

Overabsorption (“Self-absorption”), Thickness and Hole Effects in EXAFS

Matthew A. Marcus¹, Alain Manceau²

¹ Advanced Light Source, Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, California 94720, USA

² Environmental Geochemistry Group, LGIT, University J. Fourier and CNRS, 38041 Grenoble Cedex 9, France

1. Introduction

This note is a primer for users about a ubiquitous but often-misunderstood set of artifacts which can corrupt EXAFS data, but which can often be avoided by careful sample preparation. Since 10.3.2 is a micro-focused beamline, the problem of preparing good samples is a little different from what it would be on a macro beamline. While most samples of interest are dilute enough not to be of concern, the standards one might use to characterize them often aren't. Thus, it is important to understand concentration-dependent artifacts and how to deal with them.

This note is a modified section taken from a review article (Manceau et al. 2002) on environmental applications of microbeams, so tends to emphasize environmental samples. However, the considerations discussed below apply to all sorts of EXAFS.

II. Hole and thickness effects

The effects known as “hole effect” and “thickness effect” (also, “self-absorption” and “over-absorption”) are well-known from other sorts of EXAFS studies (Goulon et al. 1981), but tend to be difficult to quantify and manage when doing environmental studies, especially with a microbeam. The hole effect is seen when doing a transmission spectrum on an inhomogeneous sample. As a simple example, imagine that half the beam goes through a part of the sample for which the number of absorption lengths (μt) is 2 above the edge. For this simple example, let us neglect the pre-edge absorption. Assume that the other half of the beam goes through a blank area with no absorption. Now, the aggregate transmission above the edge is $(1+\exp(-2))/2 \approx 0.57$, whereas that below the edge is 1. The effective absorption is the negative log of this quantity, which is also about 0.57. Now, let there be an EXAFS oscillation of 10%, so that the absorption in the sample goes from 2 to 2.2. The transmission becomes 0.56, and the change in the effective absorption is only 0.0218, out of an edge jump of 0.57. Thus, we have a measured amplitude for this EXAFS wiggle of 3.8% instead of the real value of 10%. What is happening here is that the hole produces a non-linear relation between the measured absorbance and the real one. This relation displays a saturating behavior, so that small changes at the top end (where the EXAFS is) are underrepresented relative to the whole edge jump. Figure 1 shows this phenomenon graphically. In this Figure, the actual EXAFS is shown on the bottom, and its mapping to the measured EXAFS at the right is via the smooth curve in the middle. Figure 2 shows some experimental microprobe data of a ferromanganese crust (Hlawatsch et al. 2001) taken in transmission at three spots on areas of the same composition but differing thickness. We see from these data how the EXAFS amplitude can be reduced, and the pre-edge enhanced (Manceau and Gates 1997), by these effects. As will be explained below, similar effects can occur in fluorescence as well as transmission.

With this simple example as background, let us consider a more general situation. Consider a beam incident on a particle such that the thickness of material is not uniform within the beam. Let the total transmission of the beam be $T(\mu(E))$ where $\mu(E)$ is the absorption coefficient at a particular energy E . This absorption coefficient has two parts, a resonant part μ_r , which is 0 below the edge and which is modulated by the EXAFS, and a non-resonant or background part μ_b , which is continuous and slowly-varying through the edge. The EXAFS oscillations cause μ_b to be replaced by $\mu_b(1 + \chi)$ where χ is the EXAFS wiggle. What one plots is the negative logarithm of the transmission $P = -\ln(T)$. In analyzing the EXAFS, one subtracts the pre-edge background and normalizes to the smooth part of the resonant absorption. If this could be done perfectly, the result would be the effective EXAFS wiggle

$$\tilde{\chi} = \frac{\ln [T(\mu_b) / T(\mu_b + \mu_r(1 + \chi))]}{\ln [T(\mu_b) / T(\mu_b + \mu_r)]} \quad (1)$$

where the denominator represents the post-edge background subtraction. We can check this formula by noting that if the sample is uniform and of thickness t , then the transmission $T(\mu)$ is given by $\exp(-\mu t)$ and the above equation evaluates to $\tilde{\chi} = \chi$. If the EXAFS wiggle is small, we can expand Equation (1) with respect to χ and come up with

$$\tilde{\chi} = \chi \frac{\mu_r \left. \frac{d \ln T}{d \mu} \right|_{\mu=\mu_b+\mu_r}}{(\ln(T(\mu_b + \mu_r)) - \ln(T(\mu_b)))} \equiv S_t \chi \quad (2)$$

where S_t is the ratio of the amplitude of the measured EXAFS wiggle to the actual signal. Thus, if S_t is 0.8, then the coordination number will appear to be 80% of what it really is.

The above formalism is quite general, and can be used to study the effects of doing transmission EXAFS on non-uniform samples and particles of all sorts. However, the mathematics quickly become forbidding if one looks at a realistic situation such as a particle illuminated by a Gaussian beam. Such situations require numerical methods. For a simple, analytically-accessible example, imagine a uniform foil with a hole in it such that a fraction f of the beam goes through the hole. Then, we have

$$T(\mu) = f + (1 - f) \exp(-\mu t) \quad (3)$$

where t is the thickness of the hole. Turning the crank on Equation (2) yields, after some algebra

$$S_t = - \frac{\mu_r t (1 - \tilde{f}) \exp(-\mu_r t)}{(\tilde{f} + (1 - \tilde{f}) \exp(-\mu_r t)) \ln(\tilde{f} + (1 - \tilde{f}) \exp(-\mu_r t))} \quad (4)$$

where \tilde{f} is an ‘effective’ hole fraction which reduces to f for $\mu_b = 0$ and is given by

$$\tilde{f} = f / [f + (1 - f) \exp(-\mu_b t)] \quad (5)$$

which is always larger than f . It is easy to show that S_t is 1 for $\tilde{f} = 0$ or $\mu_r t = 0$ and decreases monotonically with both \tilde{f} and $\mu_r t$.

Figure 3 shows a contour map of S_t as a function of \tilde{f} and $\mu_r t$. For a thick sample, even a small fraction of beam skimming by can affect the EXAFS amplitude. Similarly, if there are harmonics in the beam, they go through the sample with less absorption than the fundamental, leading to the same effect as if there were a hole (Stern and Kim 1981). While the sample may not have holes in it, it is common to encounter particles smaller than the beam. Suppose one is dealing with a primary mineral such as magnetite (Fe_3O_4), to give a simple example. At the edge, $1/\mu_r$ is about $8.7\mu\text{m}$. Therefore, if you have a particle of $5\mu\text{m}$ size, you would want <30% of the beam to miss the particle in order to keep 90% of the EXAFS amplitude, if the data were being taken in transmission.

Since these calculations require one to evaluate the absorption coefficients (absorbances) of materials at various energies, we will now make a short diversion into how these coefficients may be calculated. There are several standard sources of tables, some of which are on the World Wide Web. Two such sets of tables are those by Henke et. al. (1993) and McMaster (1969). The latter is embodied in a FORTRAN program called `muca1`. An approximate method, good to 20% or so between 5 and 100keV, is to use the polynomial fits due to Gerward (1981), which is the source of the numbers quoted here. All of these methods yield the mass absorption coefficient $(\mu/\rho)|_{E,Z}$ (dimension cm^2/g) for a given element Z at a given energy E . To get the absorbance of a sample of a given composition, the formula is:

$$\mu(E) = \rho \sum_i (\mu/\rho)|_{E,Z_i} \quad (6)$$

where i is the index of elements and ρ is the density of the sample in g/cm^3 . The result is the absorbance in cm^{-1} . To get the resonant part, subtract the absorbance evaluated just below the edge from that just above. The non-resonant part is approximately the absorbance just below the edge. For more accuracy, extrapolate the non-resonant part to the energy of interest.

III. Fluorescence – “Self-absorption”

For such small particles, and in many other cases, one will use fluorescence instead. However, saturation effects such as we saw for transmission mode also occur in fluorescence as well (Troger et al. 1992; Castaner and Prieto 1997). The classic case here is that of a thick piece of pure metal such as Cu. In this material, the ratio of the resonant to non-resonant absorption is about 85:15. This means that for every 100 incident photons, 85 of them create K-holes and thus could stimulate fluorescence. Now, suppose the resonant absorption goes up by 10% due to EXAFS. Now the ratio is 93.5:15, or about 86.1:13.9. Thus, the resonant process accounts for 86.1% of the total, which means the fluorescence intensity only goes up by 1.3% instead of 10%. This example shows that, again, the response saturates as a function of the absorption one wants to measure

This effect is known variously as ‘self-absorption’, ‘thickness effect’ or ‘over-absorption’. An analogous effect in photochemistry is known as ‘saturation of the action spectrum’. The first term is somewhat of a misnomer because it suggests that the problem has to do with re-absorption of the fluorescence radiation, by analogy with certain effects in optical spectroscopy. Actually, the absorption of the fluorescence is independent of the incident energy, hence does not contribute to any non-linearity. What is important is that the penetration depth for the incident radiation depends on the quantity one wants to measure.

In the same spirit as the previous discussion on transmission, let us look at the general theory of thickness effects in fluorescence detection mode. The fluorescence signal received may be expressed as being proportional to the resonant absorption times a factor which would be constant for a thin sample:

$$I_f = \mu_r F(\mu_r, \mu_b, \mu_f) \quad (7)$$

where μ_f is the absorption coefficient for the fluorescence radiation. Now, the background below the edge is 0, so the EXAFS modulation is given by:

$$I_f(1 + S_f \chi) \approx \mu_r(1 + \chi) F(\mu_r(1 + \chi), \mu_b, \mu_f) \quad (8)$$

to first order in χ . Expanding this, we find a simpler formula than for transmission:

$$S_f = 1 + \frac{\partial \ln F}{\partial \ln \mu_r}. \quad (9)$$

Now let us do a simple example. Consider an infinitely-thick material oriented at an angle θ to the beam (0 = grazing) and ϕ to the detector, which is considered to subtend a small angle. The beam intensity after the beam has gone a distance z into the sample is $\exp(-(\mu_r + \mu_b)z)$, and the fraction of the fluorescence not absorbed by the sample is $\exp(-\tilde{\mu}_f z)$, where $\tilde{\mu}_f$ is an effective absorption given by $\mu_f \sin \theta / \sin \phi$. Integrating along the beam path, we find that up to constant factors, the fractional fluorescence yield is

$$F \propto \int_0^\infty dz e^{-z(\mu_r + \mu_b + \tilde{\mu}_f)} = \frac{1}{\mu_r + \mu_b + \tilde{\mu}_f}. \quad (10)$$

Carrying out the math, we find that

$$S_f = \frac{\mu_b + \tilde{\mu}_f}{\mu_b + \tilde{\mu}_f + \mu_r} \quad (11)$$

which shows that if you want to retain 90% of the EXAFS amplitude in fluorescence detection mode, the resonant absorption must be <10% of the total, including fluorescence. This treatment extends to electron-yield detection if one substitutes the appropriate mean free path for $\tilde{\mu}_f$. This also shows that by collecting the fluorescence at grazing angles to the sample, one can raise $\tilde{\mu}_f$ to the point where the thickness effect drops out and a correct EXAFS spectrum is obtained (Brewer et al. 1992). However, this method only works for smooth, flat samples, which are not always available, and it throws away a lot of signal. Still, it may be useful for certain standard minerals which can be polished and which are so concentrated one does not mind losing signal.

If the sample is of finite thickness, the formula gets somewhat more complex:

$$S_f = 1 - \frac{\mu_r}{\mu_t} + \frac{\mu_r}{\mu_t} \frac{\mu_t t \csc \theta}{\exp(\mu_t t \csc \theta) - 1}, \quad (12)$$

where t is the sample thickness and $\mu_t \equiv \mu_r + \mu_b + \tilde{\mu}_f$ is the total absorption along the incident direction. For $\mu_t t \csc \theta \gg 1$ we recover the bulk Equation (11), and for $\mu_t t \csc \theta \ll 1$ we get $S_f = 1$ as expected, because for diluted samples (regardless their thickness) the fluorescence intensity is proportional to the resonant absorption. Figure 24 shows a contour map of this formula, plotted as a function of the edge jump $\Delta\mu t = \mu_r t \csc \theta$ (proportional to the sample thickness) and the resonant fraction μ_r / μ_t (proportional to the metal concentration). We see two distinct limits, corresponding to the two branches of the contours: thick sample, in which the resonant fraction has the most effect on S_f , and thin sample, where the edge jump matters most.

Now for some examples. One of these has already been shown as Figure 1. The ‘measured’ curve in Figure 1 is an experimental fluorescence curve for Ti foil (6 μm , 45° incidence and exit angle), while the ‘actual’ curve is transmission data for the same sample. The smooth mapping curve is a fit to Equation (12). The first environmental example is Zn in a primary mineral, sphalerite (ZnS), measured at 45° incident and exit angles. For this case, the resonant fraction is 59% ($\mu_b = 160\text{cm}^{-1}$, $\mu_r + \mu_b = 700\text{cm}^{-1}$, $\mu_f = \tilde{\mu}_f = 220\text{cm}^{-1}$, so $\mu_t = 920\text{cm}^{-1}$, assuming $\rho = 4.102$). Suppose we want the amplitude to be good to 10%, so S_f must be at least 90%. Referring to Figure 4, we see that with $\mu_r / \mu_t = 59\%$, we are in the thin-sample (high [Me]) branch of the curve, and that the edge jump $\mu_r t \csc \theta$ must be 0.2 or less. Plugging in the values above, we find a maximum sample thickness of $0.2 \times \sin(45^\circ) / 920\text{cm}^{-1} = 1.5\mu\text{m}$. Fortunately, we do not need the beam to be as small as the particle in order to do fluorescence. A bigger beam would make for better stability and still yield the correct spectrum provided there are no larger particles or particles containing Zn in a different form in that beam. This example shows the importance of mapping inhomogeneous samples before measuring them.

The opposite limit is represented by a dilute mixture. For this example, let us take 1 cation % of Zn in kaolinite (used as an example of a light matrix). The empirical formula of this sample is $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8:\text{Zn}_{0.08}$. Now, the Zn resonant absorption is <5% of the total, so one is free to use any thickness. Further, non-uniformities in concentration over the beam spot would have no effect, provided that the Zn environment is uniform.

IV. What to do about it

What can be done in the case of a concentrated sample? Some possibilities include:

- (1) Look for a particle in fluorescence mode which is small enough to be in the thin-sample limit. In a fluorescence map, you do not see the thickness directly, but only the width across the beam, so one may have to make assumptions about the shape of the particle in order to decide if it is small enough. With a micron-size beam, one would look for a resolution-limited spot on a fluorescence map.
- (2) Use electron-yield detection. In the hard X-ray range, the escape depth for electrons is much less than the absorption depth for X-rays, so there is little thickness effect because the electrons are effectively probing a part of the sample which is thin compared with the absorption depth. This method can be useful for standards and other highly-concentrated samples. However, if the sample is illuminated at grazing incidence, there can be an over-absorption effect as well because then the X-rays do not penetrate much farther than where the electrons come from. Thus, the amount of material probed depends on the X-ray absorption one wants to measure, just as with fluorescence. Also, fluorescence photons are detected by photoemission, yielding a contribution to the signal which is proportional to the fluorescence and hence affected by over-absorption (Schroeder et al. 1997). Thus, it is commonly observed that the EXAFS amplitudes seen in electron yield are slightly smaller than those measured by transmission.
- (3) Use grazing-exit detection. This method, as described above, requires a very flat sample and so is not suited to most natural materials.
- (4) Measure a thin section in transmission. This works reasonably well for samples in which one wants to look at the matrix, and the matrix is uniform on the scale of the beam size.
- (5) If the effect is not too severe and the various quantities are known, then the spectrum may be corrected so the distortions are removed (Pfalzer et al. 1999). However, this correction occurs at the cost of some signal-to-noise. Also, this procedure requires knowing the various quantities in the above equations. For standards and identified

primary minerals, the composition is known, so that the resonant fraction is known. Then, if there is transmission data, the edge jump may be measured. This level of knowledge occurs less often than one might like. If transmission data are available, it is sometimes possible to do an approximate correction based on the amplitude of the first part of the transmission EXAFS signal, which is used to correct the fluorescence spectrum. This procedure is used when the transmission signal is not good enough to use on its own. Unfortunately, hole effects can cause errors in this type of correction.

The above discussion brings us to another set of problems typically encountered in environmental science, mainly those encountered when trying to look at small particles. One of these has already been described, that is beam stability. This problem can only be addressed by proper engineering of the beamline. If the particle is concentrated and has a thickness comparable to the absorption depth, then thickness effect in fluorescence mode, and hole effect in transmission mode, will cause problems. The hole effect arises because the particle will never be uniform in thickness across the beam. As a limiting case, if the beam spills over the particle, then there will be a hole effect just as described as our first example of thickness effects. The measured transmission edge jump will be smaller than the real edge jump in the thick part of the particle, so it becomes impossible to estimate the real thickness, which is what is needed for correction. The particle will appear to be thinner than it really is, so there will be saturation effects but no warning that these may occur. The beam from a typical Kirkpatrick-Baez setup has a halo which is several times larger than the nominal (FWHM) beam diameter and which carries a large fraction of the energy in the beam. Therefore, even if the FWHM of the beam is less than the particle size, a good part of the beam will pass by the particle. We see that saturation effects may be important and uncorrectable when looking at particles. Some of the measures described above may help avoid these problems. Fortunately, such concentrated particles in soils are often composed of single, simple minerals whose spectra may be recognized, even in distorted form, by comparison with standards

If the sample is thick, the particle may be buried in a matrix, which contains the same element one wants to probe in the particle (Roberts et al. 2002). In that case, the spectrum will be a weighted sum of those from the matrix and the particle. In this case, making the sample thin might help by reducing the ratio of the matrix contribution to that of the particle. Another possibility is to record μ EXAFS spectra in different spots in order to vary the proportion of each species, and to analyze the set of spectra by principal components analysis.

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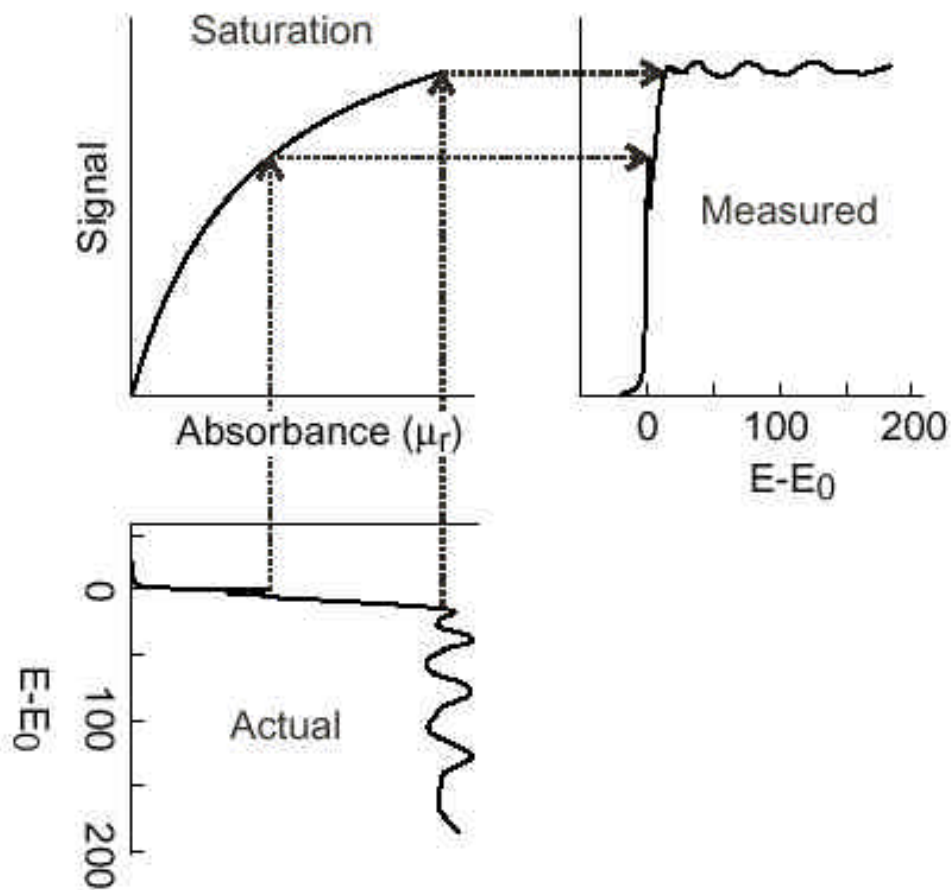


Figure 1. Illustration of the ‘thickness effect’ in X-ray absorption spectroscopy. The actual absorbance vs. energy is shown at the bottom. Due to these thickness effects, the measured signal (right) is related to the actual absorbance via a sub-linear transfer curve (Saturation). Two specific points along the curves are picked out with dotted lines and arrows, showing how the pre-edge features are raised relative to the edge. Notice also that the EXAFS amplitude in the Measured curve is reduced compared to its actual value. The Actual curve is transmission data for a Ti foil and the Measured curve is the fluorescence data for the same sample (6 μm , 45° incidence and exit angle). The Saturation curve comes from a fit between the Actual and Measured curves.

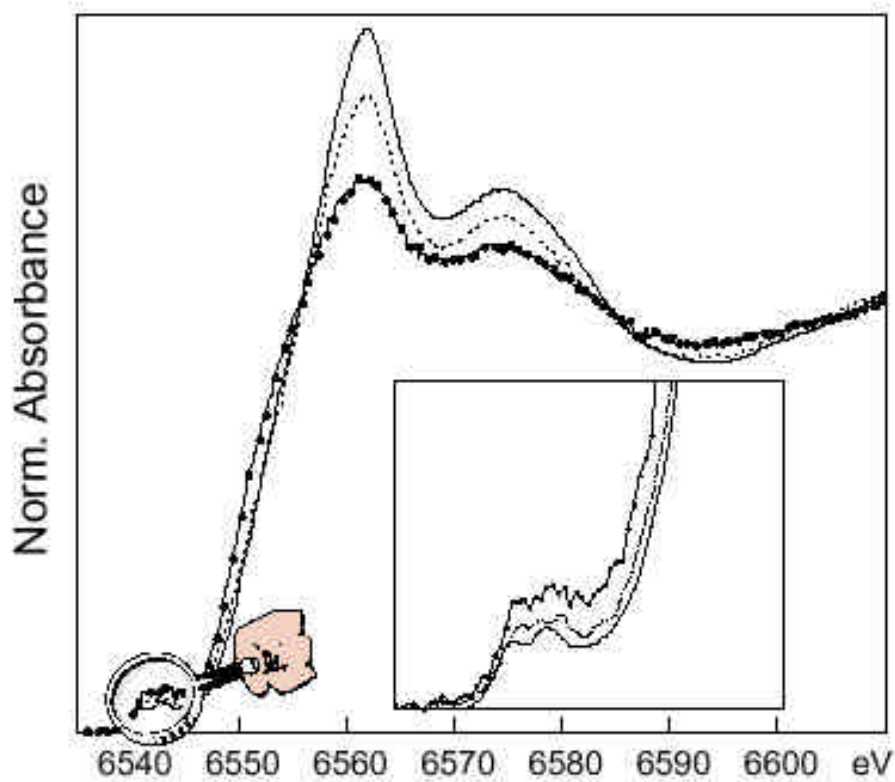


Figure 2. Micro-XANES data of a ferromanganese crust (Hlawatsch et al. 2001) recorded in transmission mode in spots of the same composition but differing thickness. The pre-edge is enhanced and the EXAFS amplitude is reduced by thickness effect

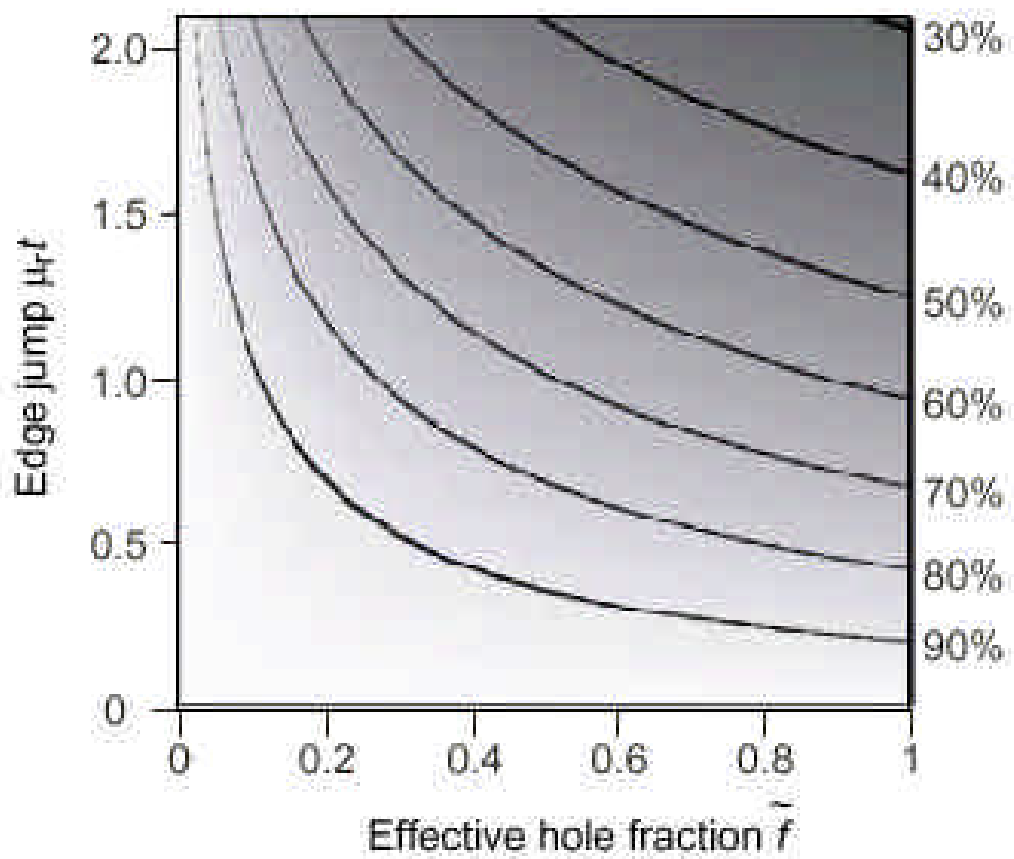


Figure 3. Reduction of the EXAFS amplitude as a function of the sample's hole fraction and the absorption edge jump. Percentages correspond to the ratio of the amplitude of the measured EXAFS wiggle to the actual signal.

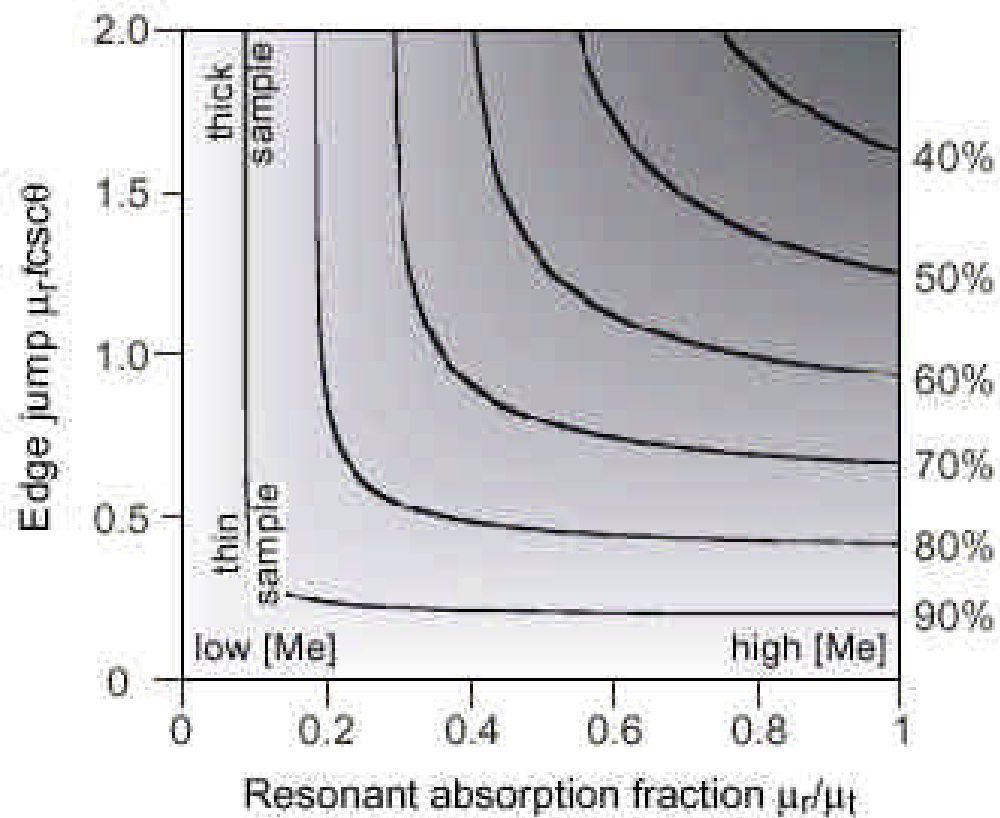


Figure 4. Reduction of the EXAFS amplitude as a function of the resonant absorption fraction (proportional to the metal concentration) and the absorption edge jump (proportional to the sample thickness and metal concentration). Percentages correspond to the ratio of the amplitude of the measured EXAFS wiggle to the actual signal.