Systematic Errors in Fluorescence EXAFS

Fluorescence detection of EXAFS is usually the most appropriate mode of detection of x-rays for dilute samples, such as biological samples. Although the signal to noise ratio in fluorescence mode is often superior to that in transmission mode, the fluorescence excitation spectra are more susceptible to systematic errors. This note describes some of the pitfalls, and steps that can be taken to avoid them.

In the conventional transmission experiment (figure 1), the flux of monochromatic x-rays incident on the sample is monitored by a semitransparent ionization chamber (I_0), and the flux of x-rays transmitted through the sample is measured by another ionization chamber (I), which is usually totally absorbent. If the sample is of uniform thickness x, the x-ray absorption coefficient $\mu(E)$ of the sample is given by $I = I_0 \exp(-\mu x)$, or $\mu x = \ln(I_0/I)$. Actually, the measured μx is the absorption coefficient of everything between the two ionization chambers, including air, entrance and exit windows, etc. Furthermore, the sensitivities of the ionization chambers decrease with increasing x-ray energy, so there are a number of extraneous factors that *multiply* the ratio I_0/I. When the logarithm is taken, these multiplicative factors are transformed into a slowly varying *additive* background, which is easily and unambiguously subtracted out in the early stages of data analysis. Thus, in transmission measurements, extraneous materials in the beam path are not of concern, as long as they do not contain the elements being measured and they do not attenuate the beam very much.

Transmission EXAFS experiment

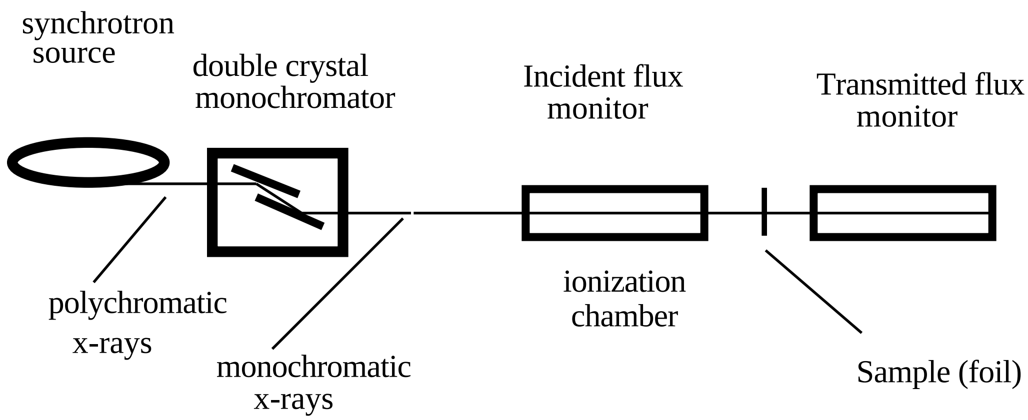

Figure 1

The situation is quite different in fluorescence mode (figure 2) because no logarithm is taken, and the spurious multiplicative factors result in altered EXAFS amplitude functions. Such effects do not cancel out even if the two detectors are identical (figure 3). The detectors are inherently functionally inequivalent because the front detector measures a monochromatic beam at the incident energy E, while the rear detector measures a combination of fluorescence at energy E_f and the scattered radiation at $E_{scat} \leq E$. Special attention therefore must be given to making sure these energy dependent factors are the same for the material under study and the standard compounds, so that they cancel out. To ensure this, the x-ray absorption properties of all of the samples should be very similar, and the physical geometry of the experiment should be the same for all materials being directly compared. Furthermore, it is very important that, for thick samples, the concentration in the sample of the element of interest (for example, Fe) not be too large. The reason is this: as the absorption of the Fe increases, the effective penetration depth of the x-rays in the sample decreases, which tends to compensate for the increase in absorption. This results in a nonlinear distortion of the measured spectra. This is worked out explicitly below. The main points are, if the sample is concentrated, it must be thin. If it is dilute, it should be thick. Fluorescence EXAFS spectra of thick, concentrated ($\mu x>1$) samples (such as metallic foils, or concentrated samples made of particles that are too large) will generally have severely suppressed amplitudes and the edge spectra will be distorted.

EXAFS experiment with ion chamber as flux monitor

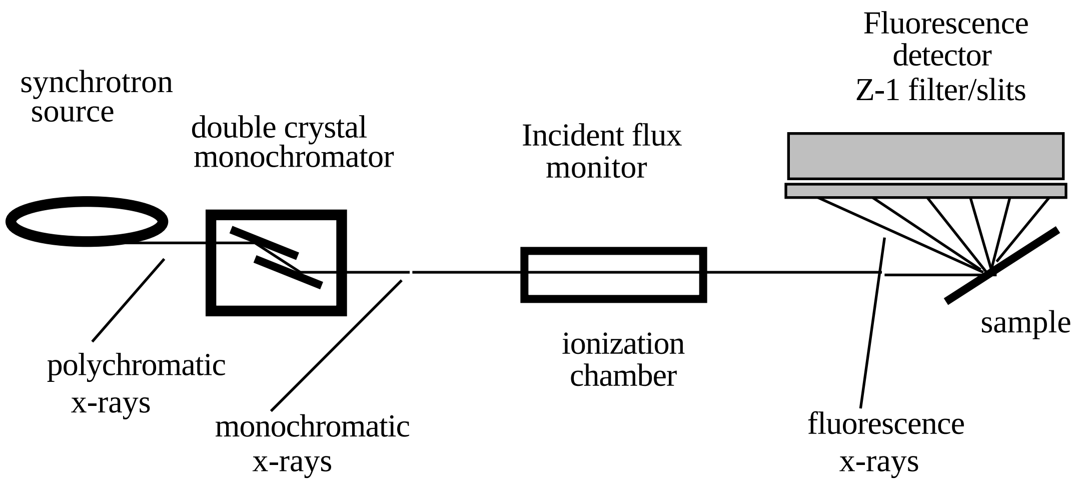

Figure 2

EXAFS experiment with scatterer as flux monitor

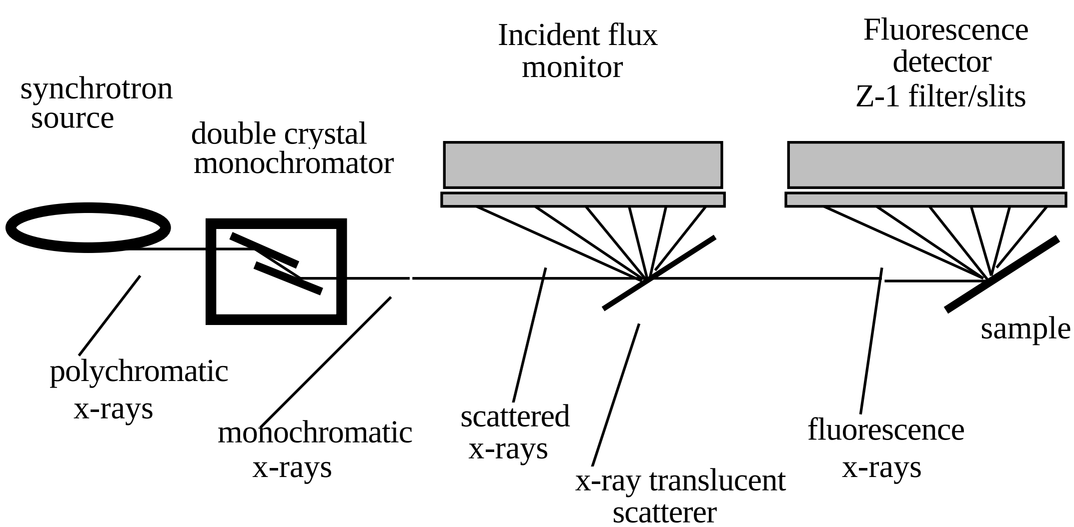

Figure 3

Example:

In the simplest experimental configuration, a slab of sample is oriented at an angle Θ with respect to the incident beam direction (figure 4). It is easy to work out the probability that a x-ray photon incident on the sample gives rise to a fluorescence photon that is collected by a detector located[1] in the direction Φ. This probability is just the probability that:

1) the photon penetrates to a depth x in the sample:

$\exp(-\mu(E)x/\sin\Theta)$

2) and that it is absorbed by the element (for example, Fe) in a layer of thickness dx:

$\mu_{Fe}(E)\, dx/\sin\Theta$

3) and as a consequence it emits with probability ε a fluorescence photon of energy E_f :

ε

4) which escapes the sample and is radiated into the solid angle Ω subtended by the detector in the angle Φ:

$(\Omega/4\pi)\exp(-\mu(E_f)x/\sin\Phi)$

5) and this product of factors is summed (integrated) over all depths x up to x_{max}:

$$(\Omega/4\pi)\,\varepsilon\,\mu_{Fe}(E)/\sin\Theta\,\exp(-\mu(E)x/\sin\Theta)\exp(-\mu(E_f)x/\sin\Phi)\;dx,$$

[1] Actually, an integral over all directions Φ that intersect the detector must in principle be done. This integral can be roughly approximated by using angle to the center of the detector, and accounting for the solid angle subtended by the detector. In practice Θ and Φ are usually both about 45˚.

That is, explicitly:

$$(\Omega/4\pi)\ \varepsilon\ \mu_{Fe}(E)/\sin\Theta \int_0^{x_{max}} e^{[-(\mu(E)/\sin\Theta\ +\ \mu(E_f)/\sin\Phi)x]}\ dx\ =$$

$$=(\Omega/4\pi)\ \varepsilon\ \mu_{Fe}(E)/\sin\Theta\ \frac{1\ -\ e^{[-(\mu(E)/\sin\Theta\ +\ \mu(E_f)/\sin\Phi)x_{max}]}}{[\mu(E)/\sin\Theta\ +\ \mu(E_f)/\sin\Phi]} \qquad [1]$$

X-rays incident on a slab of sample

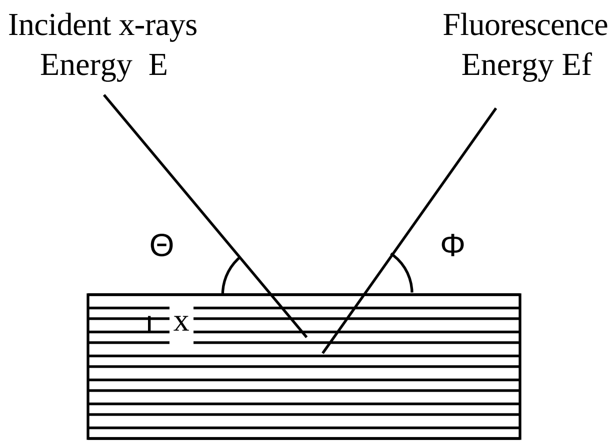

Figure 4

For thin samples (and angles that are not too small), the quantity $[(\mu(E)/\sin\Theta + \mu(E_f)/\sin\Phi)\ x_{max}\ ] << 1$, and the exponential can be approximated by the first two terms in its Taylor expansion, e.g.

$$\exp(z) = 1 + z + \ldots$$

for small z. In this case equation 1 reduces to

$$(\Omega/4\pi)\ \varepsilon\ \mu_{Fe}(E)\ x_{max}\ /\sin\Theta,$$

as it should by definition for a very thin sample.

For thick samples ($\mu x >> 1$), the exponential in equation 1 becomes negligible, and we obtain

$$\frac{(\Omega/4\pi)\varepsilon\mu_{Fe}(E)/\sin\Theta}{[\mu(E)/\sin\Theta + \mu(E_f)/\sin\Phi]} \quad . \qquad [2]$$

Now, $\mu(E)$ is the total absorption coefficient of the Fe in the sample plus everything else: $\mu=\mu_{Fe} + \mu_{else}$. The thing we are actually interested is $\mu_{Fe}(E)$. If the absorption coefficient due to Fe in the sample is only a small part of the total absorption, the denominator of equation 2 simply multiplies the desired $\mu_{Fe}(E)$ by a slowly varying function of energy (as long as no other elements in the sample have an absorption edge over the energy range of interest). On the other hand, if μ_{Fe} is not much less than μ, then serious distortions of the spectra result. For example, consider what happens if the sample is an iron foil, and the exit and entrance angles Θ and Φ are 45˚. Equation 2 gives:

$$(\Omega/4\pi)\varepsilon\frac{\mu_{Fe}(E)}{\mu_{Fe}(E) + \mu_{Fe}(E_f)} \quad .$$

If the constant $\mu_{Fe}(E_f)$ in the denominator were not present, the desired term $\mu_{Fe}(E)$ in the numerator would be totally canceled out by the same term in the denominator: one would measure a featureless spectrum, regardless of the true absorption coefficient. Because of the other term $\mu_{Fe}(E_f)$, in reality spectral features (e.g. EXAFS amplifudes) are strongly suppressed, rather than totally cancelled. Thus, when the Fe absorption increases (for example, over the absorption edge), the measured absorption increases by a much smaller amount[2].

Essentially the same problems may occur, even for samples that are dilute on average, if the element of interest is contained in concentrated particles that are suspended in a dilute matrix. If the particle size is very much larger than one absorption length, the penetration depth varies with the absorption coefficient of the species of interest, and the spectra are consequently distorted. Thus, the particle sizes must be made about one absorption length or less in fluorescence mode, just as they must in transmission[3].

The presence of the angles Θ and Φ in the equations above clearly shows that the energy dependence of the measured signals (and the EXAFS amplitudes) depend somewhat on the geometry of the experiment, e.g. the position and size of the detector. Thus, to minimize systematic errors, one should keep the experimental geometry and the composition of the sample matrices as similar as possible to each other for all materials being compared.

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2 Another effect has similar but less pronounced consequences. The elastically scattered background decreases when the absorption coefficient increases, which also tends to suppress features in the spectrum.

3 See ”Thickness and particle size effects” in this series ”Basic Techniques for EXAFS”.