Real-Life XAS Sample Preparation or What Happens If You Break the Rules

- Transmission
  - The Ideal Sample
  - Preparation Methods
  - Real Samples
- Fluorescence
- Gases and Solutions

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Matt says:

"For transmission measurements, we need a sample that is of uniform and appropriate sample thickness of ~2 absorption lengths. It should be free from pinholes. If a powder, the grains should be very fine-grained (absorption length) and uniform."

Transmission

$$I_t = I_o e^{-\rho \mu_m x}$$

μ_m	mass absorption coefficient
μ	absorption
ρ	density
x	sample thickness
I_o	incident x-ray intensity
I_t	transmitted x-ray intensity

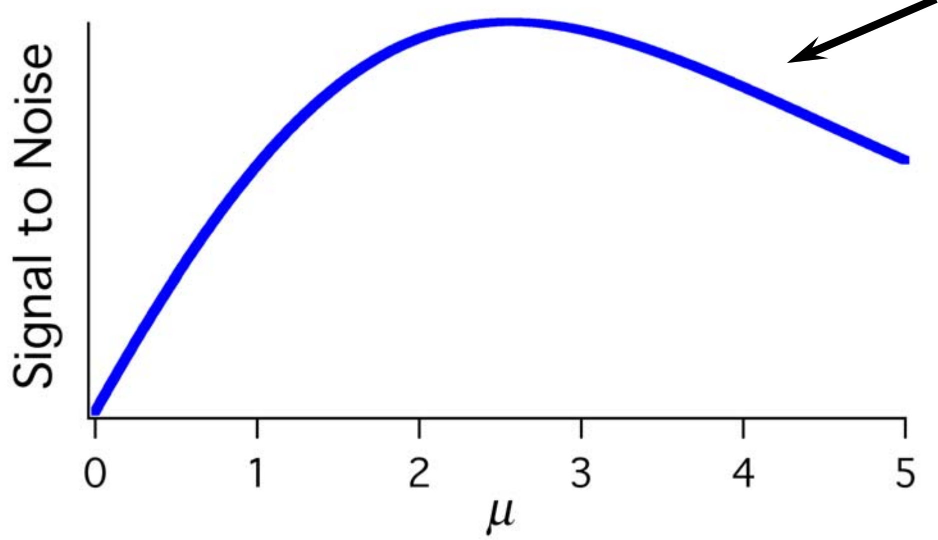
$$\mu \equiv \rho \mu_m x = \ln\left(\frac{I_o}{I_t}\right)$$

Signal to Noise

Too thick: Most photons don't get through

Too thin: Most photons don't interact

Ideal: $\mu \sim 2\text{-}3$



Leakage is a problem at high μ!

Signal to noise:

P. A. Lee, P. H. Citrin, P. Eisenberg, and B. M. Kincaid, *Rev. Mod. Phys*. **53**, 769 (1981).

Leakage:

E. A. Stern and K. Kim, *Phys. Rev. B* **23**, 3781 (1981).

Homogeneity

$$\ln\left(\frac{I_{o1}}{I_{t1}}+\frac{I_{o2}}{I_{t2}}\right)\neq\ln\left(\frac{I_{o1}}{I_{t1}}\right)+\ln\left(\frac{I_{o2}}{I_{t2}}\right)\Rightarrow$$

$$\mu_{combined}\neq\mu_1+\mu_2$$

Use as homogenous a sample as possible!

Calculating Ideal Mass

Suppose we assume we want a sample with 2 absorption length thickness:

μ_m	mass absorption coefficient
ρ	density
x	sample thickness
m	mass of sample
V	sample volume
A	sample area

$$2 = \mu_m \rho x = \mu_m \frac{m}{V} x = \mu_m \frac{m}{A} \Rightarrow$$

$$\boxed{m = \frac{2A}{\mu_m}}$$

μ_{m} values are available at
http://www-cxro.lbl.gov/optical_constants/pert_form.html

Example: $ZnFe_2O_4$

First, decide which edge is *most* important to you: let's choose Fe *K* edge.

Next, find μ_m for each element about 50 eV above Fe *K* edge (7112 eV + 50 eV = 7162 eV).

Zn: 78 cm^2/g Fe: 402 cm^2/g O: 16 cm^2/g

% by mass: Zn: 27% Fe: 46% O: 27%

Overall: $\mu_m = 0.27(78) + 0.46(402) + 0.27(16)\ cm^2/g = 210\ cm^2/g$

Suppose you are using a sample 1.5 cm x 1 cm, so that A = 1.5 cm^2.

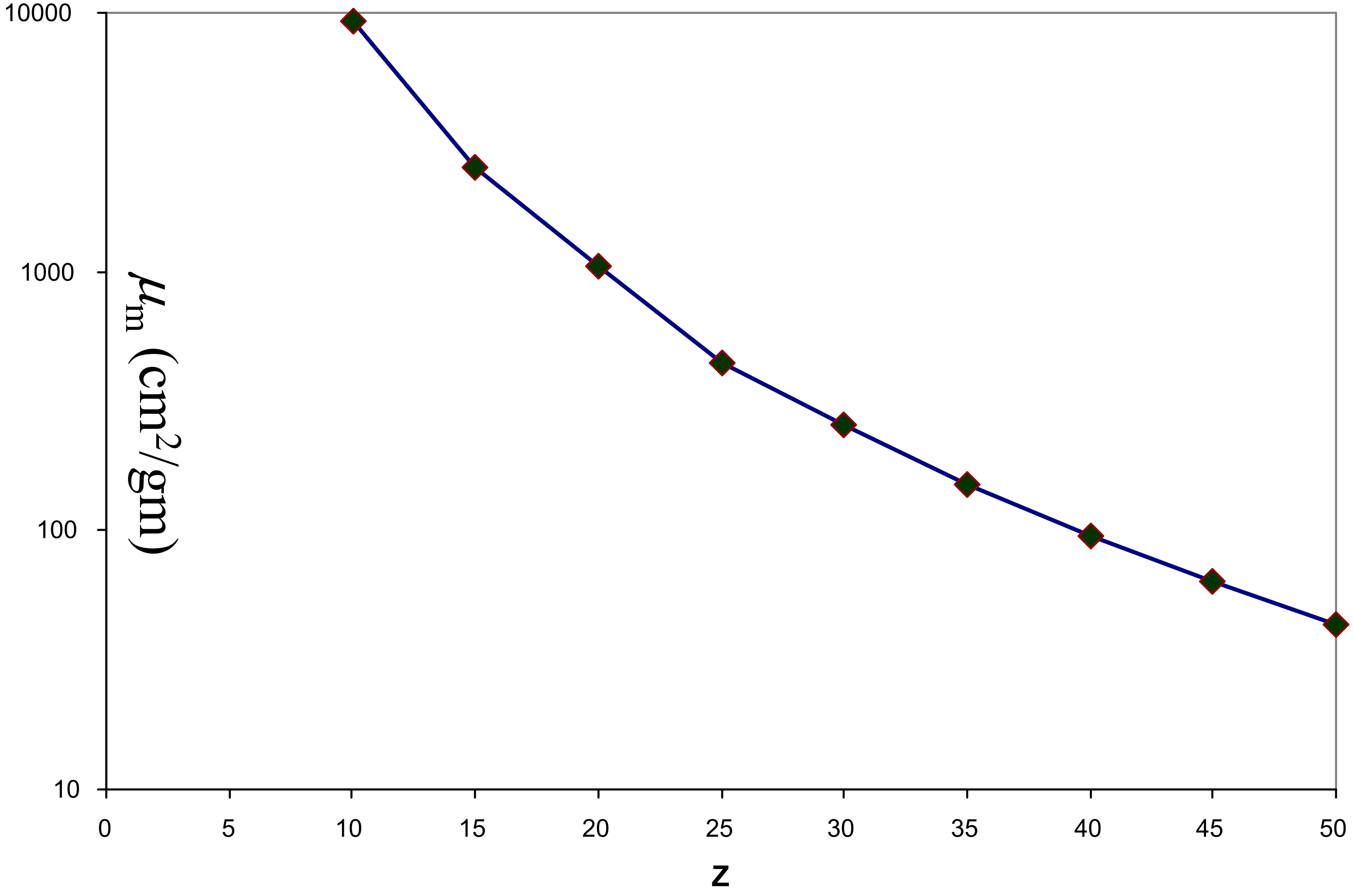
Then $m = 2A/\ \mu_m = 2(1.5)/210\ g = 0.014\ g = \boxed{14\ mg}$.

(At Zn *K* edge, a similar calculation gives 10 mg.)

Absorption Coefficient Trends

- The same element will absorb less at higher energies (e. g. tin will absorb more above its *L* edges than above its *K* edge)
- Elements with higher *Z* will absorb more at the same energy (e. g. tin will absorb more at 9000 eV than zinc)
- Elements with higher Z have their *K* edges at higher energy (e. g. the *K* edge of tin is at higher energy than the *K* edge of zinc)
- So which absorbs more: zinc 50 eV above its *K* edge, or tin 50 eV above its *K* edge?

Absorption Coefficient Trends



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Preparation Methods: Thin Layers

1. Grind the sample to a very fine powder. Some people like to use a sieve to make sure only fine particles are present.
2. Cut strips of a thin adhesive tape to the desired size. Depending on the amount of sample you have and the width of the tape, 2.5 cm x 1 cm is often good. The tape can be Kapton (thin, good thermal properties), Teflon, Mylar, or Scotch. Just make sure the tape you have does not contain any elements of interest to you and is fairly thin (i. e. does not absorb x-rays well).
3. Spread as thin and even a layer on the adhesive side of the tape as is practical. Non-metallic tools (rubber, plastic…) often work better for spreading.
4. Record the mass of the layer by measuring the mass of the tape before and after sample addition.
5. Repeat until the total mass is approximately the desired quantity. Hopefully this will require 3-20 layers of tape. Too few layers risk non-uniformity; too many layers will absorb too many of the x-rays.
6. Stack the tapes, bind them together, and place in a frame.

Preparation Methods: Dilution

1. Grind the sample to a very fine powder. Some people like to use a sieve to make sure only fine particles are present.
2. Mix the desired quantity well with a low-Z material. Typically, carbon black or boron trinitride are used. Make sure the material is not contaminated with an element you are trying to measure! This can be a particular problem with iron in carbon black.
3. Pour the mixture into a frame, using Kapton, Teflon, Mylar, or Scotch tape for the windows.

Absorption by Tapes, Windows

Absorption coefficients as a function of energy for many common materials, including teflon, mylar, glass, and water, can be found at:

http://physics.nist.gov/PhysRefData/XrayMassCoef/tab4.html

You'll find, for example, that for elements heavier than titanium, air-sensitive samples can safely be enclosed in nested and heat-sealed polyethylene (Ziploc™) bags.

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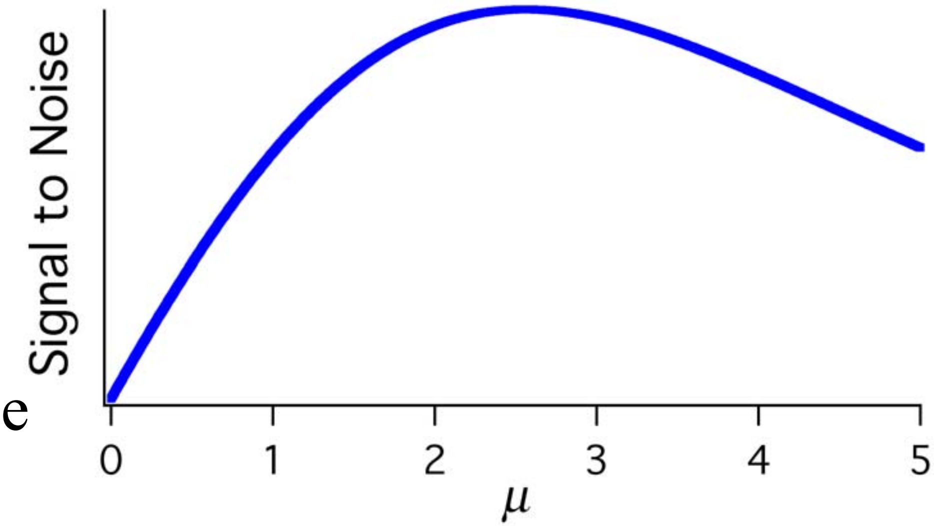
Real Samples: Thin

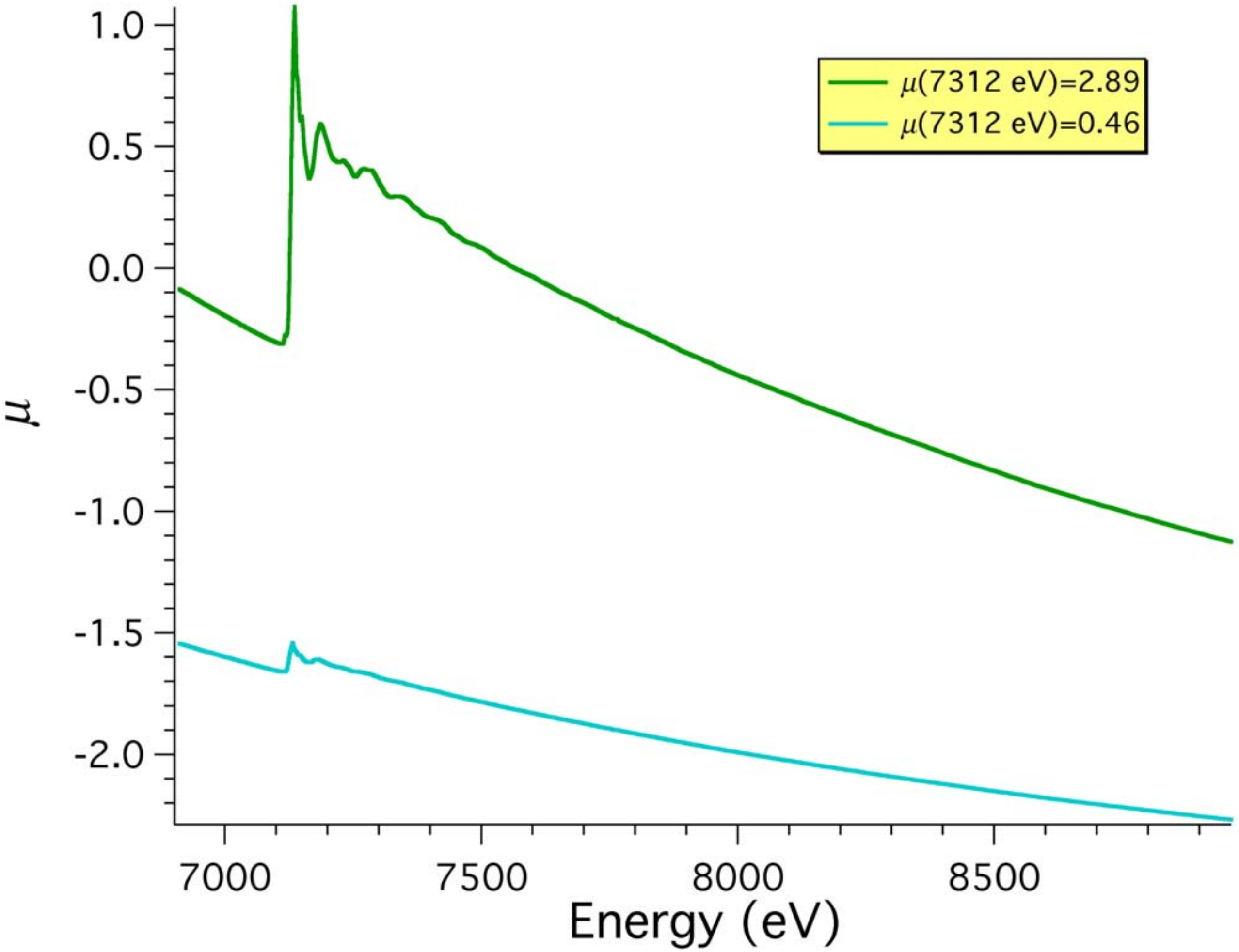
Low μ can be compensated for by

- High flux
- Long integration time
- Multiple scans
- Low expectations

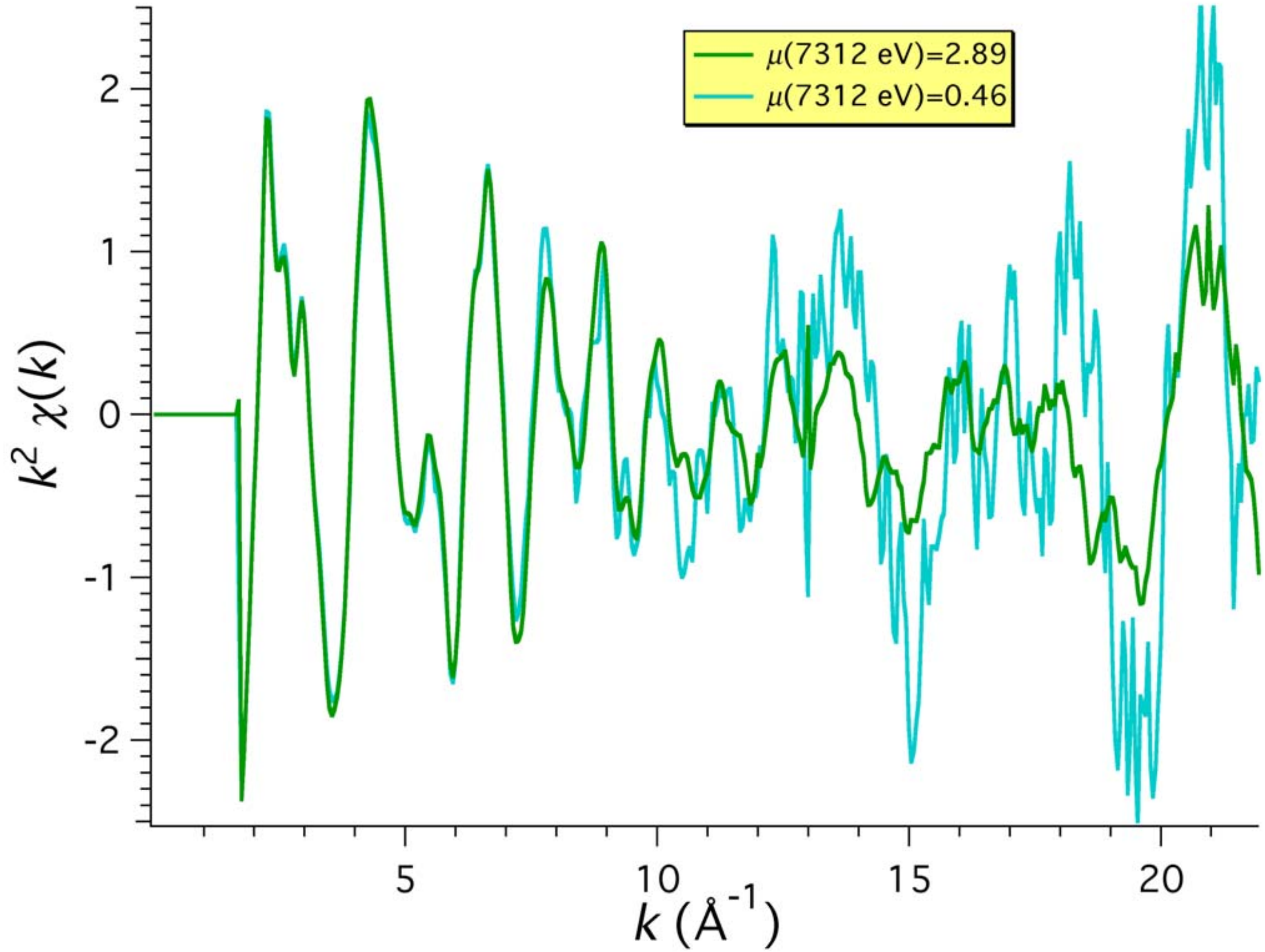
When the edge element is a large fraction of the sample, μ's as low as 0.1 do not generally require special measures



Real Samples: Thin



Real Samples: Thin



Amplitude and Phase Variables

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2 R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

Phase variables: R_j

Some physical quantities related to phase variables:

Phase identification in single-phase samples, lattice parameters, bond lengths

Amplitude variables: N_j, σ^2_j

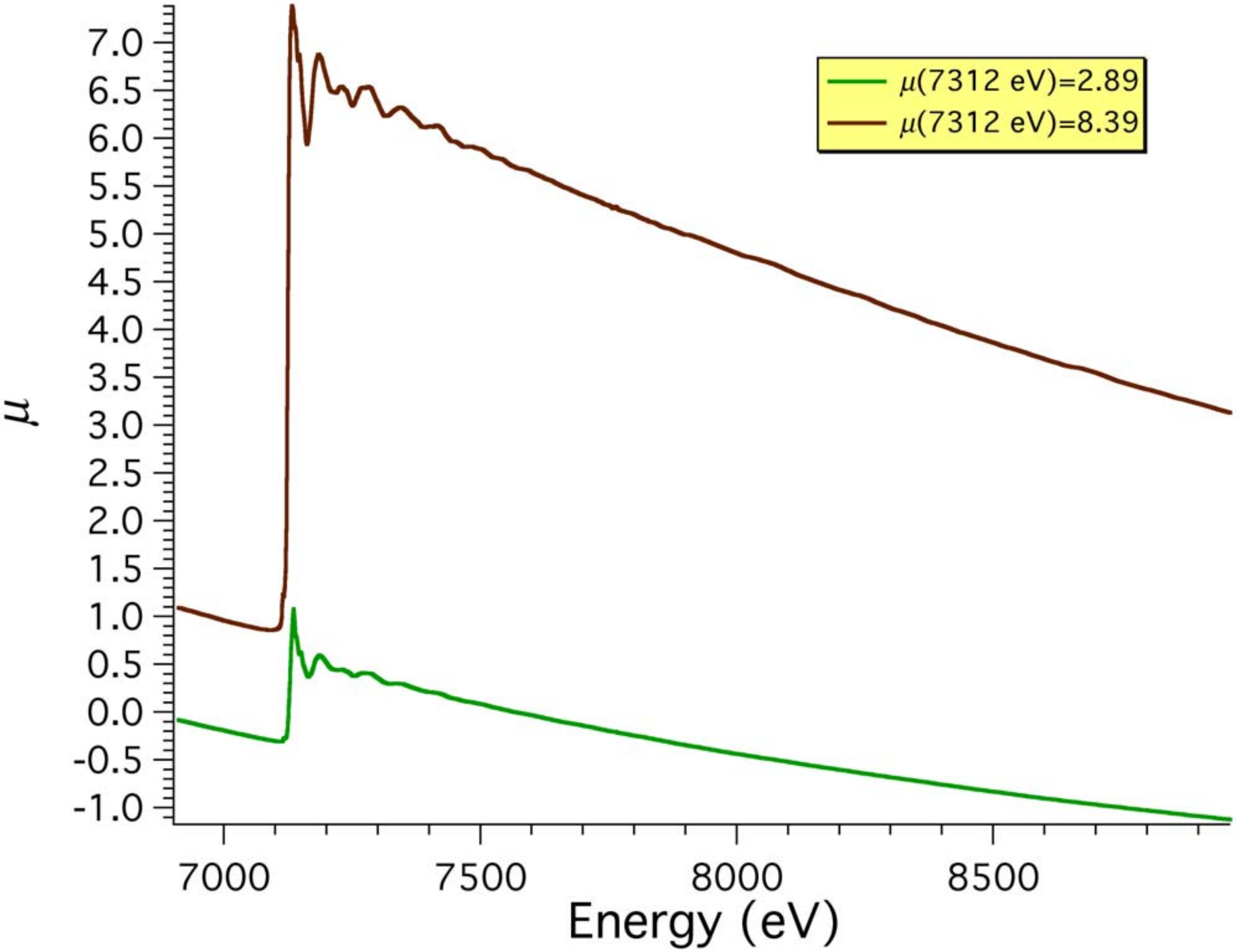
Some physical quantities related to amplitude variables:

Coordination numbers, fractional phase composition, static and thermal disorder

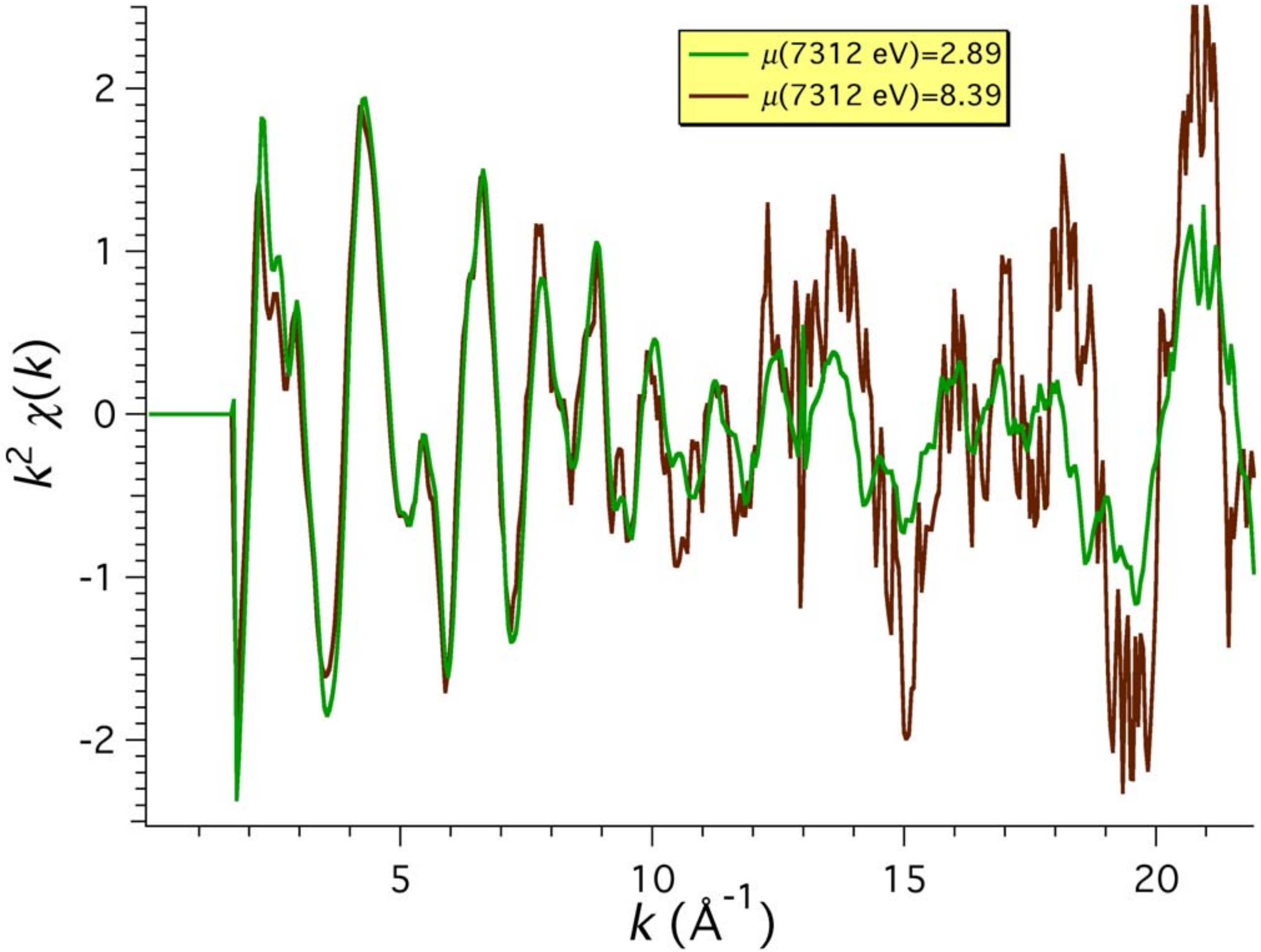
Real Samples: Thick

- Above μ of 4 or so “leakage” can be a serious problem. This can be caused by thin spots in the sample, harmonics in the beam, resolution limits of the monochromator, or x-rays scattering in the hutch.
- Expect serious errors in amplitude variables, although phase variables may be OK
- Consider using fluorescence if phase variables are desired

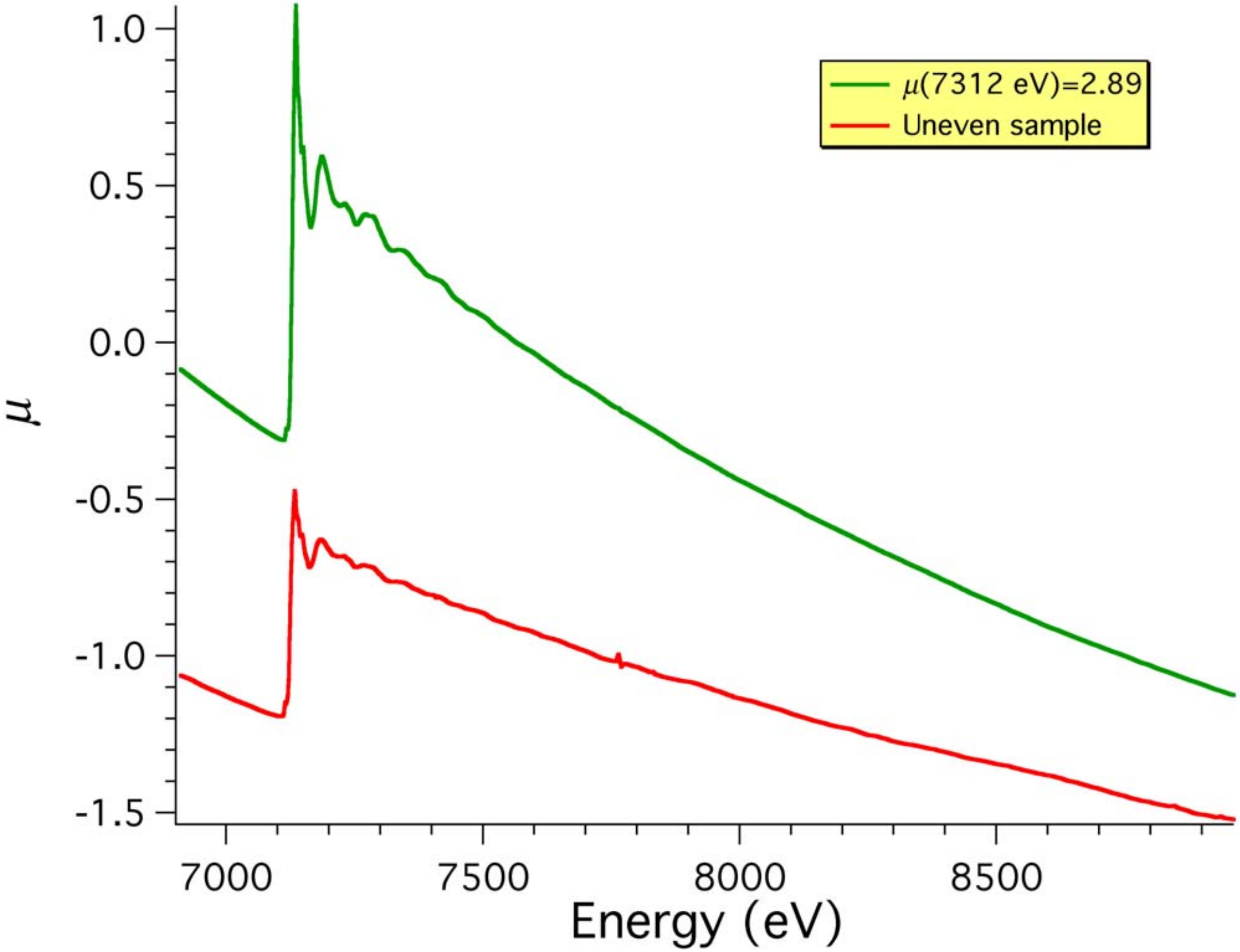
Real Samples: Thick



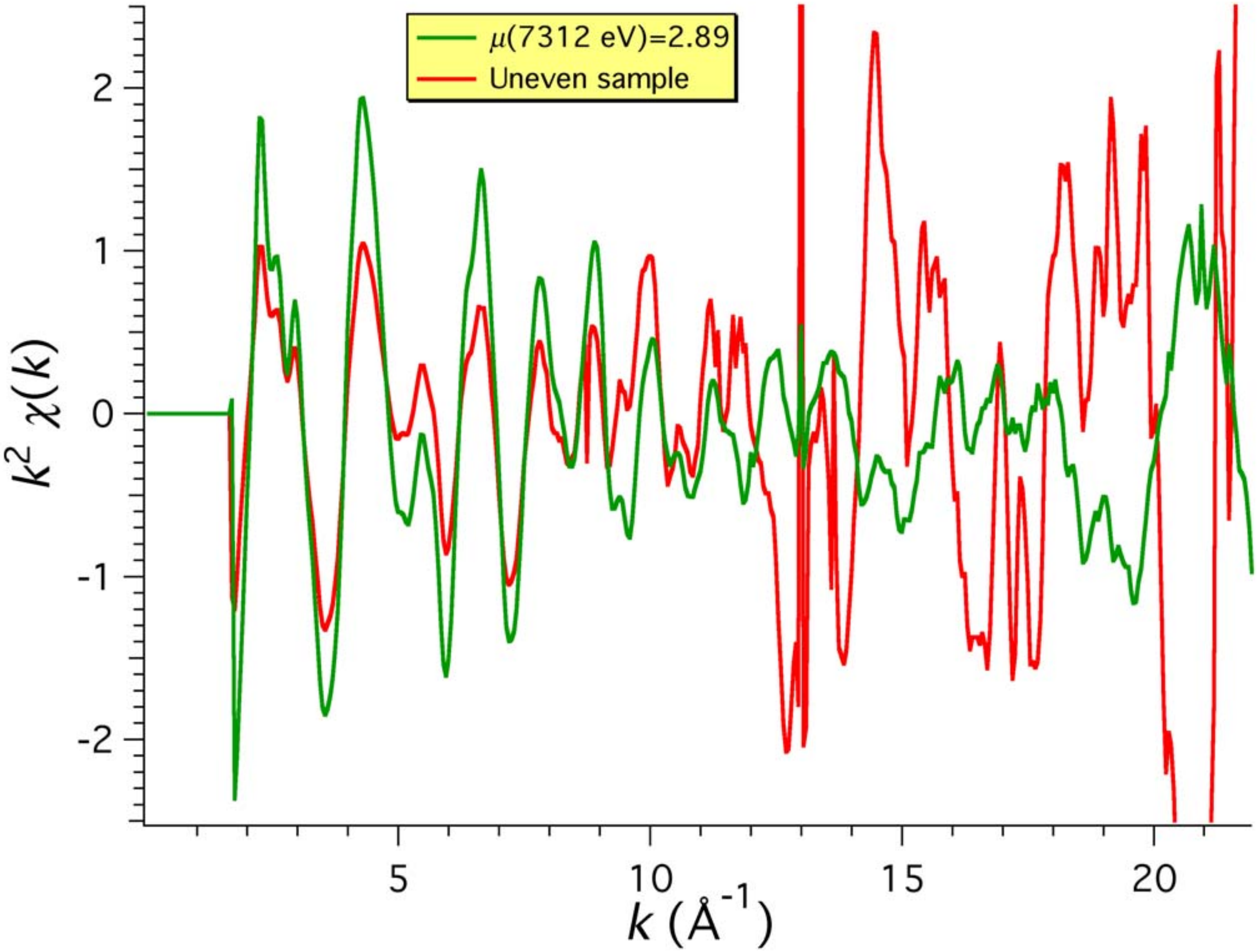
Real Samples: Thick



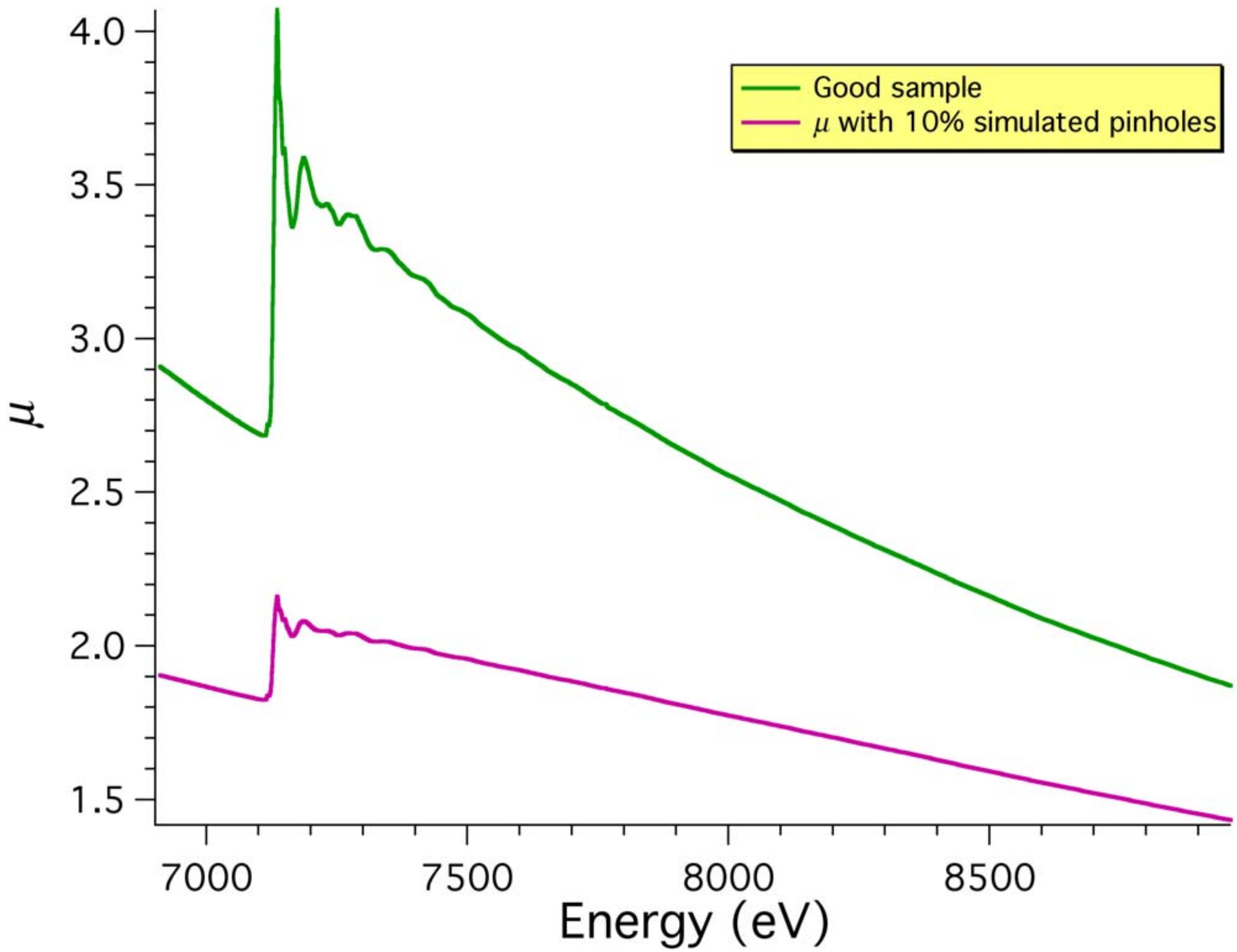
Real Samples: Uneven



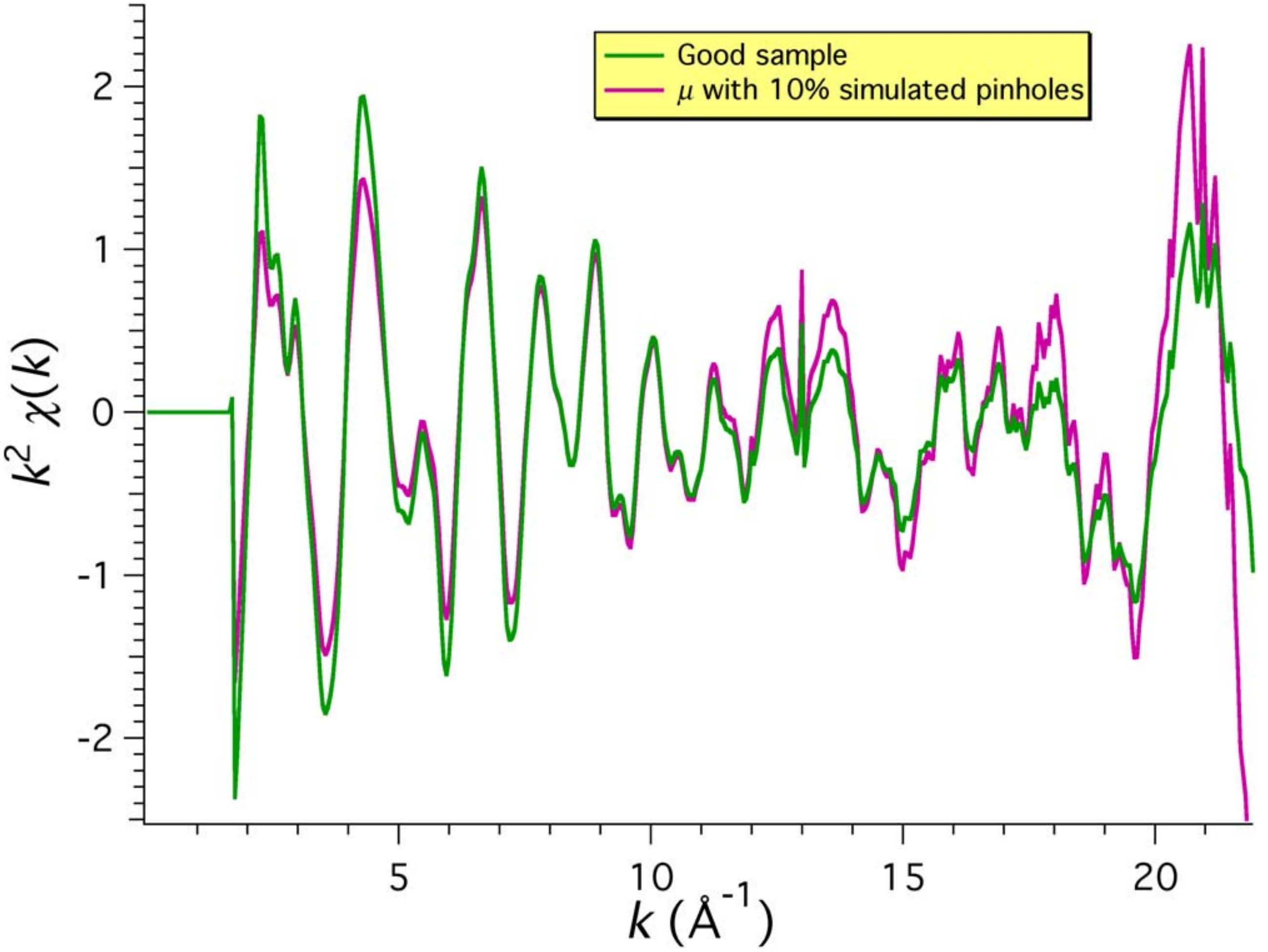
Real Samples: Uneven



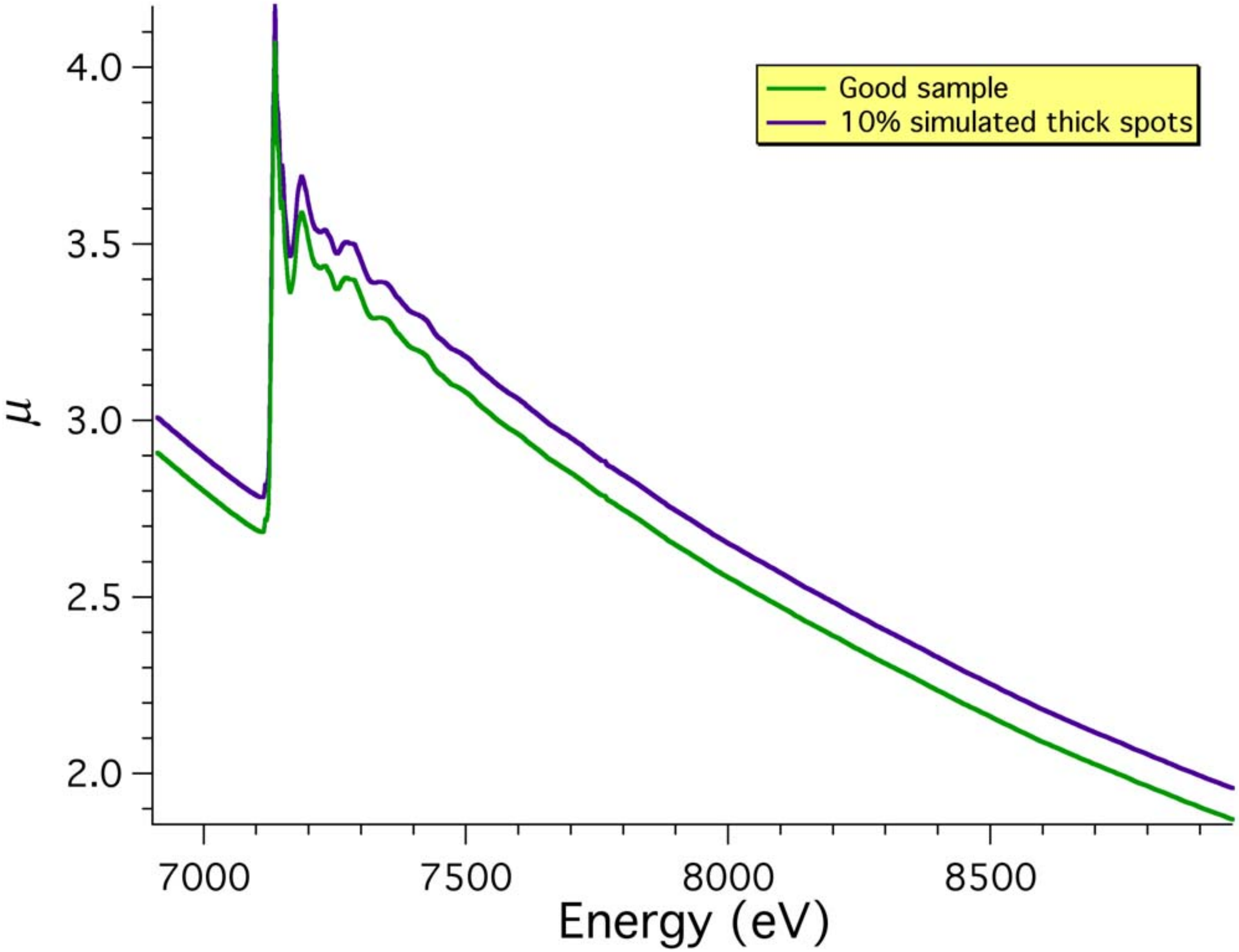
Is it pinholes?



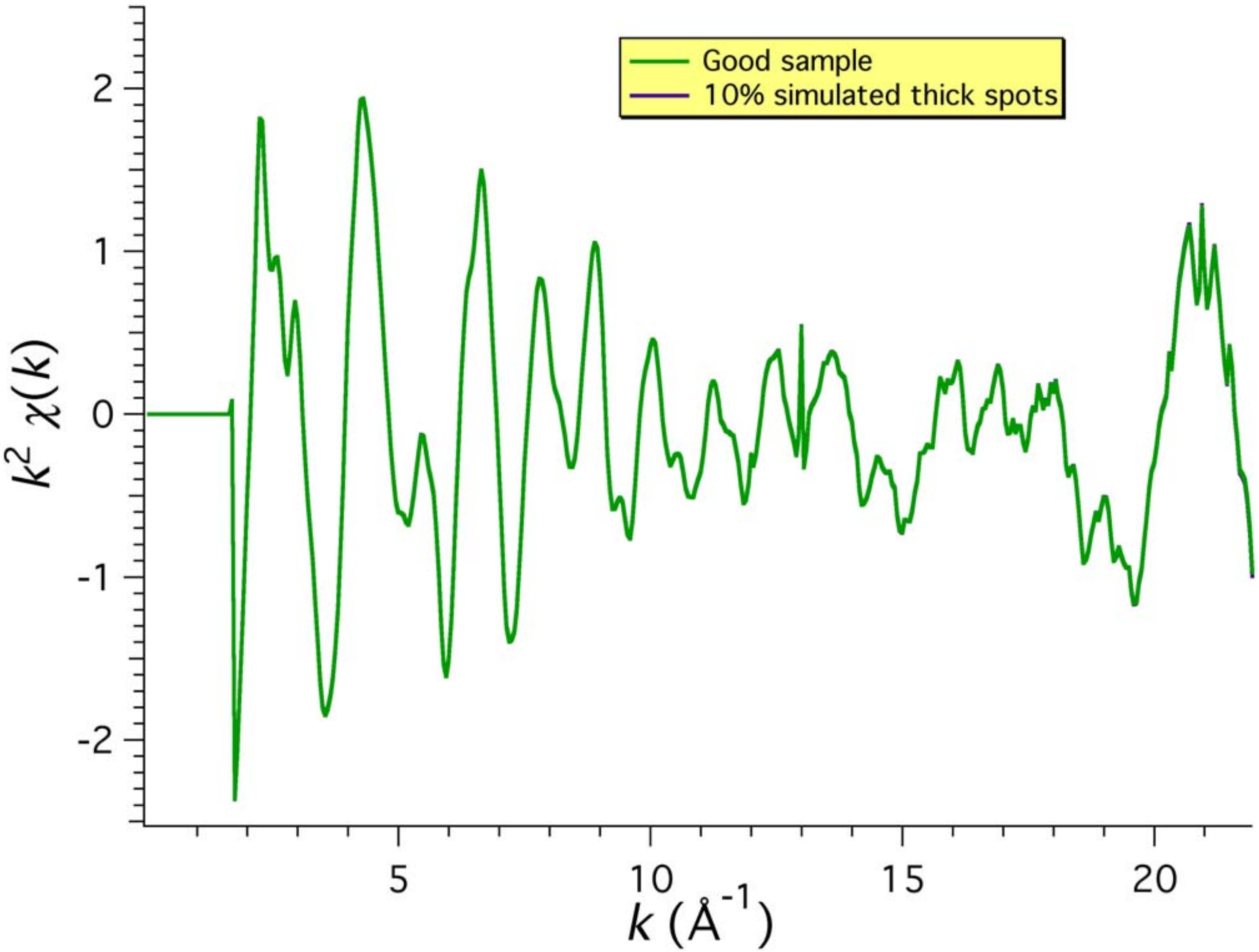
Is it pinholes?



Or is it thick spots?



Or is it thick spots?

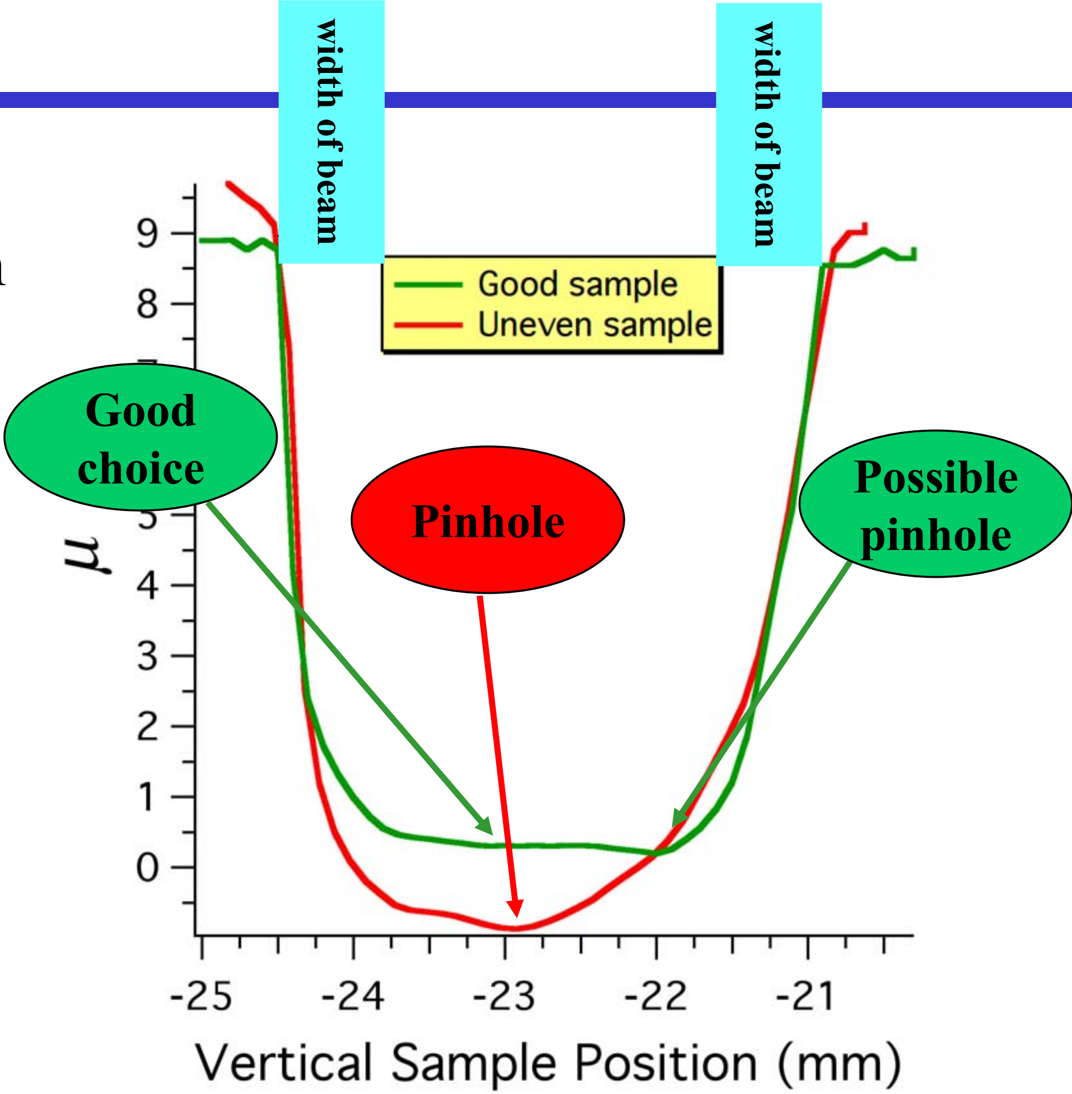


Real Samples Summary

- In general, the quality of samples may be ranked as follows:
  - Ideal > uneven due to thick spots > thin and even > thick and even > uneven due to pinholes
  - Therefore avoid pinholes at all costs! Somewhat thick samples, or samples with occasional thick grains, are OK. Thin, even samples are OK, but often hard to prepare. Very thick samples should be measured in fluorescence.
- Poor samples affect amplitude variables much more than phase variables

Checking for pinholes

Scan absorption as a function of sample position (both horizontal and vertical). If you'd really like to be sure, narrow the exit slits for this measurement.



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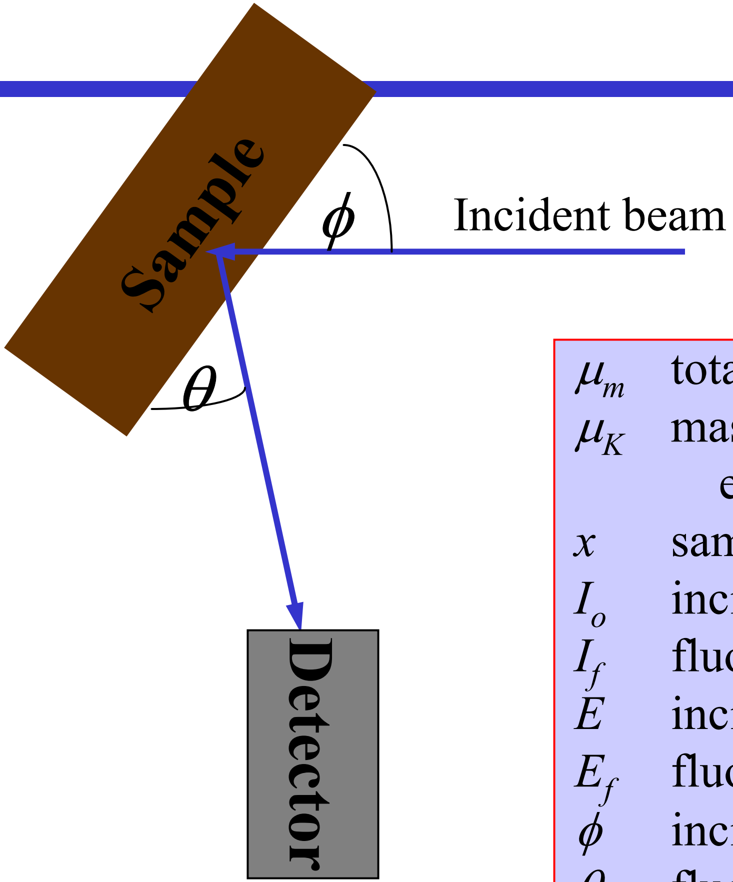
Fluorescence



P. Pfalzer, J.-P. Urbach, M. Klemm, S. Horn, M. L. denBoer, A. I. Frenkel, and J. P. Kirkland, *Phys. Rev. B* 60, 9335 (1999).

μ_m	total mass absorption coefficient
μ_K	mass absorption coefficient for edge element
x	sample thickness
I_o	incident x-ray intensity
I_f	fluorescent x-ray intensity
E	incident x-ray energy
E_f	fluorescent x-ray energy
ϕ	incident angle
θ	fluorescent angle

$$I_f \propto I_o \left(\frac{\mu_K(E)}{\mu_m(E) + \mu_m(E_f)^{\sin\phi / \sin\theta}} \right) \left\{ 1 - \exp\left[-\left(\frac{\mu_m(E)}{\sin\phi} + \frac{\mu_m(E_f)}{\sin\theta} \right) x \right] \right\}$$

Fluorescence: Thick Dilute

Fluorescence:

$$I_f \propto I_o \left(\frac{\mu_K(E)}{\mu_m(E) + \mu_m(E_f)^{\sin\phi}/_{\sin\theta}} \right) \left\{ 1 - \exp\left[-\left(\frac{\mu_m(E)}{\sin\phi} + \frac{\mu_m(E_f)}{\sin\theta} \right) x \right] \right\}$$

Thick sample:

$$I_f \sim I_o \left(\frac{\mu_K(E)}{\mu_m(E) + \mu_m(E_f)^{\sin\phi}/_{\sin\theta}} \right)$$

If the sample is also dilute, then the oscillatory part is almost all in the numerator, and the EXAFS oscillations are largely due to:

$$\Delta\left(\frac{I_f}{I_o} \right) \propto \Delta\left(\frac{\mu_K(E)}{\mu_m(E) + \mu_m(E_f)^{\sin\phi}/_{\sin\theta}} \right) \sim \Delta\mu_K(E)$$

Fluorescence: Thin

Fluorescence:

$$I_f \propto I_o \left(\frac{\mu_K(E)}{\mu_m(E) + \mu_m(E_f)^{\sin\phi}/_{\sin\theta}} \right) \left\{ 1 - \exp\left[-\left(\frac{\mu_m(E)}{\sin\phi} + \frac{\mu_m(E_f)}{\sin\theta} \right) x \right] \right\}$$

Thin sample:

$$I_f \sim I_o \left(\frac{\mu_K(E)}{\mu_m(E) + \mu_m(E_f)^{\sin\phi}/_{\sin\theta}} \right) \left(\frac{\mu_m(E)}{\sin\phi} + \frac{\mu_m(E_f)}{\sin\theta} \right) x$$

So again

$$\frac{I_f}{I_o} \propto \mu_K(E)$$

Fluorescence: Grazing Exit

Fluorescence:

$$I_f \propto I_o\left(\frac{\mu_K(E)}{\mu_m(E)+\mu_m(E_f)^{\sin\phi}/_{\sin\theta}}\right)\left\{1-\exp\left[-\left(\frac{\mu_m(E)}{\sin\phi}+\frac{\mu_m(E_f)}{\sin\theta}\right)x\right]\right\}$$

For small detection angle:

$$I_f \propto I_o\left(\frac{\mu_K(E)}{\mu_m(E_f)^{\sin\phi}/_{\sin\theta}}\right)\left\{1-\exp\left[-\left(\frac{\mu_m(E_f)}{\sin\theta}\right)x\right]\right\}$$

So once again

$$\frac{I_f}{I_o} \propto \mu_K(E)$$

Fluorescence Summary

- Easiest with:
  - Thick, dilute
  - Thin, concentrated
- Sample uniformity is not as important as for transmission

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Gases

- Ideal substances for transmission!
  - Very uniform
  - Long absorption lengths
- Beware of deposition on windows
- Consider safety issues well in advance! (Many hutches vent to office space…)

Solutions

- Short absorption length and need for windows with structural integrity may make transmission difficult.
- If gases are evolved, bubbles are a serious concern.
- If precipitates are formed, solution becomes inhomogeneous. Transmission XAS will primarily probe thinner spots; it will be the “last to know” about particles forming out of solution.
- Fluorescence and a deep sample chamber will largely solve both the bubble and inhomogeneity problems.
- In either case, precipitates may deposit on the window, which may or may not be a problem depending on the experiment.

Final Words

- Pinholes are the worst enemy of transmission measurements, followed by uniformly thick samples.
- Very dilute, very thick, or pinhole-ridden samples should be measure in fluorescence.
- Self-absorption is the enemy of fluorescence; try to make sample thick and dilute or thin and concentrated; if that’s not possible, measure at multiple angles if a correction is desired.
- Do not be afraid to try “bad” samples, but be prepared to estimate the degree and type of error. Estimations can be made by theory, simulation, or experiment.
- Phase variables are generally less affected by sample quality than amplitude variables.