



Chapter 3.35

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X-ray fluorescence detection for EXAFS

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For dilute atomic species, detection of X-ray fluorescence is often the preferred method of measuring X-ray absorption fine-structure (XAFS) spectra. Detectors optimized for the detection of X-ray fluorescence are described along with different approaches for the isolation of the fluorescence signal from scattered X-rays and spurious fluorescence from other atomic species.

1. Secondary processes

An introduction and a description of the physics of secondary-process detection is described in Chantler (2024). In the X-ray region, the primary interaction for photons is the photoelectric effect, where atoms are directly excited by the X-ray photon (see, for example, Markowicz & Grieken, 2001). This results in prompt photoelectrons being emitted, but also leaves excited atoms which later de-excite, resulting in fluorescence X-ray photons or Auger electron emission. Both of these emissions can also precipitate an ionization cascade, which produces copious numbers of low-energy secondary electrons.

2. Fluorescence photons

This is the most common technique for measuring secondary processes and was first described in the context of XAFS by Jaklevic *et al.* (1977). Note that the energy of the fluorescence photons is fixed by the electronic binding energies of the fluorescing atoms and is largely independent of the energy of the exciting radiation. Heald (2015) has made a study of the ultimate limitations of the technique, particularly in the context of high-flux beamlines.

2.1. Total versus partial yield

The largest fluorescence signal is obtained by the collection of all X-ray energies. This signal is unfortunately contaminated with elastic scattering, Compton scattering and fluorescence from atoms that are of no direct interest. For concentrated samples this may not be a problem, but for dilute samples where the desired fluorescence signal is small this is a problem. The solution is to use some sort of energy discrimination to detect only the X-ray photons of interest.

There are three main approaches to this: *X-ray filters*, *X-ray analyzers* and *discriminating/counting detectors*.

The first two methods restrict the energies of the X-rays reaching the detector. The last method relies on energy discrimination in the detector and associated instrumentation.

X-ray bandpass filters are of two general flavours: high-resolution, usually using Bragg diffraction for a narrow energy bandpass, and low-pass X-ray filters for rejecting elastically scattered X-rays.

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The low-pass filter is typically a lower Z (typically $Z - 1$) thin film on a low- Z substrate such as Kapton. The quasi-elastic scattered X-rays have an energy close to the probe X-ray energy, which is higher than the desired fluorescence energy. If the absorbing atom has an absorption edge at an energy greater than the fluorescence energy and lower than the elastic scattered energy, then the elastic background will be reduced relative to the fluorescence signal. For example, the $K\alpha$ transition for iron is at 6.40 keV, while the iron absorption edge is at 7.11 keV. The absorption edge of manganese at 6.54 keV falls nicely between them, and is suitable as a filter for the iron edge (Fig. 1).

After traversing the energy filter, the X-rays are then detected by an ion chamber or some other detector, which

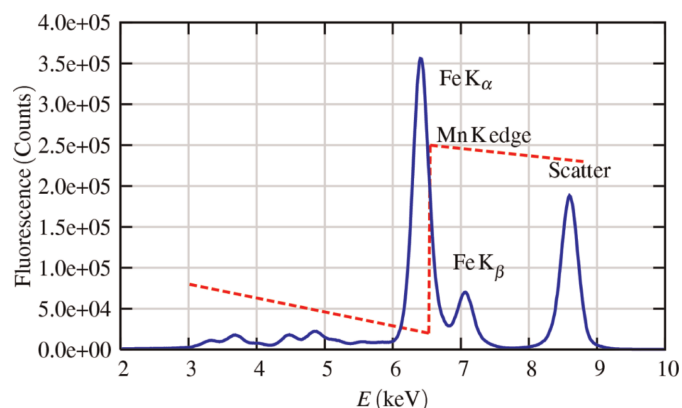


Figure 1
The effect of a ' $Z - 1$ ' filter on a measured iron fluorescence spectrum. A filter of manganese placed between the sample and the detector will absorb most of the scatter peak, while transmitting most of the Fe $K\alpha$ emission. For samples dominated by the scatter peak, such a filter can dramatically improve the signal-to-noise level. (Figure courtesy of M. Newville.)

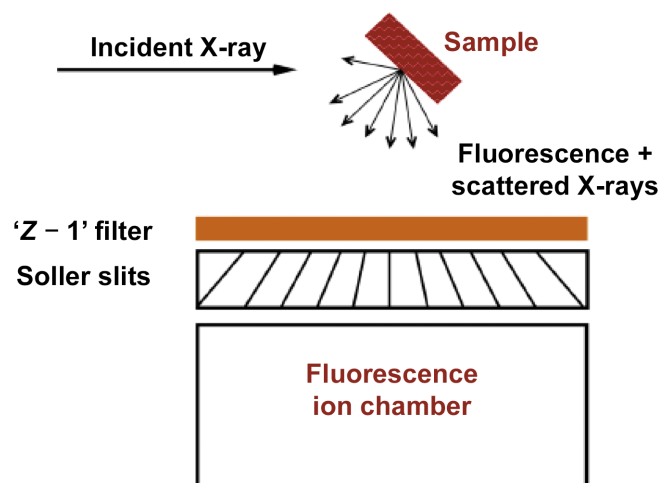


Figure 2
A schematic of the geometry of X-ray fluorescence detection. The incident X-rays excite atoms in the sample, and fluorescence and scattered radiation are emitted over a large solid angle. The ' $Z - 1$ ' filter selectively absorbs higher energy X-rays such as elastically scattered photons. Soller slits are used to suppress refluorescence from the filter. (Figure courtesy of M. Newville.)

need not have energy discrimination itself. This technique is enhanced by geometrically suppressing refluorescence from the filter by the use of Soller slits (Stern & Heald, 1979). Besides relative simplicity, this allows the use of detectors that are capable of extremely high X-ray fluxes. To optimize path length through the fill gas while allowing a reasonable path length for ions and electrons to the electrodes, these chambers are usually designed with multiple subchambers that the X-ray beam transits (Fig. 2).

Ion chambers are typically used in an integrated current mode, with the small direct current being fed to a current-to-voltage amplifier, with the resulting output voltage recorded by a computer as a function of monochromator position.

Pulse-counting detectors, on the other hand, use the detector itself for energy discrimination. These detectors, along with their limitations, are described more completely in this volume by Kappen *et al.* (2024).

2.2. Medium energy resolution

Another approach to using crystal analyzers is a bent-Laue optic, which has a larger acceptance angle than the flat optical elements because of crystal distortion in the strain of the bent crystal. Although these devices are somewhat tunable for energy, they are generally suited to a particular range of energies (see, for example, Zhong *et al.*, 1999).

2.3. High energy resolution

High energy resolution (10 eV) can be used for a number of specialized purposes, such as inelastic X-ray scattering or suppression of core-hole lifetime broadening. The instrumentation is described more completely by Glatzel & Ghiringhelli (2024). The suppression of lifetime broadening has been described by Hämäläinen *et al.* (1999).

3. Nonradiative processes: Auger and secondary electrons

Detection of either higher energy Auger electrons or low-energy secondary electrons is another method of measuring the X-ray absorption as a function of incoming X-ray energy. Total electron yield is the measurement of the total electric current from the negatively biased sample and is proportional to the absorbed X-ray flux. Partial electron yield is usually measured using an analyser specialized for this purpose, for example a cylindrical mirror analyser (see, for example, Gorelik, 2023) or angle-resolved hemispherical analyser (see, for example, Isomura *et al.*, 2022). This is particularly useful for enhancing surface sensitivity for surface XAFS, as the mean free path for escaping electrons is relatively short.

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