Biophysics Collaborative Access Team
Basic Techniques for EXAFS
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Optimizing X-ray Filters

X-ray filters are an essential, but often neglected, part of the apparatus for fluorescence EXAFS experiments. The relative ease by which one can fabricate a serviceable filter has led to a widespread neglect of filter quality. The filter quality is an important parameter: it can make or break an experiment. The purpose of this note is to define filter quality, describe its effects, and derive equations and rules of thumb for choosing the correct filter thickness during an experiment.

Filters are used to preferentially absorb the x-rays that are scattered from dilute samples. Statistical fluctuations in the number of scattered photons are a principal source of noise in EXAFS experiments, and it is therefore desirable to minimize the scattered background as much as possible, without attenuating the signal significantly. Normally the main constituent of a filter is an element which has an absorption edge that falls between the strongest fluorescence lines and the absorption edge of the element of interest (see figure). In many cases (but not all) a suitable filter can be constructed using the element of atomic number (Z) one less than that in the sample (a “Z-1 filter”). For example, one uses a Mn filter (Z=25) for Fe (Z=26) K-edge studies. A well-made filter strongly absorbs the elastically scattered background at excitation energy, but it only slightly attenuates the desired signal at the (lower) fluorescence energy.

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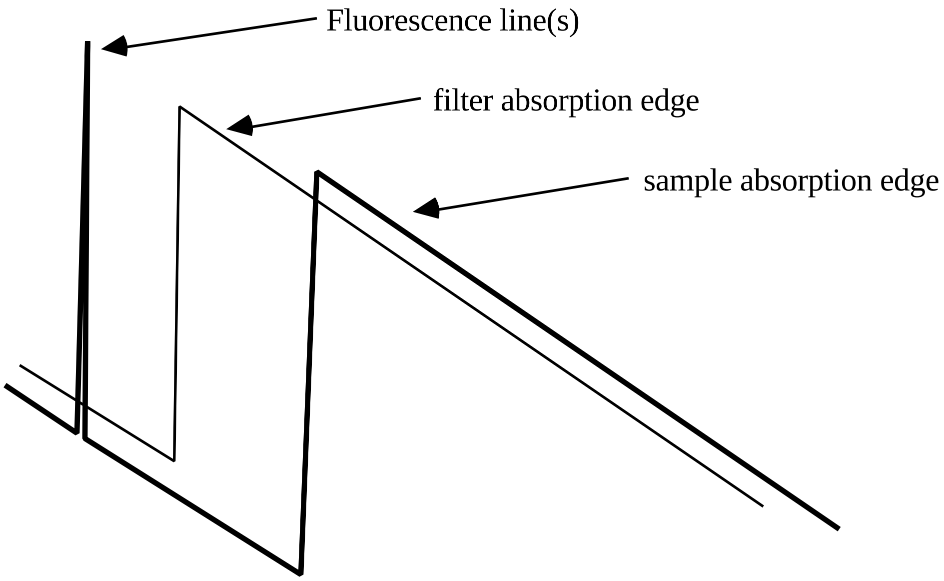

Unfortunately, for every photon that is absorbed by the filter, some fraction (the fluorescence yield, which is about 30% for Fe and elements of similar Z) is re-emitted by the filter as its own fluorescence. The fluorescence yield increases with the Z of the absorber, and generally is greater for K-edges than L-edges. The fluorescence radiation is re-emitted in all directions, so automatically half of the refluorescence goes away from the detector and is not collected. To a first approximation, elements are transparent to their own fluorescence (since the fluorescence is always below the absorption edge edge), and therefore the refluorescence is largely unattenuated as it escapes from the filter. Thus, for iron, about 15% of the scattered background that is absorbed by the filter will still be detected. Therefore an upper limit for the reduction in background is about 1/.15 ≈ 7 or so. This is fine, but it is not enough for dilute specimens, for which the background to signal ratio may be 50 or 100.

Stern and Heald[1] proposed a clever method of preferentially blocking most of this refluorescence by using soller-type slits that focus on the sample. This trick works because the refluorescence is isotropically radiated from the filter (which is placed as close as possible to the detector), while the signal radiates from the sample which is a slight distance away from the detector. It is not difficult to reduce the refluorescence by a factor of 10 using such slits, which results in a maximum background reduction of a factor of about 70. This is appropriate for most enzyme samples in the millimolar concentration range.

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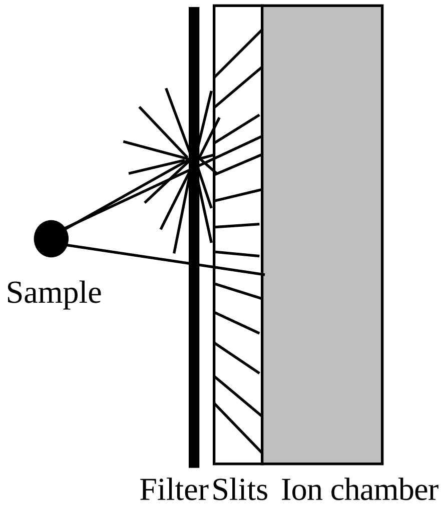
[1] E.A. Stern and S.M. Heald, Rev. Sci. Inst. **50** (1979) 1579. Stern and Heald's paper is the original reference on this topic; this technical note differs basically in emphasis and notation.



Slits permit the fluorescence signal photons to travel from the sample to the detector, but block most of the filter refluorescence.

Filters unfortunately not only attenuate the background, they also attenuate the signal to some extent. For most pure elements of interest, the ratio of the absorption coefficient $\mu(E)$ above the K-edge to that below the edge is in the range 6-8. This imposes fundamental limits on how effectively a filter can work. We can define a figure of merit for a filter, the "Quality", $Q = \mu(E_a)x/\mu(E_b)x$, where $\mu(E)$ is the absorption coefficient of the filter at energy E, x is its thickness, E_a is near the midpoint of the energy range of the scan (e.g. 7,500 eV for Fe), and E_b is the average energy of the fluorescence lines (6,400 eV for the average Fe Kα fluorescence)[2]. For a filter constructed of a homogeneous foil of a pure element, Q is typically in the range 4-6, as mentioned above, which is a fundamental upper limit for a particular element. Most filters in practice are non-uniform, and also contain stuff (plastic, or Duco cement) that absorbs essentially the same fraction of signal and background. Thus many filters in common use have quality factors of Q=3 or so, and it is well worth the trouble to do better than that. Mediocre filters can easily degrade the signal to noise ratio by a factor of 2 relative to good filters.

It is important to note that the Quality of a filter is not proportional to its thickness, because the factor x divides out in the ratio $Q = \mu(E_a)x/\mu(E_b)x$. Two filters of the same Q stacked together are equivalent[3] to one (thick) filter of the same quality Q.

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[2] It is usually more convenient in practice to measure the absorption right above and right below the filter's absorption edge, and scale the result, accounting for the approximate $1/E^3$ energy dependence of the filter absorption coefficient. For example, suppose we are measuring Fe fluorescence, and the ratio of the measured absorption coefficients immediately above and below the Mn edge at 6.54 KeV is 6. Appropriate choices for E_a and E_b are 7.50 KeV and 6.400. Then $Q= 6\,(6.54/7.50)^3\,(6.40/6.54)^3 = 6\,(6.40/7.50)^3 = 6\,(.62)$, or Q=3.7.

[3] In general, when a number of filters (i) of thickness $(\Delta\mu x)_i$ and quality Q_i are stacked together, they are equivalent to a single filter of quality $Q= \Sigma_i\, Q_i\, W_i \,/\, \Sigma_i\, W_i$, with $W_i = (\Delta\mu x)_i \,/\, (Q_i - 1)$.

It is straightforward to write an equation[4] for the "number of effective counts" N_{eff}, in the case in which we have N_b background counts and N_s signal counts (i.e. sample fluorescence) collected by the detector:

$$N_{eff} = \frac{N_s^2}{N_s + N_b}$$

If we place a filter between the sample and the detector, the background is reduced by the factor $\exp(-\mu_a x)$, and the signal is reduced by the factor $\exp(-\mu_b x)$, where $\mu_a \equiv \mu(E_a)$ and $\mu_b \equiv \mu(E_b)$. The refluorescence is proportional to the number of photons absorbed, and a fraction η finds its way into the detector and are counted, where $\eta \approx .15$ if no slits are used, and $\eta \approx .02$ if slits are used ($\eta \approx 0$ for energy dispersive detectors if they are set to resolve only the fluorescence signal). Combining these observations, we can write the number of effective counts as

$$\frac{N_{eff}}{N_s} = (1-\eta)\frac{(e^{-\mu_b x} + \gamma)}{1 + A\left(\frac{e^{-\mu_a x} + \gamma}{e^{-\mu_b x} + \gamma}\right)} \qquad [1]$$

where $A \equiv N_b/N_s$ and $\gamma \equiv \eta/(1-\eta)$. It is convenient to reexpress μ_a and μ_b in terms of the "filter thickness" $\Delta\mu x \equiv \mu_a - \mu_b$ and quality $Q \equiv \mu_a/\mu_b$, or $\mu_a = \Delta\mu x(Q/(Q-1))$, $\mu_b = \Delta\mu x(1/(Q-1))$.

The number of effective counts depends on the background to signal ratio (before the filter is put in), the thickness $\Delta\mu x$ and quality μ_a/μ_b of the filter, and the effectiveness of the slits η. We plot this function for various typical values of these parameters in the figures below. These curves can be used during your experiment to choose the optimum filter thickness, provided you have previously measured the thickness and quality of your filters.

We can find the optimum value by taking the derivative of equation [1] with respect to $\Delta\mu x$, setting it to zero, and solving for $\Delta\mu x$. However, unless somewhat dubious further approximations are made, this gives a transcendental equation that has no analytical solutions. Numerical solutions however can be readily obtained, and are presented in the appendix as tables and graphs. The figures have the additional advantage of showing how "soft" the optimum filter thickness is.

Simple analytical solutions are readily obtained when η approaches zero. this is appropriate when a solid state detector is used to reject filter refluorescence[5], or if the slits are able to block nearly all of the filter refluorescence. In that case (η=0) the optimum filter thickness is given by the simple expression:

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[4] See the note "Sources of Noise in EXAFS experiments" in this series.

[5] It is often beneficial to use filters and slits in conjunction with solid state detectors, so that scattered background radiation does not saturate the detector. In this case the strategy is to use just only as thick a filter as needed to prevent saturation.

$$\Delta\mu x(\text{best}) = \ln\left[\frac{N_b}{N_s}(Q-2)\right] \qquad [2]$$

These equations indicate that if the filter quality is 2.0 or less, one is better off without it: it actually degrades the signal to noise ratio. Another consequence of this equation is that, for a filter quality of 3.0, the best signal to noise ratio is obtained when the signal and background are about equal. If the filter quality is 4, the optimum S/N ratio occurs when the background is half the size of the signal. Although the equation is approximate, it is useful during the experiment for estimating how thick a filter to add or remove in order to improve the signal to noise ratio. For example, suppose that you are already using some filters, and the background has been reduced to 3 times the signal, and the filters you have left are of quality Q=4. The equation indicates that you should add a filter of $\Delta\mu x \approx 1.8$ to obtain optimal S/N.

The exact expression (equation 1) is plotted vs filter thickness in the accompanying figures. Using these curves is probably the best way to estimate the proper filter thickness under given experimental conditions. Note how strongly the filter quality affects the optimum achievable S/N ratio. One can readily double the effective number of counts by using a high quality (Q=5) filter rather than a mediocre one. The thickness of the filter must also be correct, however, and it is very important that slits be used if the filter is close to the detector. Also it is striking how low the efficiency of use of signal photons actually is: clearly there is a need for energy dispersive detectors of large solid angle and higher maximum count rate.

Having made the point that filter quality is a very important experimental parameter, we now describe the most important factors that affect filter quality. Considering only x-ray characteristics, the ideal filter would be a uniform, self supporting foil of the appropriate element. In most cases this is not practical, however. Usually the appropriate foil thickness is only a few microns, and such a foil usually is easily damaged under experimental conditions. Excellent filters can often be constructed by thermally evaporating metals on a 0.5-1.0 mil Kapton™ plastic film (1 mil =.001 inch). The quality Q is higher for thicker filters because the absorption of the substrate is present regardless of the coating thickness. In general, one wants to minimize the absorption of signal by the support and other material. Uniformity is very important, because thin regions will allow leakage of background photons through the filter and degrade its effectiveness, particularly for thick filters.

One can alternatively use fine particles of the appropriate element applied to adhesive tape (Scotch Magic Transparent tape works well), or uniformly suspended in a slurry of Duco cement and thinner that is painted (or sprayed) on a thin support. One can use the cement itself as a support, but care should be taken that it not be too thick and absorb too much of the fluorescence signal.

If “fine” particles are used, it is very important that they be fine *enough* : the particle size should be not be much larger than one absorption length (μ^{-1}). For example, if one uses MnO to construct a filter for use at the Fe K edge, the particle size should be not much larger than 5 microns. A -400 mesh sieve permits particles smaller than 38 microns to pass through. Although these particles make up a very fine dust, they are still about ten times larger than needed. In short, one must first calculate what one absorption length is, and then figure out some way to obtain particles that size. Just grinding up the material until the particles seem small usually results in a low quality filter (Q=2–3). Large particles do not effectively filter out the background, and moreover, they unnecessarily block out the signal. Finer particles can be separated by sedimentation, for example by mixing particles with methanol or acetone, stirring the mixture up, letting the larger particles fall to the bottom for a minute or so, and decanting and drying the ultrafine particles that remain suspended. Paradoxically it is sometimes better to use a compound or complex salt (which has more “junk” in it), because particles of the appropriate size are more easily prepared. In this case attenuation by the other elements in the filter should of course be minimized. For example, a few oxygen atoms may be ok, but a few sulfurs are not.

The final step in filter preparation is to measure: A) the filter thickness $\Delta\mu x$, and B) the filter quality $(\mu x)_{above}/(\mu x)_{below}$. These numbers, and equations [1] and [2] above, and the accompanying figures then allow one to systematically optimize the filter thickness during the experiment.

To determine filter quality Q, it is necessary to make absolute measurements of the filter absorption coefficient, rather than the relative measurements that are normally carried out in XAFS experiments. It is straightforward and fast to do so by the following procedure. Move the monochromator to the fluorescence energy and measure the ion chamber reading with the filter placed in front of the detector (I_b), and also without it (I_{b0}). Then move to an energy in the middle of the EXAFS scan range (say 400 eV above the edge) and again measure the fluxes with (I_a) and without (I_{b0}) the filter. After subtraction of dark currents (“offsets”) (and correction for air absorption if needed) the filter quality can be calculated as $Q=\ln(I_a/I_{a0})/\ln(I_b/I_{b0})$. The measurements should be done without large time delays between the readings so that the incident flux does not appreciably change. Alternatively the incident flux can be measured simultaneously and each flux above can be normalized by the incident fluxes. Several measurements on different parts of the filter should be taken to check uniformity. As in a transmission measurement, care should be taken to eliminate harmonic contamination of the beam, otherwise filter quality will be underestimated.