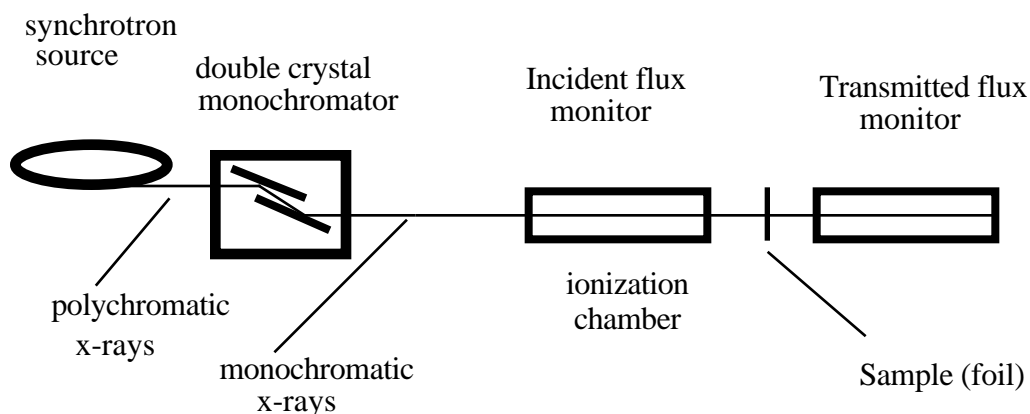


### Systematic Errors in Fluorescence EXAFS

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  $\mu x$  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  $E_{\text{scat}} = E$ . 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 samples (such as metallic foils, or concentrated samples made of particles that are too large) will generally be severely distorted.

#### EXAFS experiment with ion chamber as flux monitor

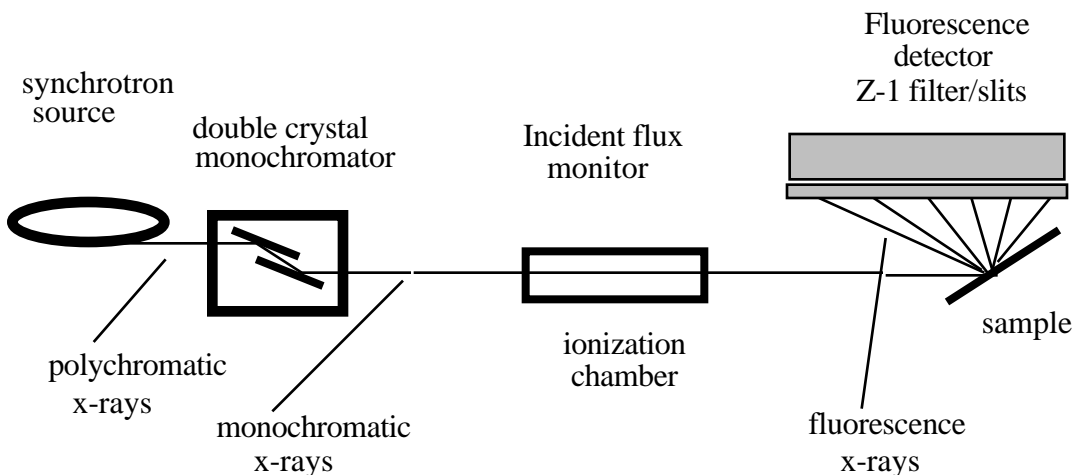
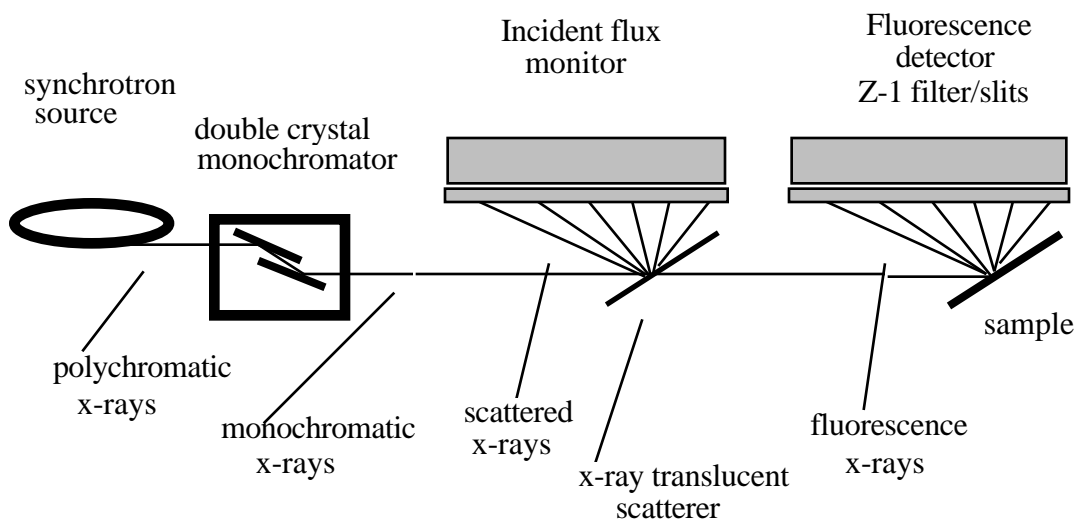


Figure 2

## EXAFS experiment with scatterer as flux monitor



**Figure 3**

### Example:

In the simplest experimental configuration, a slab of sample is oriented at an angle with respect to the incident beam direction (figure 4). It is easy to work out the probability that a fluorescence x-ray photon incident on the sample will be collected by a detector located<sup>1</sup> in the direction  $\theta$ . 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  $dx$ :  
 $\mu_{\text{Fe}}(E) dx$
- 3) and as a consequence it emits with efficiency  $\omega$  a fluorescence photon of energy  $E_f$ :
- 4) which is radiated into the solid angle  $\Omega$  subtended by the detector in the angle  $\theta$ :  
 $(\Omega/4\pi) \exp(-\mu(E_f)x/\sin \theta)$
- 5) and this product of factors is summed (integrated) over all depths  $x$  up to  $x_{\text{max}}$ :

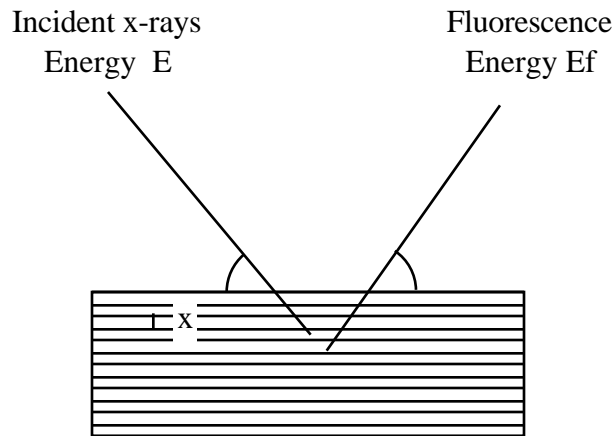
$$\int_0^{x_{\text{max}}} (\Omega/4\pi) \mu_{\text{Fe}}(E) \exp(-\mu(E)x/\sin \theta) \exp(-\mu(E_f)x/\sin \theta) dx,$$

<sup>1</sup> Actually, an integral over all directions  $\theta$  that intersect the detector must be done, at least in principle. The integral can be roughly approximated by using the angle to the center of the detector, and accounting for the solid angle subtended by the detector. In practice the average  $\theta$  and  $\Omega$  are usually both about  $45^\circ$ .

That is, explicitly:

$$\begin{aligned}
 \left( \frac{1}{4} \right) \mu_{\text{Fe}}(E) \int_0^{x_{\text{max}}} e^{[-(\mu(E)/\sin \theta + \mu(E_f)/\sin \theta_f)x]} dx = \\
 = \left( \frac{1}{4} \right) \mu_{\text{Fe}}(E) \frac{1 - e^{[-(\mu(E)/\sin \theta + \mu(E_f)/\sin \theta_f)x_{\text{max}}]}}{[\mu(E)/\sin \theta + \mu(E_f)/\sin \theta_f]} \quad [1]
 \end{aligned}$$

### X-rays incident on a slab of sample



**Figure 4**

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

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

for small  $z$ . In this case equation 1 reduces to

$$\left( \frac{1}{4} \right) \mu_{\text{Fe}}(E) x_{\text{max}},$$

as it should, by definition, for a very thin sample.

For thick samples ( $\mu x \gg 1$ ), the exponential in equation 1 vanishes, and we obtain

$$\frac{(\cos \theta / 4) \mu_{\text{Fe}}(E)}{[\mu(E)/\sin \theta + \mu(E_f)/\sin \theta]} \quad [2]$$

Now,  $\mu(E)$  is the total absorption coefficient of the Fe in the sample, plus everything else:  $\mu = \mu_{\text{Fe}} + \mu_{\text{else}}$ . The quantity we are actually interested is  $\mu_{\text{Fe}}(E)$ . If the absorption coefficient due to Fe in the sample is only a small part of the total absorption, the denominator of equation 2 just multiplies the desired  $\mu_{\text{Fe}}(E)$  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  $\mu_{\text{Fe}}$  is not much less than  $\mu$ , 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  $\theta_i$  and  $\theta_f$  are  $45^\circ$ . Equation 2 gives:

$$\frac{\sqrt{2}(\cos \theta / 4) \mu_{\text{Fe}}(E)}{[\mu_{\text{Fe}}(E) + \mu_{\text{Fe}}(E_f)]}$$

If the constant term  $\mu_{\text{Fe}}(E_f)$  in the denominator were not present, the desired term  $\mu_{\text{Fe}}(E)$  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, in reality one observes a strong suppression of features in the spectrum rather than total cancellation. Thus, when the Fe absorption increases (for example, over the absorption edge), the measured absorption increases by a much smaller amount<sup>2</sup>. In short, use of a thick, concentrated sample results in severely distorted EXAFS amplitudes and XANES spectra.

Essentially the same problems occur even for dilute samples, if the element of interest is contained in concentrated particles that are suspended in a dilute matrix. If the particle size is larger than about one absorption length, the penetration depth varies with the absorption coefficient of the species of interest, and the spectra are nonlinearly distorted as a consequence. Therefore the particle size must be made sufficiently small in fluorescence mode, just as it must in transmission mode<sup>3</sup>.

The presence of the angles  $\theta_i$  and  $\theta_f$  in the equations above shows that the energy dependence of the measured signals (and the EXAFS amplitudes) depend on the geometry of the experiment, e.g. the size of the detector and its position relative to the sample. Also note that the equations above refer to a planar sample; a sample of different shape would give a somewhat different equation. To minimize systematic errors, one should keep the experimental geometry and the sample matrices as similar as possible to each other for all

<sup>2</sup> 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.

<sup>3</sup> See "Thickness and particle size effects" in this series "Basic Techniques for EXAFS".

materials being compared. In polarized EXAFS and XANES measurements, care should be taken to ensure that such effects are calibrated out when the sample is rotated.

These considerations show that special care must be taken to obtain consistent EXAFS amplitudes when obtaining fluorescence EXAFS spectra. If attention is paid to such experimental details, higher accuracy should be obtainable in determining coordination numbers and EXAFS Debye Waller factors.