Sample Preparation for EXAFS Spectroscopy

lecture notes for NSLS EXAFS course, September 23-25, 2002

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Types of samples examined by EXAFS and XANES

Source of sample:

- Materials - minerals, ceramics, polymers, glasses
- Synthetic molecules - coordination complexes, compounds of heavier main-group elements
- Biomolecules - metalloproteins, metal + nucleic acid complexes
- Heterogeneous systems - soils, catalysts, coatings, whole cells

State of interest:

- Gas or liquid state (rare)
- Solution
- Frozen solution
- Unoriented powder
- Suspension or emulsion
- Oriented crystal
- Surface

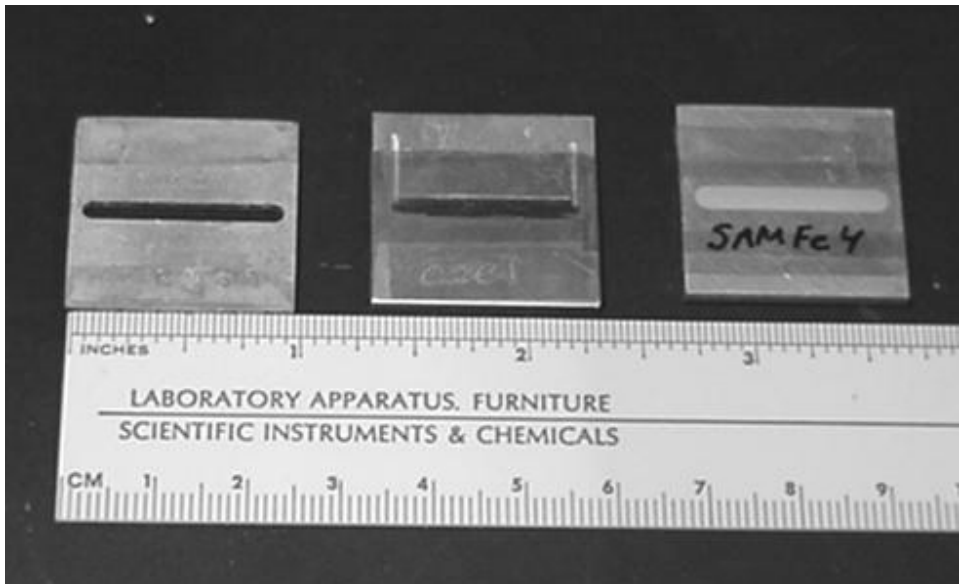
Very simple sample holder designs

Body

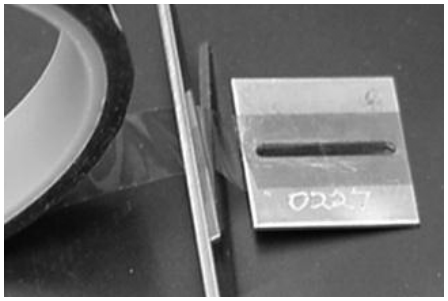
- Aluminum alloys
  - 6061 - Fe 7, Cu 4, Mn 1.5, Mg 12, Cr 3.5, Zn 2.5, Ti 1.5 ppt
  - 5052 - Fe 4, Cu 1, Mn 1, Mg 28, Cr 3.5, Zn 1 ppt
  - 2024 - Fe 5, Cu 44, Mn 8, Mg 15 ppt
- Copper
- Gold-plated copper
- Lucite, polypropylene, polycarbonate

Coverslips

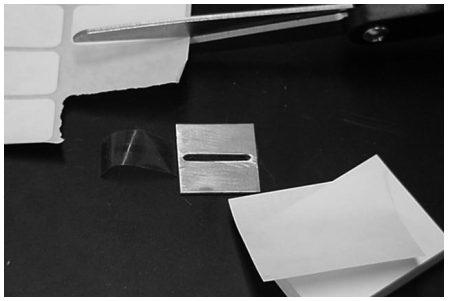
- Mylar, Kaptan or Polyethylene film (+ epoxy)
- “Scotch” tape
- Polyimide (Katpan) electrical tape
- nothing (frozen samples)



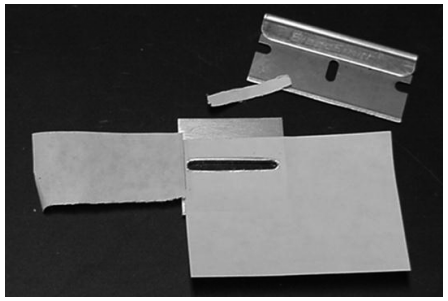
Preparation of solid powders (diluted with BN)



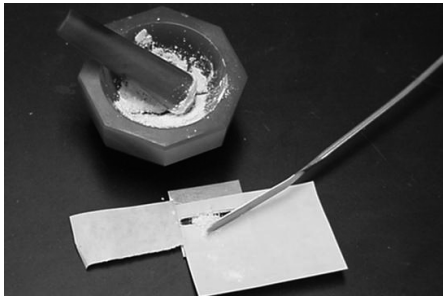
1) Wrap tape tightly; foldextra tape on itself to create a non-sticky tab.



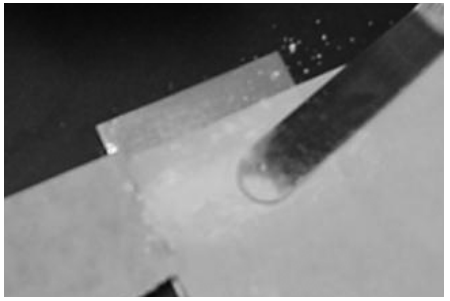
2) Peel tape from one side and protect it with waxed label-backing paper.



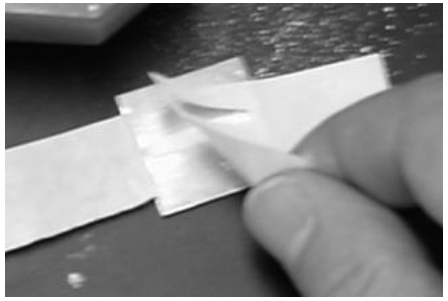
3) Cut “mask” from “Post-it” note. Mask hole slightly larger than slot.



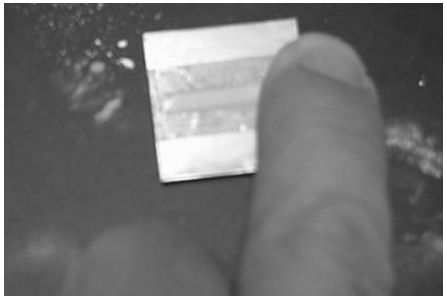
4) Grind sample with BN or other dilutant and transfer to slot.



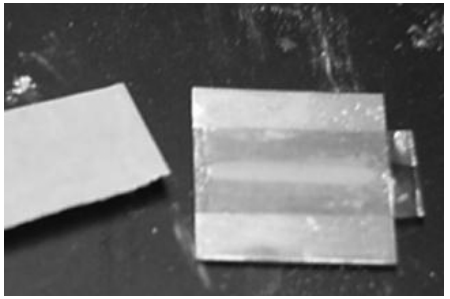
5) Pack sample into slot. Scrape excess from top of “Post-it” note.



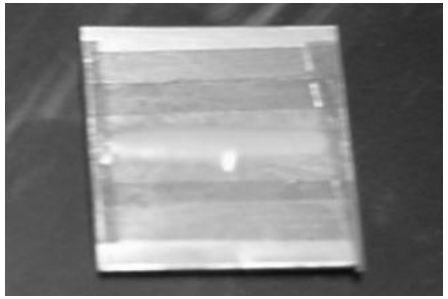
6) Carefully peel back “Post-it” note. Keep powder off surface of holder



7) Peel backing off tape and carefully flatten it over sample (from L to R).

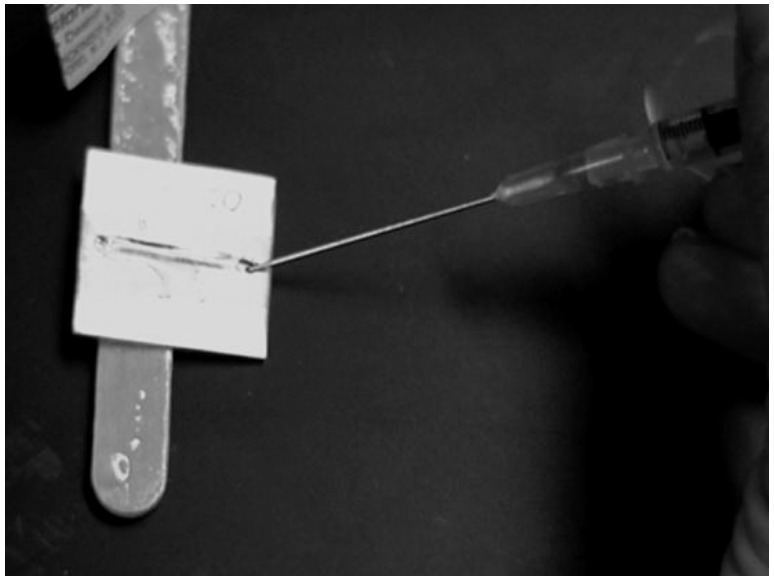


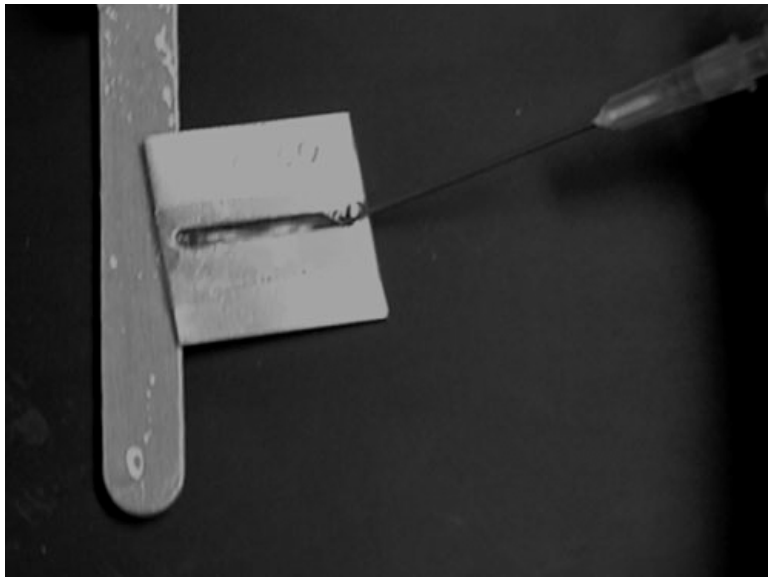
8) Use razor blade to trim excess tape (tab).



9) Dust off any adhering powder and tightly wrap edges with extra tape.

Frozen solution samples





For high-surface tension liquids (water):

Two (21 gauge) needle holes, opposite ends.

Holder at slight slope; load from lower end.

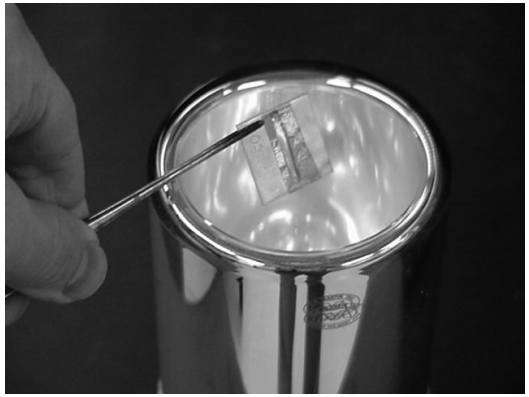
For low-surface tension liquids (organics):

Two (25 gauge) needle holes same end.

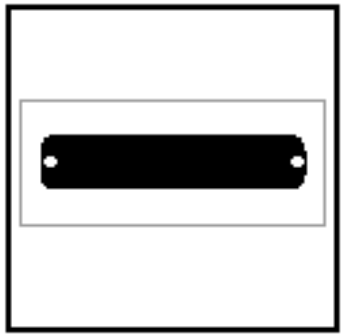
Load from high end (liquid will flow down).

Careful: don't puncture back cover-tape; avoid air bubbles.

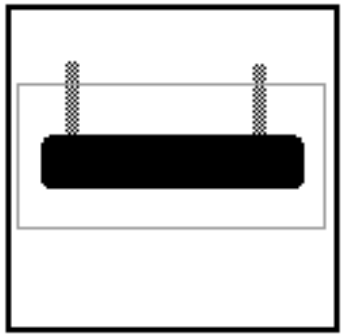
Freeze organics from one end to avoid large cracks (gaps).



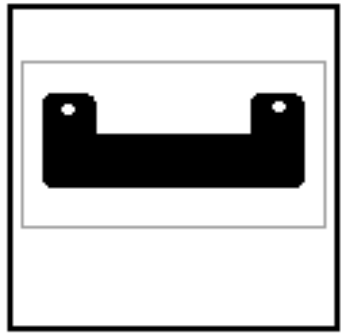
Variations on basic design



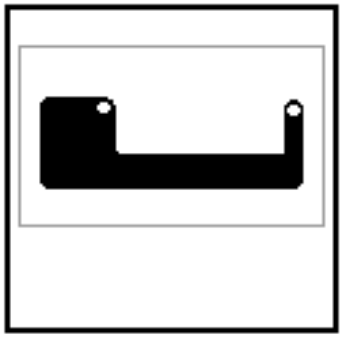
Needle-holes for introducing aqueous sample



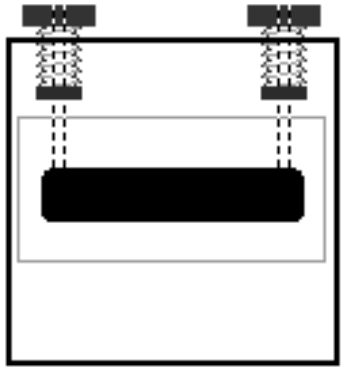
Beveled-slots for introducing liquid samples



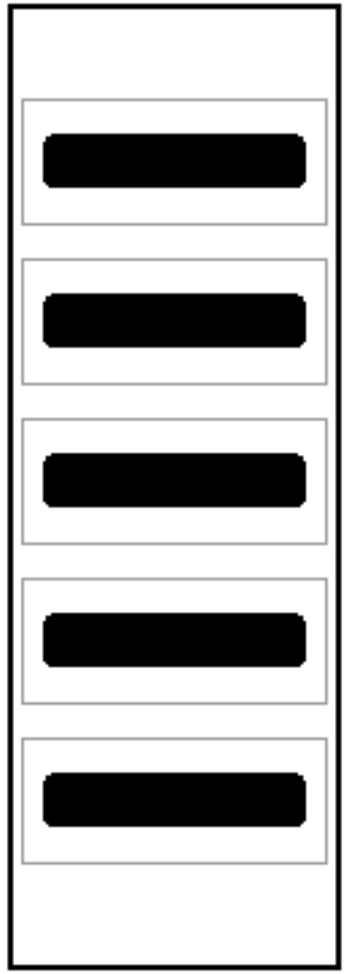
For studies of (non-frozen) liquid samples



Built-in mixing chamber for titration studies



Needle-ports with rubber gaskets for air-sensitive samples



Multiple sample holder for automated sample changes

How high and wide should the slot be?

The X-ray beam at most beamlines is ca. 2 × 30 mm (find out).

Beam height affects resolution

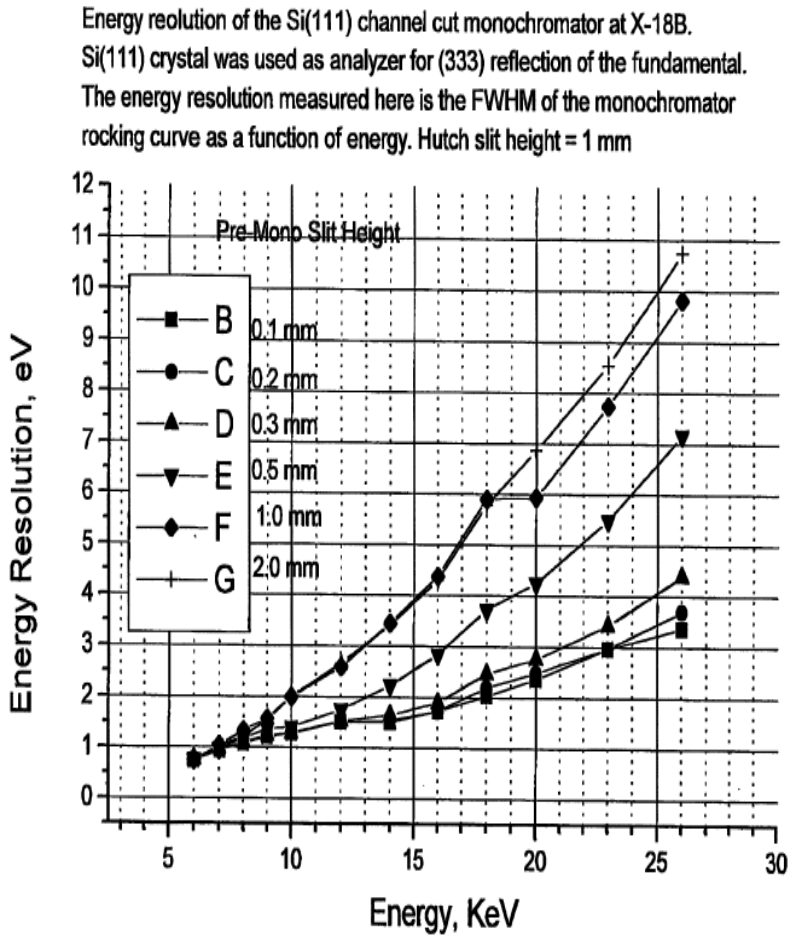
- At most beamlines, best resolution achieved with height ≤ 0.5 mm
- If focussing mirror in place, resolution may not depend on height.

Width consideration:

- Cryostat may limit width of sample holders.
- If fluorescence detection used, multiply beam width by 1.4 (sqrt(2)).
- Stray radiation (diffraction peaks, etc) more likely to cause problems when full width of beam is used.

Add 1 mm at each edge of slot for ease of alignment.

(I use 3 × 20 mm slots with 0.5 × 12 mm beam).

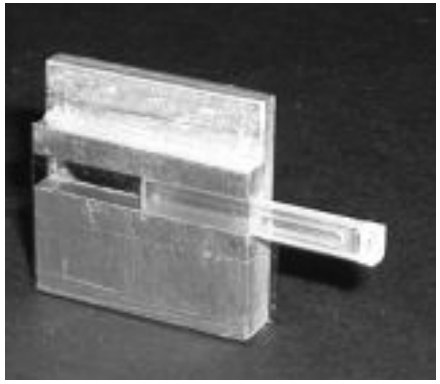


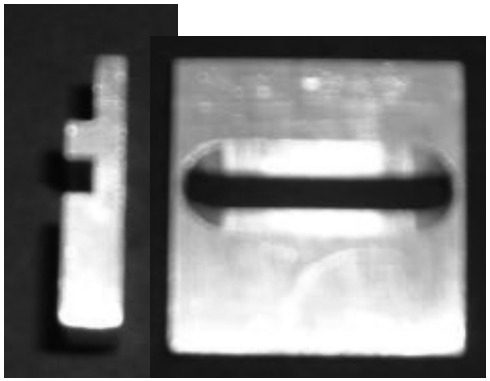
A more sophisticated sample holder

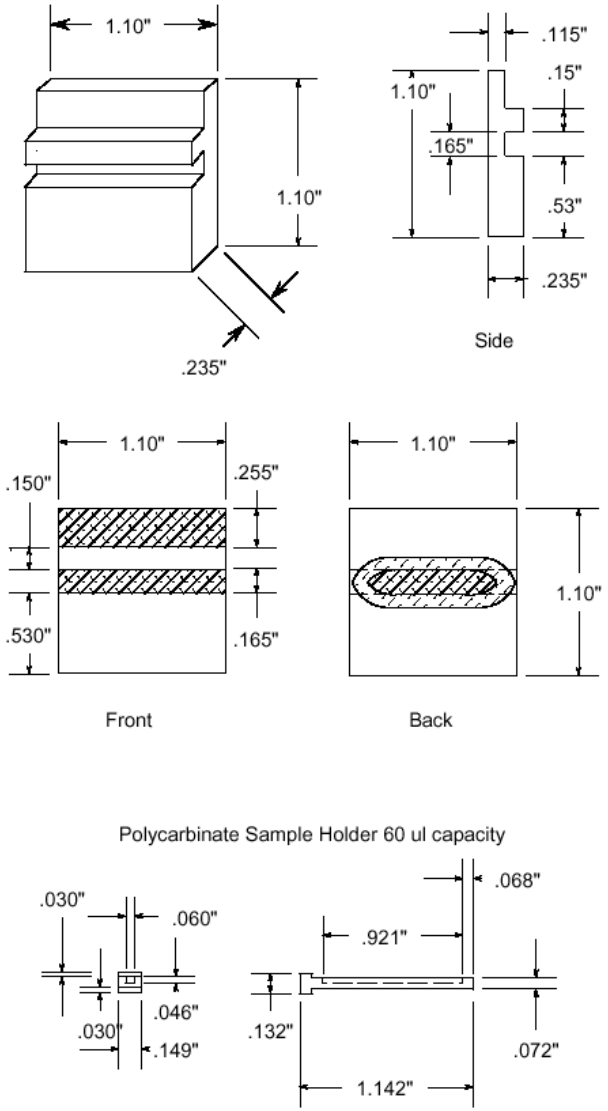
Polycarbonate inserts slide between the aluminum heat-sink and the Kaptan film epoxied to the side.

Inserts fit into EPR tubes!

Thanks to Prof. Mike Maroney, University of Massachusetts, Amherst, for these plans and pictures.







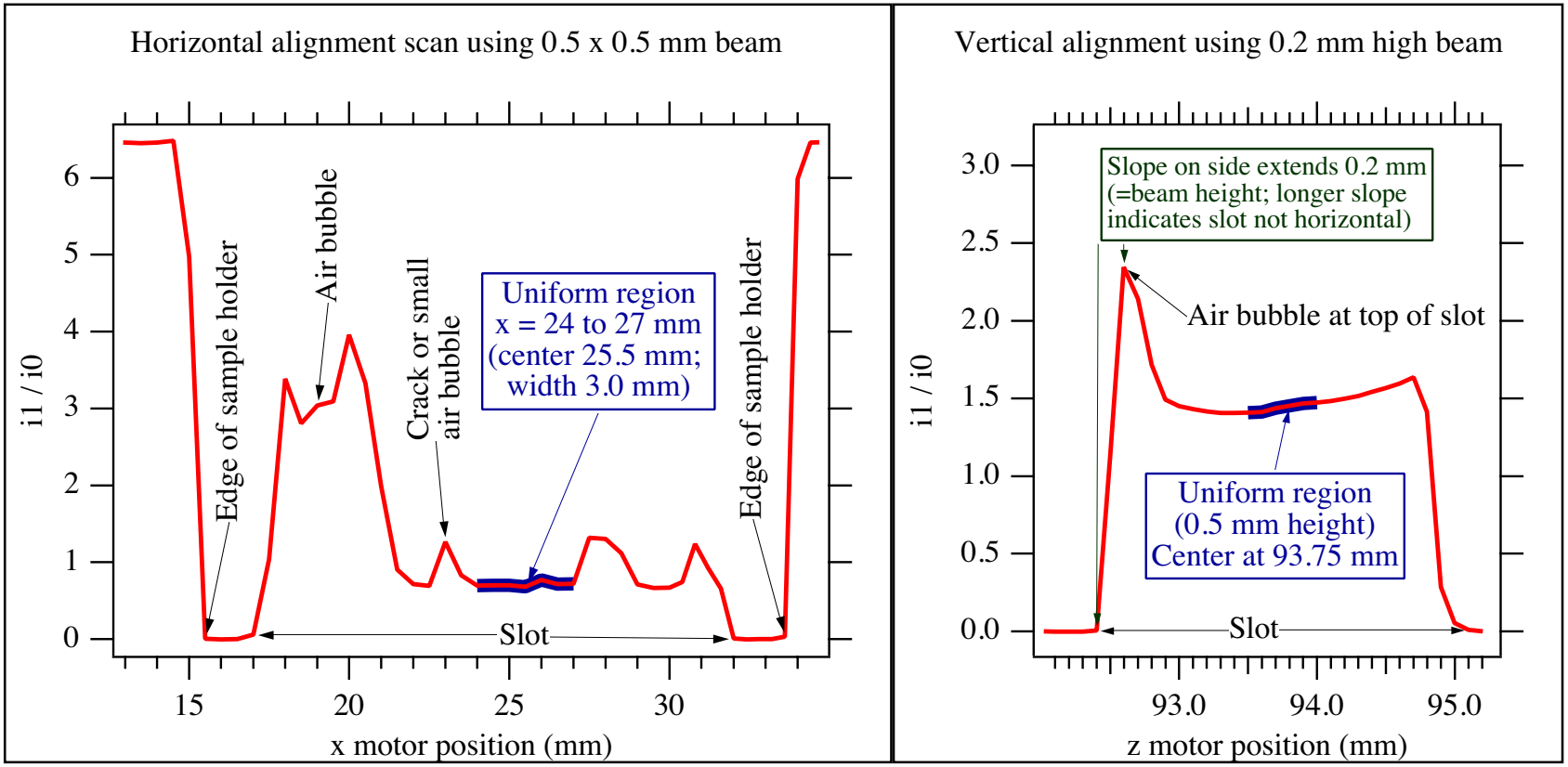
Using motorized X-Z stage for sample alignments

Computer-controlled motorized stages make sample alignment easy

X-ray beam is made thin in direction of scan to give sharp "image" of sample

Uniform thickness is important (±25 % - *vide infra*)

Record x-z stage positions and beam size in log file comments (not recorded automatically)



How thick should sample be?

Statistical considerations:

Assumption:

noise(photon counts) = (# photons)$^{1/2}$

$$\frac{N}{S} = \frac{1}{t I_0^{1/2}} \left(\frac{1}{f} + \frac{e^{\mu t}}{1-f} \right)^{1/2}$$

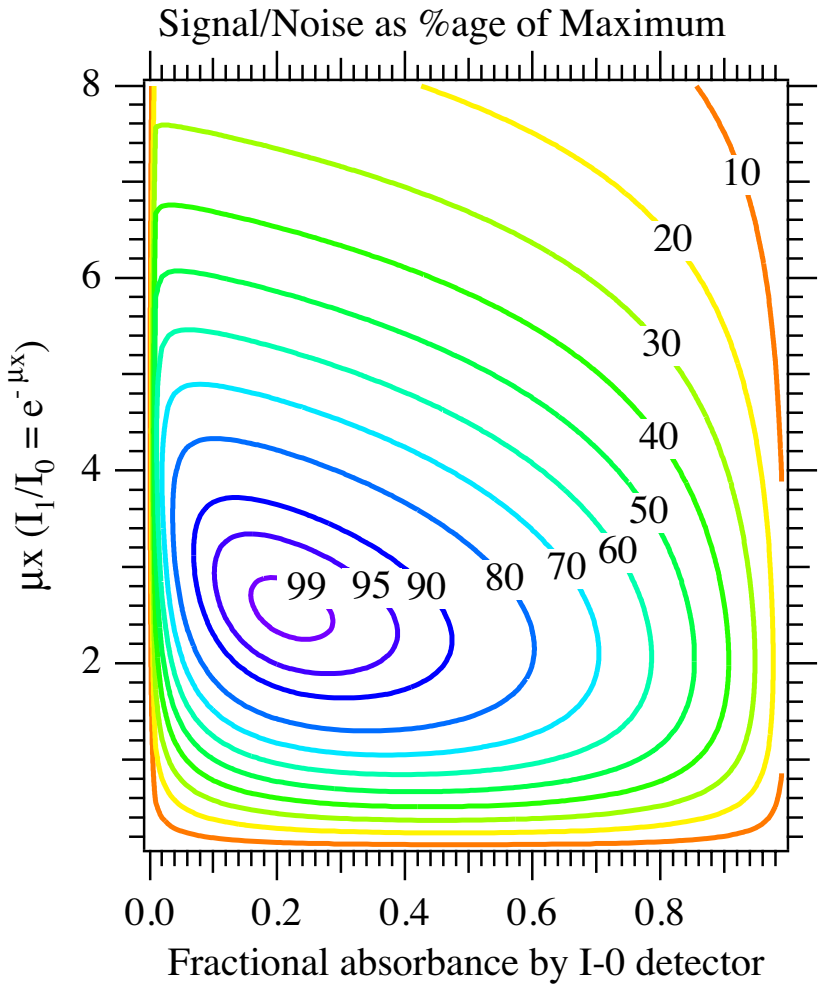
Heald, S. M. In *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*; D. C. Koningsberger and R. Prins, Eds. ; John Wiley & Sons: New York, 1988; pp 87-118.

Variables

μt = absorption thickness of target compound (t = sample thickness, also called x in some sources and figure on right)

f = fraction of X-rays absorbed by I_0 detector

I_0 = # of photons entering I_0 detector



If counting noise predominates, optimal μx = 2 to 2.5

A more complete equation:

Variables

μt = abs. thickness of target cmpd.

f = fract. of X-rays abs. by I_0 detector

I_0 = # of photons entering I_0 detector

Additional variables:

b = background abs. ($\Sigma\mu x$) from air, windows, and solvent or dilutant.

g = fract. of X-rays abs. by I_1 detector

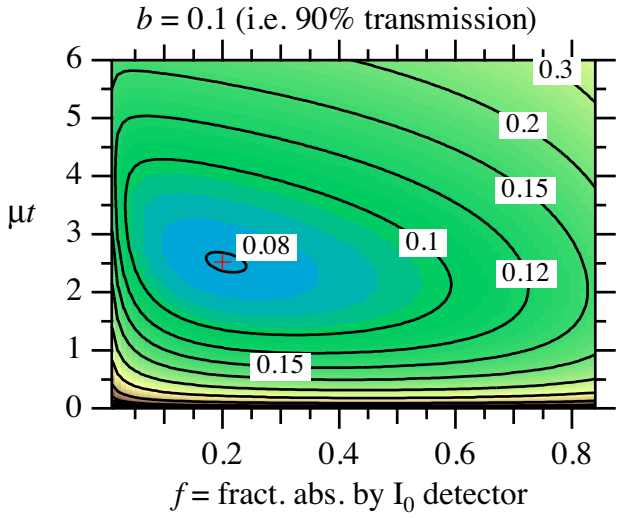
$h = \Delta\mu_{edge} / \mu_{high\ k}$

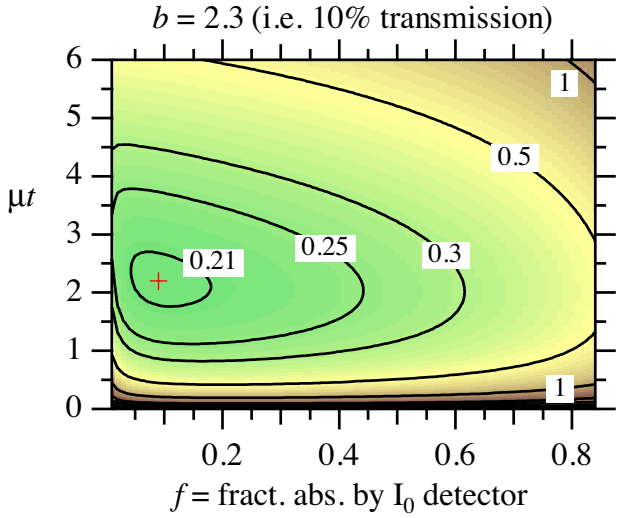
Equation below is for noise in EXAFS at high k limit (500 - 1000 eV above edge):

$$N(\chi)_{hi\,k} = \frac{1}{h(\mu t) I_0^{1/2}} \left(\frac{1}{f} + \frac{e^{\mu t} e^{b}}{(1-f) g} \right)^{1/2}$$

Calculations shown at right are for noise in $k^3\chi$ at k = 16 Å^{-1} (i.e. 1000 eV above edge)

Both graphs assume $I_0 = 10^{10}$, $g = 0.9$, $h = 1$





If electronic (A-D) noise predominates, optimal $\mu t \approx 1\text{-}1.3$

For all calcs.:

$I_0 = 10^{10}$

$h = 1$; $g = 0.9$

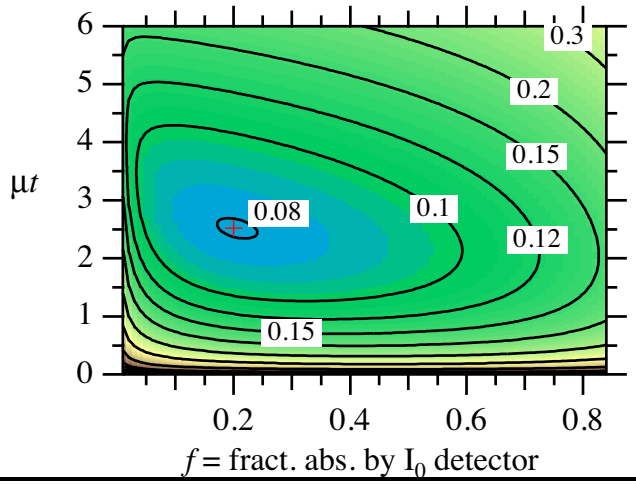
Assuming $N(\text{detector}) = \sqrt{\#\ \text{photons}}$

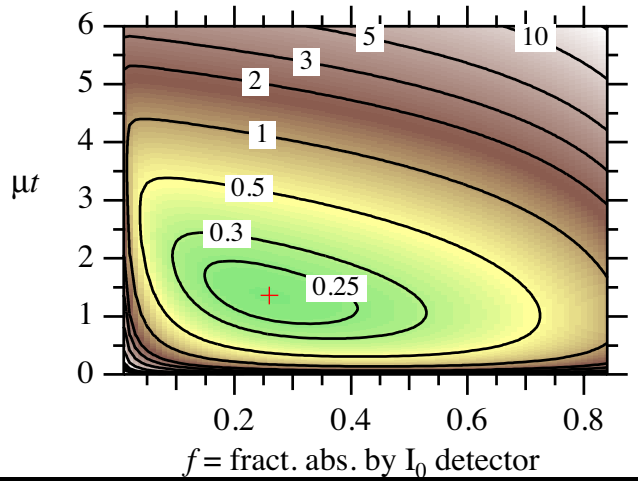
$$N(\chi)_{hik} = \frac{1}{h(\mu t) I_0^{1/2}} \left(\frac{1}{f} + \frac{e^{\mu t} e^{b}}{(1-f) g} \right)^{1/2}$$

Assuming $N(\text{detector}) = \text{constant } (c) = 10^5$

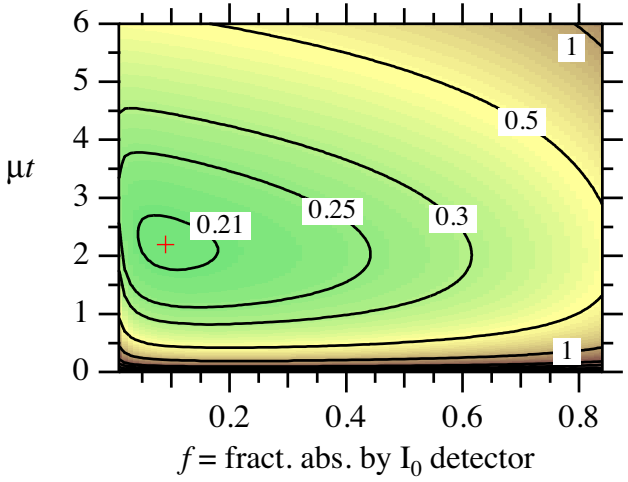
$$N(\chi)_{hik} = \frac{c}{h(\mu t) I_0} \left(\frac{1}{f^2} + \frac{e^{2\mu t} e^{2b}}{(1-f)^2 g^2} \right)^{1/2}$$

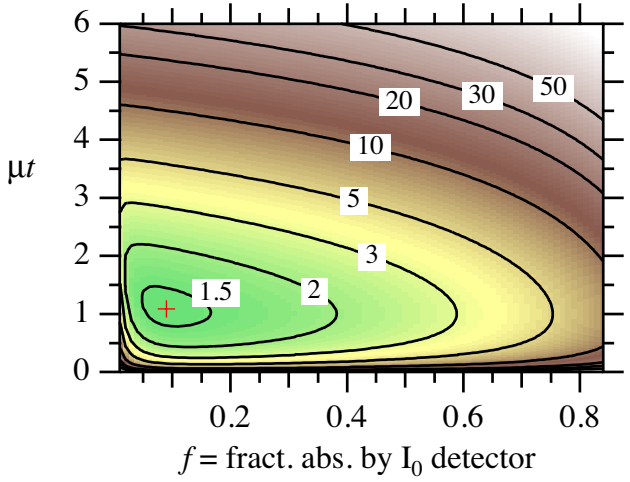
Background absorbance $b = 0.1$ (i.e. 90% transmission)





Background absorbance $b = 2.3$ (i.e. 10% transmission)





Possible systematic errors suggest keeping $\Delta\mu_0 t < 1.5$

The following are sources of extra signal in the I_1 (transmission detector)

"Pinholes" (air bubbles, cracks, etc.)

Monochromator overtones (if not removed completely by low angle mirror or detuning)

Monochromator resolution spread (important in near edge region)

"Stray" radiation (incl. scattered and fluoresced radiation entering transmission detector)

These extra signal sources cause a systematic lowering in the measured $\mu t = \ln(I_0 / I_1)$

The effect is most pronounced when μt is large (> 2)

More discussion of these effects may be found in Heald, S. M. In *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*; D. C. Koningsberger and R. Prins, Eds. ; John Wiley & Sons: New York, 1988; pp 87-118.

Heald (ref. above) suggests preparing samples so that the transmission edge jump, $\Delta\mu_0 t < 1.5$

For most coordination complexes, the $\Delta\mu_0$ (edge jump) is within ±20% of μ at 800 eV above the edge (where optimizing S/N is most crucial), so this rule is roughly equivalent to the rule to aim for μt between 1 and 1.5 (see next slide).

Suggestion for transmission: aim for $\mu t \approx 1$ to 1.5

Graph shows concentration required for μ = 1 per mm (μt = 1.2 for 1.2 mm thick).

S/N most important at high k region of EXAFS spectrum (600 - 1000 eV above edge).

First row T.M.: [M] ≈ 0.4 M

Second row T.M.: [M] ≈ 1.2 M

(K edge studies)

If holders are ≈1.2 mm, use concentrations shown.

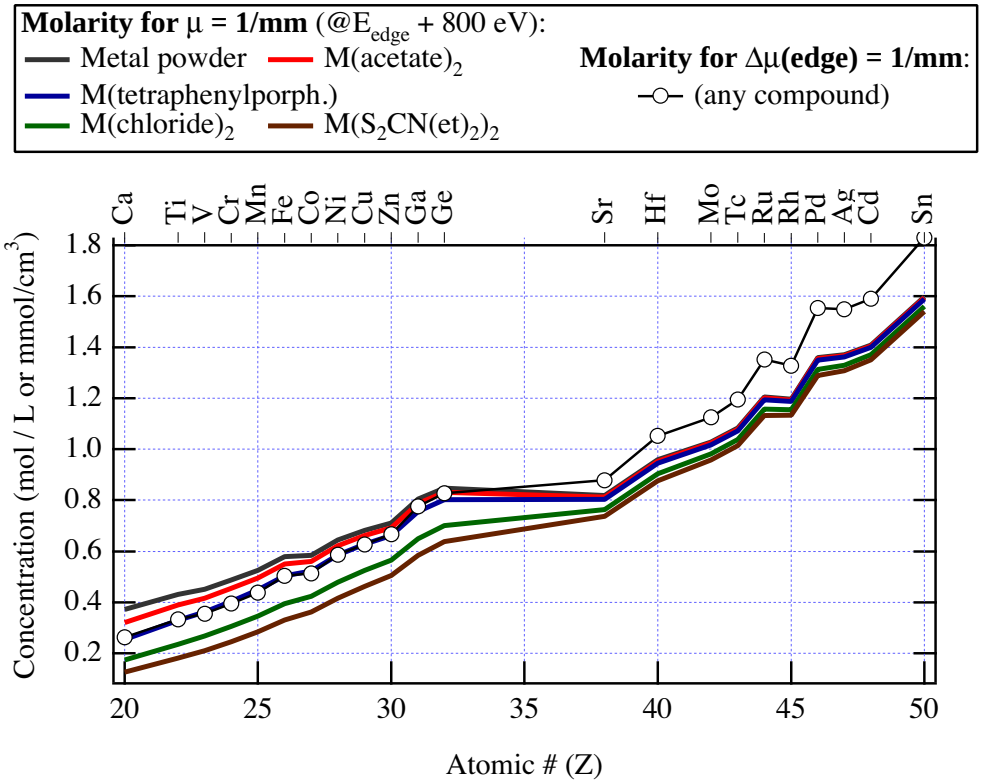
For 3 mm thick holders, decrease [M]

Ex. for BN powder (0.7 g/cc packed)

$ZnO_mN_nC_pH_q$ (300 amu)

Assume holder thick 3 mm:

$$0.6\frac{mmol}{cc}\left(\frac{1.2}{3}\right)\left(\frac{0.300g}{mmol}\right)\left(\frac{1cc}{0.7g\,\mathrm{BN}}\right)=\left(\frac{0.10g}{g\,\mathrm{BN}}\right)$$



EXCEL spreadsheet used for the calculations shown here: http://www.haverford.edu/chem/Scarrow/XAS/

Web resource for calculating μ: http://physics.nist.gov/PhysRefData/Xcom/Text/XCOM.html

cross section (cm^2/g) × density (g/cm^3) = μ in cm^{-1}

Choice of dilutants, solvents and windows

Dilutants (powders)

- Boron Nitride
- Cellulose
- Mineral Oil

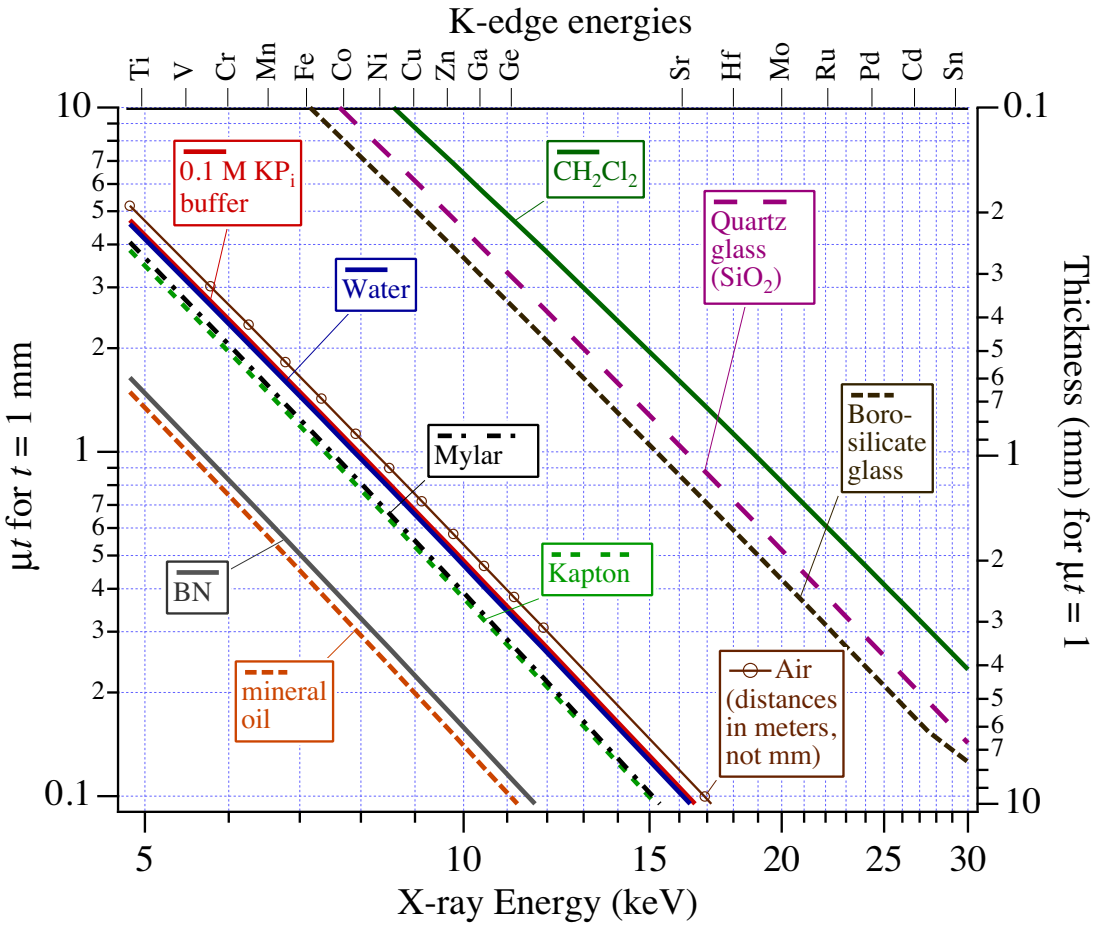
Solvents

- Organics more transmissive than water
- Avoid chlorinated solvents
- Buffer salts cause only minor change in water transmission

Windows

- 1 mil (0.025 mm) Mylar or Kaptan give μt <0.1 for E>4.5 keV; $\mu t \approx 1$ at E=2.1 keV (P-K)
- Glass windows may be useful for higher E studies.

Air - minimize pathlength for E<10 keV

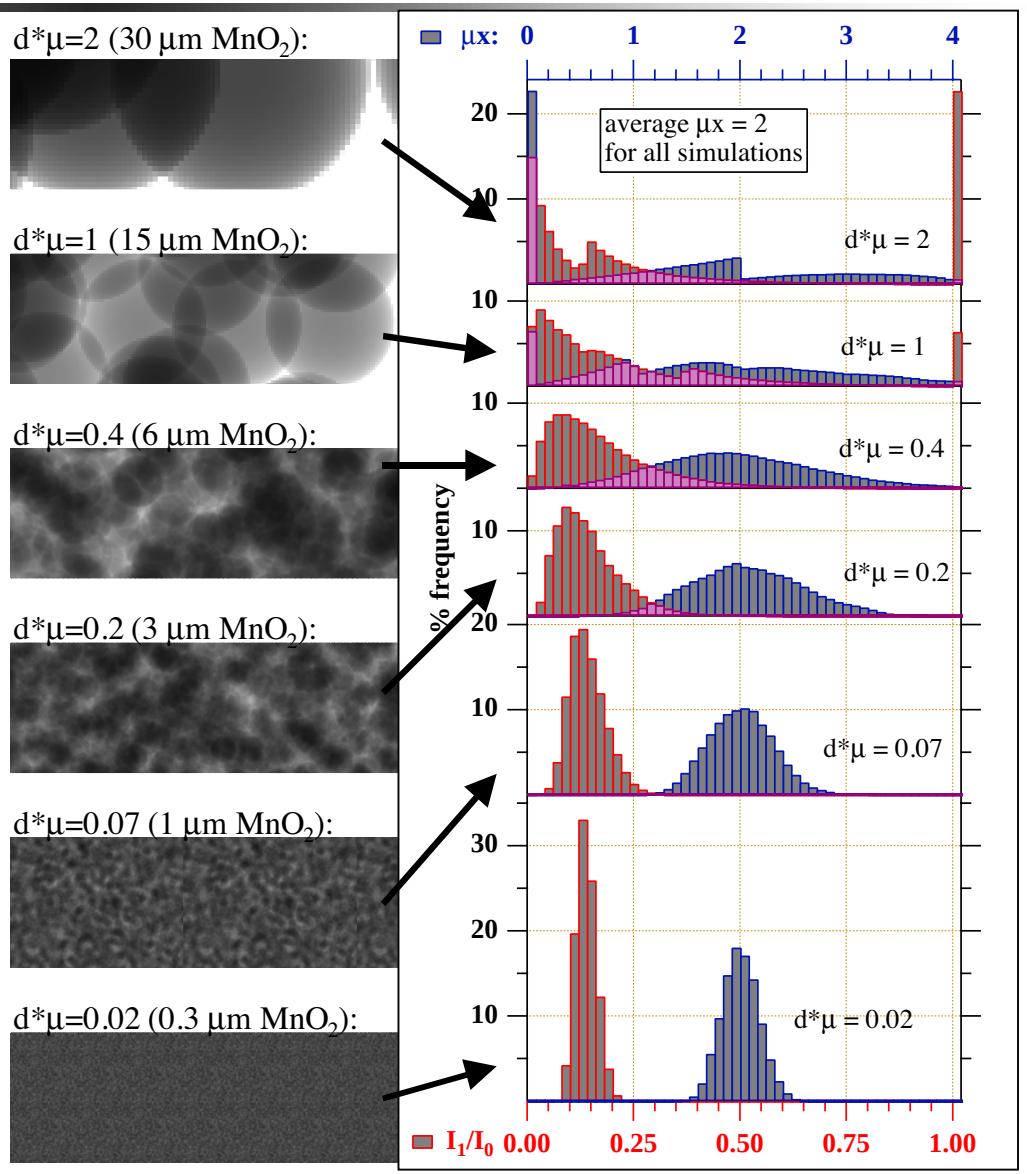


Importance of small particle size for uniform thickness

Uniform thickness of samples is needed for accurate determination of XAS and EXAFS (χ) from transmission measurements. ±20% variations in thickness of cause only minor errors in χ, but variations larger than this may occur if the particles are not finely ground.

The simulations at right assume spherical particles dispersed randomly in a thick BN matrix. *x* refers to the total distance that a transmitted X-ray travels through particles of sample (not BN). The particle diameters are scaled relative to the absorption thickness of the material (=1/μ). As an example, particle diameters are specified for MnO_2, for which $\mu \approx 67\ mm^{-1}$. In each case, the same amount of material is added, and the average $\mu x = 2$.

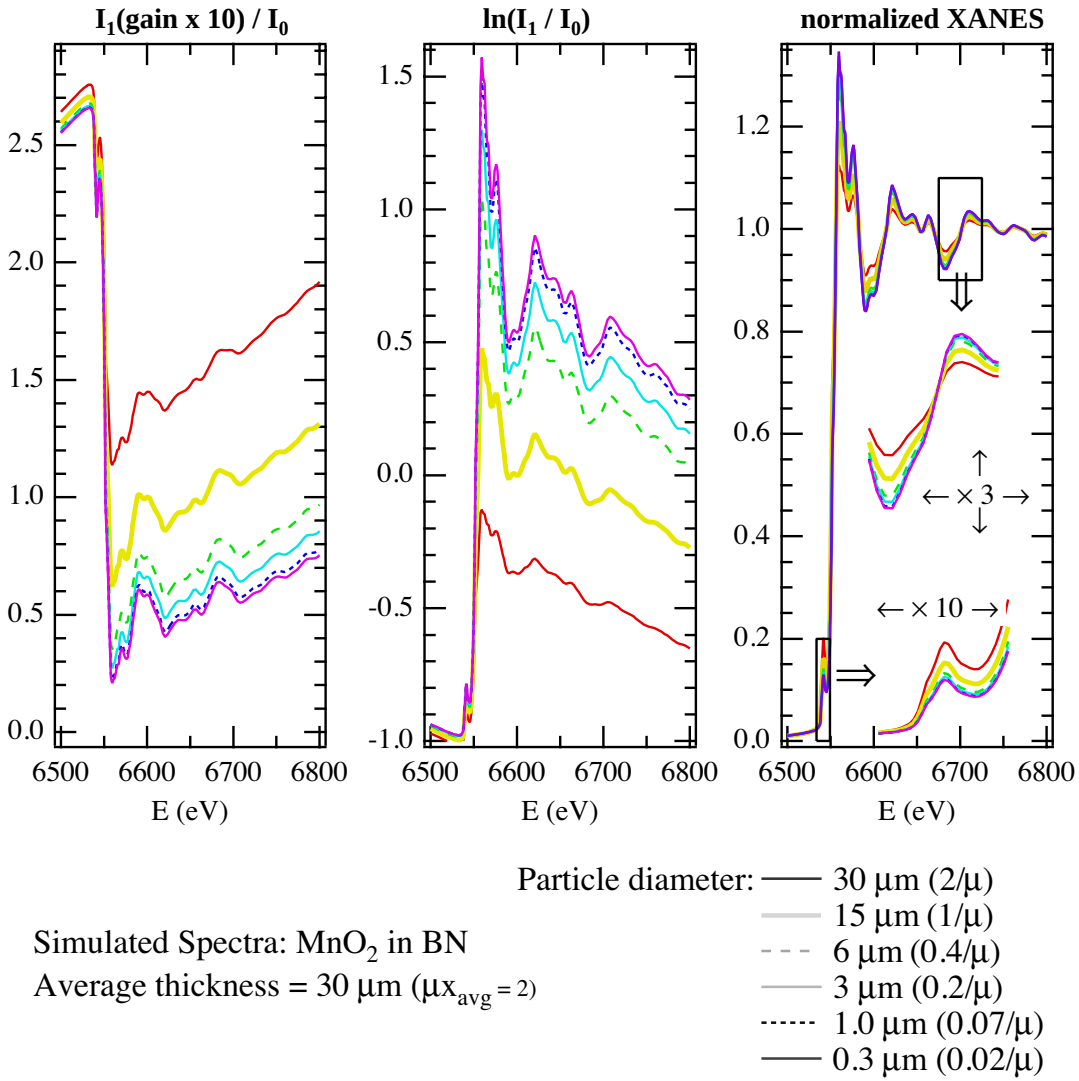
The histograms show the uniformity (or lack thereof) in the **absorbance coefficient (μ*x*) of various "pixels"** and in the **intensity reaching the I_1 detector**.



Effects of non-uniform thickness on the measured XAS

Spectral simulations at right are based on a measured XAS spectrum of MnO_2, and show the effects of variations in thickness on the spectrum that would be measured.

Large particle sizes (large variations in effective thickness) diminishes the apparent size of the edge jump. When converted to XANES and EXAFS, the pre-edge peak(s) appear larger, and the EXAFS appears smaller than it really is.



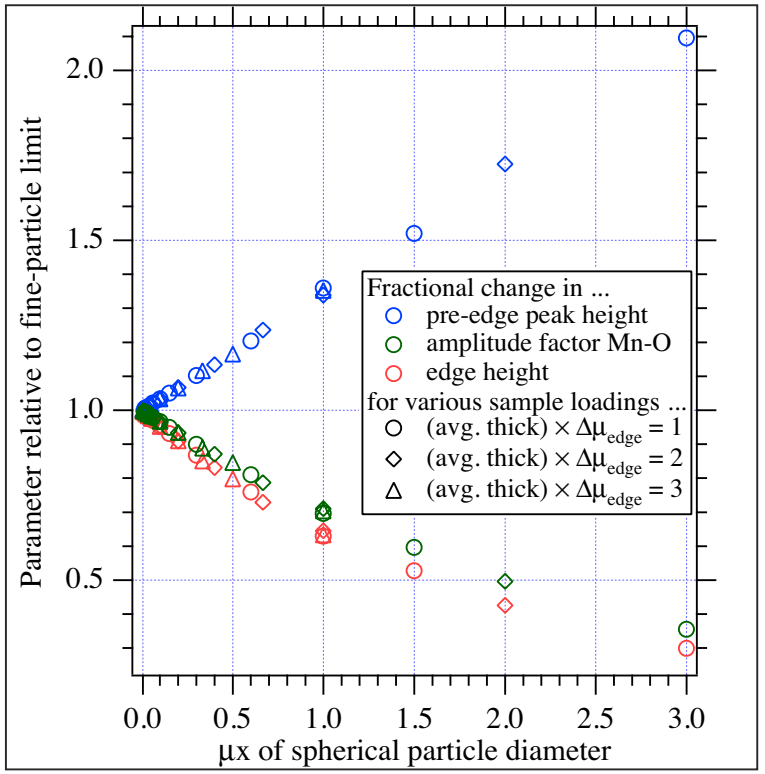
Errors from large particles are independent of thickness

The relative (%) variation in thickness depends on the ratio (particle diameter / avg. thickness), so it is tempting to increase the avg. thickness (i.e. increase μx) as an alternative to reducing the particle diameter.

However, simulations of MnO_2 spectra for average $\Delta\mu_0 x = 1$, 2 or 3 show that the errors in derived pre-edge peak heights and EXAFS amplitude factors are significant when diameter > $0.2 / \Delta\mu_0$, but that they are not affected by the average sample thickness. ($\Delta\mu_0$ refers to the edge jump)

The equation at right is given by Heald (quoting earlier work by Stern and Lu). D is particle diameter, μ_1 is for just below the edge, and $\Delta\mu$ = μ(above edge) - μ_1.

BOTTOM LINE: GRIND PARTICLES FINELY



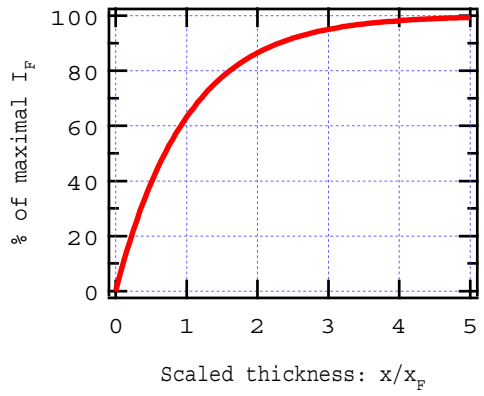
$$\frac{\chi_{obs}}{\chi_{true}} = \frac{2 - \dfrac{(\mu D)^2 e^{-\mu D}}{1-(1+\mu D)e^{-\mu D}}}{(\Delta\mu)\mu \ln\left\{\dfrac{\mu^2\left(1-(1+\mu_1 D)e^{-\mu_1 D}\right)}{\mu_1^{\,2}\left(1-(1+\mu D)e^{-\mu D}\right)}\right\}}$$

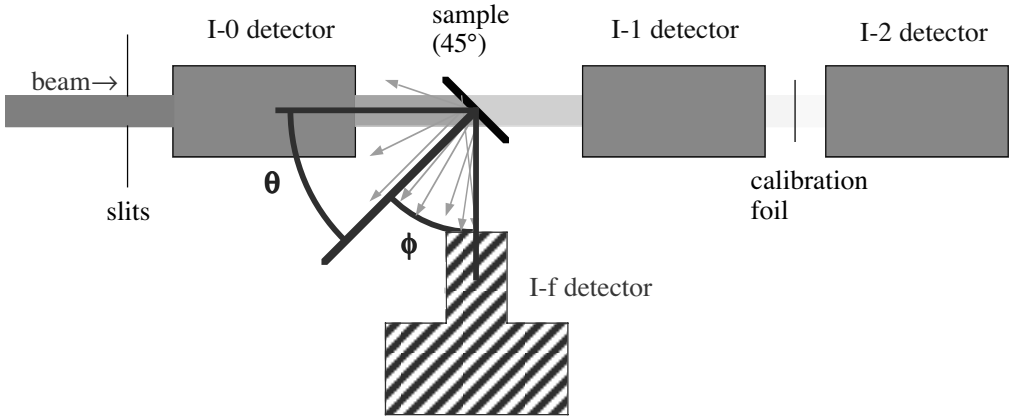
Fluorescence Samples

Usual geometry (looking down from above) involves sample holder at $\theta = \phi = 45°$:

Fluorescence signal increases with sample depth, but only to a certain extent:

- μ_K = K-edge absorbance of interest
- μ_T = total absorbance (incl. μ_K)
- μ_F = absorbance at $E_{fluorescence}$
- c = fluor. yield × fract. solid angle
- I_{in} = photon flux entering sample





Define $x_F \equiv \dfrac{1}{\mu_T + \mu_F \, \cos\phi / \cos\theta}$ = effective fluorescence depth

Then $\dfrac{I_f}{I_{in}} = c\mu_K x_F \left(1 - exp\left\{- t / x_F\right\}\right)$

(t is beam pathlength through sample = $holder\ t \div \cos\theta$)

Thick vs. Thin Fluorescence Samples

Thin samples: $t < 0.2 \times x_F$

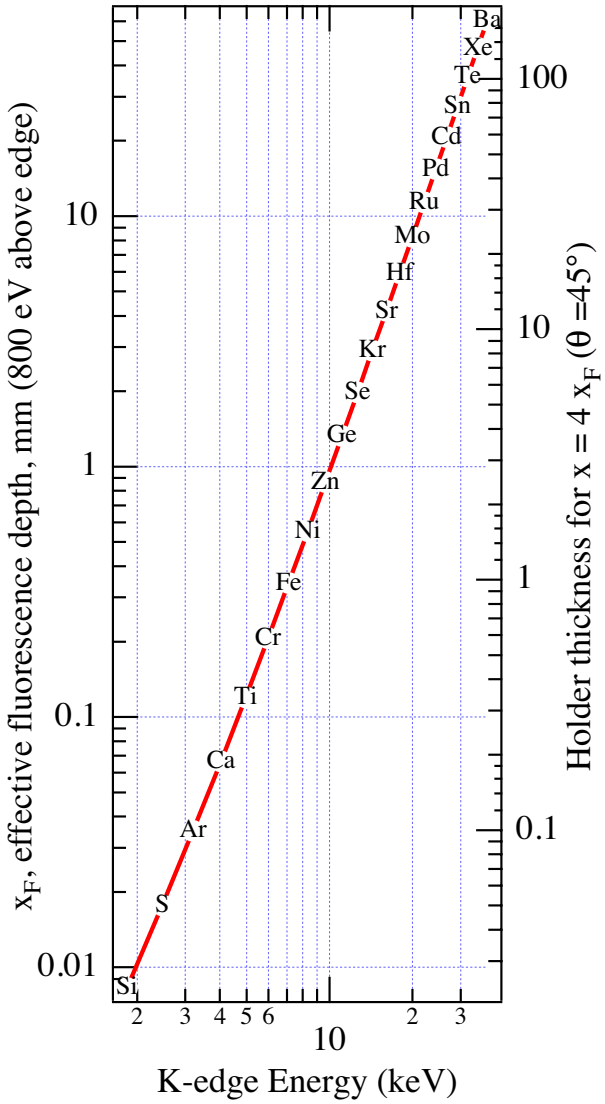
- Finely divided powder on Scotch tape, for instance
- Data workup relatively simple: $\mu_K = c'(I_f / I_{in})$

Thick samples: $t > 4 \times x_F$

- This is the best method for dilute samples (mM or lower in edge element)
- Measurement of μ_T and μ_F (or calculations) needed to obtain accurate μ_K from I_f/I_0
  - Use blank scan: $t\mu_T(E) = \ln(I_0/I_1) - \ln(I_0/I_1)_{blank}$
  - $t\mu_F$ determined by extrapolation of $t\mu_T(E)$ back to $E = E_F$
  - In cases where $\theta = \phi$, $\mu_K = c'(I_f / I_{in})(t\mu_T + t\mu_F)$
- When sample is not dilute ($t\Delta\mu_{edge} > 0.1$), it is particularly important to use measured $t\mu_T$
  - (In these cases transmission data is often comparable or better in quality anyway)

Intermediate thicknesses ($0.2 < t / x_F < 4$)

- When sample is both dilute and precious (metalloprotein), can optimize signal/sample ratio by keeping $t \approx x_F$.



Avoiding unwanted signals in Fluorescence data

Scattering (from sample) followed by fluorescence from nearby metal surface (containing the element of interest as at least an impurity) can be a problem with mM samples

Detecting the problem:

Run a blank containing solvent or dilutant, but no sample.

Solutions:

Avoid element of interest (or Z+1 element) in sample holders, cryostat chamber, etc.

Lead tape can be used to selectively mask metal parts

Window materials should be checked (very low levels of Mn, Zn in Mylar, Fe in Kapton have been found, but probably vary from batch to batch)

Detecting the problem:

Run a blank containing windows only. Hopefully, no edge will be seen, but data from this run is useful for determining the $x\mu_T$ needed for correction of the fluorescence data.

Solutions:

Change to a different window material, or avoid windows altogether for frozen solutions.

Fluorescence from in-line calibration foil should not get to the fluorescence detector.

Solution: use lead shielding. In addition, place 3 abs. thickness of paper or plastic (etc.) in front of the foil to reduce reference signal to the lowest detectable level.

Summary of Sample Preparation Notes

Sample holder designs range from simple to moderately complex

Height and width are governed by beam size

- Don't forget to multiply beam width by ca. 1.5 if holders will be used for fluorescence
- Leave at least 1 mm around edges so that alignment is not so critical
  - this also minimizes secondary fluorescence problems

Thickness and concentration considerations

- For transmission measurements
  - Aim for μt (for compound of interest) $\approx$ 1 to 1.5 (also $\Delta\mu_0 t < 1.5$)
    - For t = 2 mm, [M] $\approx$ 0.2 M for first row TM, [M] $\approx$ 0.6 M for 2nd row TM (K edge)
  - Consider also μt of water, organic solvents, or dilutants such as BN. Try to keep below 1 if possible.
- For fluorescence, no additional signal gained if $t > 4\, x_F$.
  - Useful for concentrations 0.1 - 10 mM or higher (see suggestion below).

Sample uniformity

- Grind solid samples as small as possible ($<0.2 / \Delta\mu_0$).
- Avoid air bubbles, cracks, pinholes. (Sample thickness variations of ±10% are OK).
- If suspect thickness effect problems, try comparing fluorescence and transmission spectra.