chain is usually composed of a current-to-voltage amplifier with gains ranging from $10^3$ to $10^{11}$ V A$^{-1}$. Velocity and linearity of the amplifiers over several orders of magnitude is essential. These amplifiers have a small offset from gain to gain (the accuracy of the gain may count for 1%) which prevents auto-ranging during a measurement. The voltage produced by such an amplifier should be reasonably offset from zero to avoid zero error; this ‘dark-current’ value depends on the amplifier gain and is measured and subtracted at the software level. Not correcting for dark current ($d$) biases the evaluation of $\mu$ through the relation $\mu = \log((I_0 + d_0)/(I_1 + d_1))$. For small $I_1$ the value of $d_1$ dominates and nonlinearly attenuates the effective absorption; this is particular evident when measuring elements with a strong white line (for example Pt $L_3$), where the maximum peak absorption may exceed twice the edge jump, or in the case of strong monochromator glitches. Once the current has been amplified and transformed in voltage its value may be directly read by an analogue-to-digital converter (ADC) and saved to the buffer memory of a computer. This method is fast and is particularly adapted to fast extended X-ray absorption fine-structure (QEXAFS) measurements (see below), but it is much more effective to use a voltage-to-frequency converter (VTF) for longer counting times (tenths of a millisecond per point and above). In a VTF the voltage is digitized and the proportional output frequency is read by a scaler. Modern and fast VTFs have the possibility to ‘infinitely’ improve the precision of the measurement by extending the integration time (Hino et al., 2013; Yurish, 2008), while still being usable at a few milliseconds. A similar procedure may be performed by a computer-based ADC at the expense of reading data at maximum speed and then applying numerical filters such as the Savitzky–Golay filter, for instance (Savitzky & Golay, 1964).

This is obviously a computationally intense and extremely ineffective procedure for long measurements, which may produce a huge amount of data and constitute a potential computational bottleneck.

Finally, we report on some important issues related to QEXAFS and their solutions, since these measurements are of increasing importance and are easily accessible at new synchrotron-radiation beamlines. The time response of an ion chamber depends on the position of the ionization event, since the time of arrival of the electrons is much shorter than that of the cations; this phenomenon produces a characteristic shape of the ion-chamber pulse where a rapid onset due to the arrival of electrons is followed by a longer rise time due to cations. Increasing the voltage only partially solves the problem and may increase the noise. Position sensitivity may be cancelled by increasing the time constant of the amplifier, but this is not compatible with fast measurements. Current QEXAFS setups are capable of measuring 1 keV at more than 10 Hz, i.e. at the maximum speed in an oscillation it takes 17 $\mu$s per electronvolt, where 10 eV compares with the width of extended X-ray absorption near-edge structure (XANES) features. If the detector has a rise time of several hundredths of a microsecond, as is common for ion chambers, it will cause a virtual loss of resolution which will be strongly velocity-dependent (Müller et al., 2013), while still being usable at a few milliseconds. A similar procedure may be performed by a computer-based ADC at the expense of reading data at maximum speed and then applying numerical filters such as the Savitzky–Golay filter, for instance (Savitzky & Golay, 1964).

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sum of the movements of cations and electrons as in ordinary ion chambers, while only electrons move between the grid and the collector. Müller et al. (2013) have demonstrated the benefit of this experimental setup for QEXAFS measurements, obtaining a rise time of about 5 μs. This value (plus the rise time of the current amplifier) may still play a role in resolution when compared with the achievable 50 Hz or even 100 Hz speed of recent QEXAFS setups, decreasing the time to 3.4 or 1.7 μs per electronvolt, but it is a two-order-of-magnitude improvement compared with a parallel-plates ion chamber without a Frisch grid.

2. Issues related to fluorescence-detector orientation

XAS is widely used to obtain short-range structural information on elements that are highly diluted in a sample. In this case the XAS spectrum is usually measured in fluorescence mode, i.e. detecting the intensity of a specific fluorescence emission from the element of interest present in the sample with atomic concentration c. Consider an X-ray beam of energy E and intensity I₀ incident at an angle ϕ on the surface of a thick (i.e. completely absorbing the incoming X-ray beam) and homogeneous sample and a detector of area A placed at an angle α to the sample surface at a distance r (with $A^{1/2}/r \ll 1$). The fluorescence intensity $I$ of energy $E_{\text{flu}}$ onto the detector is

$$I/I_0 \propto \Delta \Omega \varepsilon_{\text{flu}} \frac{\mu_{\text{ph}}(E)}{\mu_{\text{tot}}(E) + \mu_{\text{tot}}(E_0) \sin \phi / \sin \alpha},$$

(1)

where $\Delta \Omega$ is the solid angle of detection, $\varepsilon_{\text{flu}}$ is the fluorescence efficiency and $\mu_{\text{ph}}$ and $\mu_{\text{tot}}$ are the photoelectric and total absorption coefficients, respectively (Pfalzer et al., 1999).

If the concentration $c$ of the element of interest is low, the denominator in the formula is only slightly dependent on the incident energy, and so the intensity of the fluorescence emission is proportional to the absorption coefficient with a constant factor.

From an experimental standpoint, it is often essential to use collimators between the sample and the detector in order to ensure that scattering and fluorescence from the sample only can reach the detector. In addition, the detection apparatus for fluorescence should be able to isolate the fluorescence signal of interest from all of the other contributions, including in particular other fluorescence emissions, as well as elastic and Compton scattering.

To limit the detection of fluorescence emission from other lighter elements that are present in the sample, an aluminium filter can be very effective. In this case, the lower the atomic number of the other elements, the higher the achievable filter performance.

A simple strategy to increase the fluorescence detection with respect to elastic and inelastic scattering is to exploit the fact that the fluorescence emission is isotropic while the elastic and inelastic scattering are not. If the incident beam is linearly polarized, as is usually the case for synchrotron radiation, the detector should be placed to collect the fluorescence along the polarization vector, where the Compton scattering is minimum and the elastic scattering is absent (see Fig. 1). Then, to increase the fluorescence signal, the detector can be placed close to the sample. Nevertheless, it should be considered that by increasing the solid angle of detection, the increase in the scattering signal that hits the detector is greater than the corresponding increase in fluorescence. For example, if the maximum collection angle $\theta$ is increased from $10^\circ$ to $20^\circ$ the fluorescence increases by a factor of 4, while the elastic scattering increases by a factor of $\approx 16$. Depending on the energy resolution of the detector, the scattering contribution to the total signal can lead to a high background in the XAS spectrum. That is, for detectors with no or moderate energy resolution (such as solid-state detectors, for which $\Delta E/E \simeq 1$–$2\%$), the increase in the fluorescence signal cannot be obtained without decreasing the fluorescence/background ratio. A proper trade-off between these two effects has to be found when choosing the collection angle, while also avoiding detector saturation.

To limit the elastic and Compton scattering on the detector more than the fluorescence contribution, a filter with an absorption-edge energy between the fluorescence line of interest and the incident beam can be placed between the sample and the detector. To measure a $K$-edge XAS spectrum from an element with atomic number $Z$, a filter made of a $Z - 1$ element can be used. The fluorescence contribution from the filter itself has to be eliminated by placing Soller slits between the filter and the detector. This configuration, which combines a $Z - 1$ filter with Soller slits and a large area detector, is known as a Lytle detector (Lytle, 1989; Lytle et al., 1984).

As an alternative, the scattering contribution that constitutes the background in the XAS signal can be made very low if the energy resolution of the detection setup is increased. This is achievable, for example, by coupling an X-ray detector with bent crystal analyzers working either in Laue geometry, (bent crystal Laue analyzers; BCLAs; $\Delta E/E \simeq 0.4\%$; Karanfil et al., 2012) or in Rowland geometry ($\Delta E/E \simeq 0.01–0.02\%$). Nevertheless, in these two systems the solid angle of detection is usually low (about 1–$2\%$) and the diffraction efficiency is about 20–30%, so that this setup is extremely interesting especially if coupled with brilliant third-generation synchrotron light sources (Karanfil et al., 2012; Heald, 2015).

A relevant case for discussion is the collection of the XAS spectrum from elements diluted in thin films deposited on surfaces or buried at a moderate depth (10$^{-2}$–1 μm); most of the film, the crystal cannot be taken out from the substrate without breaking. In this case it is convenient to confine the incoming X-ray beam close to the sample surface as much as possible to maximize the fluorescence intensity and to reduce spurious signals originating from scattering by and/or fluorescence from other components in the substrate. When the surface flatness allows it, experiments in or very close to total reflection conditions for either the incoming X-ray or for the outgoing fluorescence have been demonstrated to be very helpful (Heald et al., 1988; Noma & Iida, 1994 and references cited therein).
Nevertheless, working far from total reflection but still in grazing-incidence geometry is very simple and is often convenient: if the X-ray extinction length is much longer than the film thickness, the intensity of the fluorescence signal from the dopant in the film is proportional to the beam-footprint area, i.e. to $1/\sin \varphi$. Thus, if the sample surface is large enough, it is sufficient to use an incidence angle of $1^\circ$ to obtain a net gain of a factor of 40 in the fluorescence yield with respect to the standard XAS geometry ($\varphi = 45^\circ$). Moreover, a setup that couples a grazing incidence with a grazing collection geometry is extremely advantageous (Fig. 1b). With respect to the standard geometry (Fig. 1a), it allows enhancement of the fluorescence signal without a corresponding increase in the elastic scattering contribution from the matrix. Indeed, because of the low collection angle, it can be shown that the scattering contribution that is not absorbed by the sample itself and thus hits the detector is that from a thin surface layer (Fig. 1c). In this way, the signal-to-background ratio is considerably enhanced (Maurizio et al., 2009).

Measurement of the absorption spectrum through detection of the fluorescence emission is also used in special cases for concentrated systems. With the standard detection geometry (Fig. 1a) the XAS spectrum suffers from self-absorption, which leads to a significant reduction of the amplitude of the EXAFS signal. This is because the fluorescence signal is emitted from a layer whose thickness depends on the X-ray energy in a nonmonotonic way. Indeed, in equation (1) the energy dependence of the denominator has to be considered. The importance of the self-absorption effect can be reduced if the sample surface is normal to the X-ray beam as in Fig. 1(d), with a grazing angle of detection (Pfalzer et al., 1999). In this geometry the detector collects the fluorescence from a surface layer whose thickness (approximately) does not depend on the X-ray energy. The unavoidable residual self-absorption, which is related to the nonzero solid angle of collection, can be then corrected by proper data analysis, providing that the stoichiometry of the sample (with a planar surface) is known (Pfalzer et al., 1999; Tröger et al., 1992).

### 3. Issues related to fluorescence-detector nonlinearity/pile-up

Any detection system is characterized by a minimum amount of time necessary to discriminate two events and record them as independent pulses. This small time interval is called ‘the dead time’ of the counting system (Knoll, 1989). The progress made in synchrotron-radiation source design, leading to the delivery of higher and higher X-ray flux on the sample, has taken place in parallel with the issue of pulse pile-up in detection. The detectors developed for fluorescence-mode XAS are particularly affected by this problem because the need to discriminate the fluorescence line of the element under study from the other fluorescence lines and the elastic and inelastic scattering background requires the signal-processing electronics to perform a pulse-height analysis, with consequent intrinsic non-negligible dead times. Even though fluorescence-detector technology and the associated electronics have made consistent progress in the last 40 years (especially with regard to single-photon counting detectors), the fastest energy-resolving solid-state fluorescence detector systems that are now available may still need to deal with the pulse pile-up issue when used at third-generation synchrotron-radiation sources. This happens either in the study of concentrated samples or when the fluorescence line of interest represents only a minor fraction of the photons scattered from the sample, forcing the user to perform the experiment with a large number of total photons impinging on the detector in order to obtain a sufficient count rate in the region of interest. Due to this issue, in some cases where the sample concentration and/or geometry are not suitable for transmission-mode measurements and high energy resolution in fluorescence detection is not required, integrating detectors such as the Lytle detector (Lytle, 1989; Lytle et al., 1984) or passivated implanted planar silicon (PIPS) detectors can provide better data quality than a single-photon-counting solid-state detector: these solutions have the advantage of a large detection area and high linearity, respectively.

There are two common models of dead-time behaviour for pulse-counting systems: the paralyzable and the nonparalyzable response (Knoll, 1989). It is recognized that the solid-
state detectors used for XAS and the associated electronics follow the paralyzable response, sometimes with variants depending on the electronic cards used. For a paralyzable response function a dead time $\tau$ is assumed to follow each true event that occurs during the live period of the detector. True events that occur during the dead period, although not recorded as counts, extend the dead time by another period $\tau$ following the last lost event. If we call $n$ the true count rate \textit{(i.e.} the real rate of photons impinging on the detector), $m$ the apparent count rate \textit{(i.e.} the rate measured by the pulse-counting electronics) and $\tau$ the system dead time, statistical considerations lead to the following relation for the system throughput, also called the nonlinearity (NL) curve:

$$m = n \exp(-n\tau). \hspace{1cm} (2)$$

This relation is, strictly speaking, valid for energy-integrated count rates. If we want to relate the count rate in the region of interest of the selected fluorescence line to the true count rate, equation (2) has to be modified to introduce a constant factor and/or an offset (Ciatto et al., 2004a) depending on the origin of the background counts to be rejected (discrimination of $K\alpha$ from $K\beta$ photons from the same element, fluorescence of other elements, elastic and inelastic scattering). Fig. 2 shows a typical experimental NL curve for a detector system obtained by varying the intensity of the beam impinging on the sample which can be fitted with a dead-time parameter $\tau = 9.1$ $\mu$s. The plotted function increases monotonically until $n = 1/\tau$, where it has a maximum, after which it decreases and goes to zero as $n$ increases further; the true count rate corresponding to the maximum of the NL curve can be considered to be a characteristic frequency of the acquisition system. The true count rate $n$ in equation (2) was approximated by the count rate detected by using a fast amplifier channel with negligible dead time and no energy resolution (ICR; input count rate); this is a very good approximation except for fast detector systems used at very high count rates, for which the fast channel dead time also has to be considered (Cramer et al., 1988; Warburton, 2004; Ciatto et al., 2004b). In modern digital X-ray processors, the ICR can be recorded as a function of the incident energy during an XAFS scan, along with the energy-integrated apparent count rate (OCR; output count rate).

The importance of dead-time effects when high count rates are used in fluorescence-mode XAFS has been known for a long time, with the most relevant issue being an artificial decrease of the amplitude of the XAFS signal. The need for, and the possibility of, the application of dead-time corrections to recover such errors was also observed by different groups at the end of the last millennium (Cramer et al., 1988; Nomura, 1998; Farrow et al., 1998). Ciatto et al. (2004a) performed a quantitative and systematic study of the effect of dead-time losses on the structural parameters extracted from XAFS data and of the reliability of dead-time corrections in recovering the correct structural information. Three methods to correct the data taken at high count rates with a high-purity multielement germanium detector coupled to XIA digital electronics were discussed and compared. The first correction, which is now probably the most widely used, consists of using the ratio $OCR(E)/ICR(E)$ measured experimentally during the XAFS scan to determine the system throughput $\exp(-n\tau)$ in equation (2). If we assume that the fast-channel dead time in measuring the energy-integrated count rate is negligible and that the ratio $OCR(E)/ICR(E)$ obtained from the energy-integrated count rates is applicable to any subset of photons \textit{(i.e.} dead-time losses are independent of energy), then the true count rate in the region of interest $n_T$ is obtained at each energy from the measured count rate in the same region $m_T$, as $n_T = m_T[ICR(E)/OCR(E)]$. The second method consists of numerically inverting the system-throughput relation in equation (2) to extract the true count rate $n(E)$ from $m(E)$. This requires previous knowledge of the dead time $\tau$, which can be extracted by fitting the NL curve, and proper modification of $m_T$ to mimic the magnitude of the OCR in order to perform the inversion on the correct point of the nonlinearity curve. A third strategy is based on linearization of the system-throughput function, which leads to the following expression for the true XAFS $\chi(k)$ signal as a function of the measured signal $\chi_m(k)$:

$$\chi(k) \simeq \chi_m(k)\left( \frac{1}{1-\tau J} \right). \hspace{1cm} (3)$$

Here, $J$ is the true fluorescence ‘jump’, \textit{i.e.} the discontinuity in the absorption coefficient at the absorption edge, and the expression is valid for moderate pile-up only ($\tau J \ll 1$). According to this expression the dead-time correction of the XAFS signal is an overall amplitude factor, so that the only effect predicted on the structural parameters is a reduction of the estimated coordination numbers, which can be corrected \textit{a posteriori} by multiplying by the correction factor $1/(1-\tau J)$.

Analysis of the XAFS data recorded on a model sample demonstrated that the first two correction methods allow one to recover reliable structural information working up to a count rate equal to approximately 60% of the inverse of the dead time ($1/\tau$), while the third method allows the evaluation

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**Figure 2**
Nonlinearity curve for a fluorescence-detector system fitted with a dead time $\tau$ of 9.1 $\mu$s. Modified from Ciatto et al. (2004a).
of reliable coordination numbers (within the experimental uncertainty) up to 38% of 1/τ. Fig. 3 shows uncorrected XAFS spectra taken at increasing count rates (Fig. 3a) and the same spectra corrected with the numerical inversion strategy (Fig. 3b): the recovery of the signal amplitude upon correction is evident.

Woicik et al. (2010) tested NL corrections on a fast detector system consisting of a four-element SDD coupled to customized electronics, working up to very high count rates. The authors took the dead time of the fast channel into consideration and concluded that, for optimal operation, the incoming count rate should not exceed ~70% of the maximum throughput. They also implemented dead-time corrections into some of the most popular software for XAFS data analysis (ATHENA; Ravel & Newville, 2005, 2020). Fast energy-dispersive fluorescence detectors include monolithic multi-cell SDDs which, with respect to traditional multi-element detectors, are able to cover large fractions of the total solid angle with minimized dead regions between the detector cells. As observed by Welter et al. (2009), the use of these detectors may imply a modification of the NL curve, with a reduction factor in front of equation (2) accounting for a count-rate independent dead time owing to the specific readout scheme (Hansen et al., 2008). Nevertheless, multi-cell SDDs allow very a high count rate per mm² of area. The possibility of working at high count rates, although without optimal energy resolution, is of great importance, for example for in situ fluorescence-mode XAFS, where one may need to count a fraction of second per point to improve time resolution.

We conclude by noting that equation (2) is valid for flat filling of the synchrotron ring, where bunches of electrons are separated by a time $\tau_B \ll \tau$. The flat-fill case is perceived by the detector as uniform and random delivery of X-rays in time since there is, on average, much less than one detectable event per bunch. Bateman (2000) proposed an extension of the NL formulation for alternative fillings such as single bunch and gapped beam, where the circulation period can be comparable with $\tau$, especially when using fast detector systems and large synchrotron rings. For the single-bunch mode, different formula can be derived depending on whether $\tau$ is longer or shorter than $\tau_B$ while the gapped mode is analytically intractable and can only be dealt with based on a modelling approach. Walko et al. (2011) also performed an empirical study of dead-time corrections for different operation modes including hybrid singlet modes. The results found for these alternative modes may be of interest for time-resolved studies.

References


