

# Preparing samples for XAFS data collection

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Types of samples

Potential problems

Methods of preparation

## Types of samples:

### Solids

- powder
- foil
- ingot
- tissue

### Liquid

### Thin Film/Surface

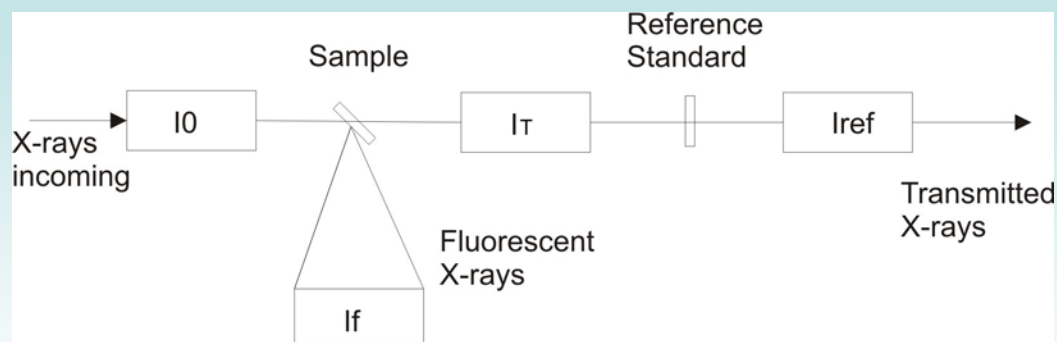
### Microprobe

- solid, as above
- thin (thick) section

## Potential Issues:

- Particle Size
- Uniformity (or lack thereof)
- Beam damage
- Background
- Concentration of target
- Containment
- Crystallinity
- Penetration/Escape

## Typical XAFS set-up



Measured quantities:

$I_0$  - incident intensity – after beam defining slits, before sample

$I_T$  - transmitted intensity – after sample

$I_f$  - Fluorescence intensity (or electron yield, optical luminescence) from the sample

$I_{ref}$  - Reference signal (in transmission above) for energy calibration and comparison with sample

## Absorption Process

$$IT(E) = \iint_{\substack{\text{Beam} \\ \text{Area}}} dx dy [B(E, x, y) \exp(-\mu(E)t(x, y))]$$

$B(E, x, y)$  = beam flux incident on sample at point  $(x, y)$

$t(x, y)$  = thickness at  $(x, y)$

$\mu(E)$  = absorption co-efficient

Simplify: Uniform beam density,  $B = I_0 / A$

$$IT(E) = \frac{I_0(E)}{A} \iint_{\substack{\text{Beam} \\ \text{Area}}} dx dy [\exp(-\mu(E)t(x, y))]$$

Transmission measurement: consider  $-\ln \frac{IT}{I_0}$

Ideal case: uniform thickness,  $t$   $IT = I_0 \exp(-\mu t)$

$$-\ln \frac{IT}{I_0} = \mu t$$

optimum  $t \sim 1 - 2$  absorption lengths

Simple non-uniform case: pinholes

$t = 0$  for fraction,  $f$ , of beam area

$t = t$  for fraction  $(1-f)$

$$IT(E) = I0(E)[f + (1 - f) \exp(-\mu(E)t)]$$

$$= I0(E) \exp(-\mu(E)t) * [f \exp(\mu(E)t) + (1 - f)]$$

$$-\ln \frac{IT}{I0} = \mu t - \ln[f \exp(\mu(E)t) + (1 - f)]$$

↑

[Always  $\geq 1$ ]

$$= \mu t_{\text{effective}}$$

↑

[Always  $\leq \mu t$ ]

*Non-uniformity reduces exafs amplitude in transmission measurements*

## What about Fluorescence?

$I_f \propto I_0 - IT$  Fluorescence signal is proportional to the amount absorbed

$$\frac{I_f}{I_0} \propto (1 - \exp(-\mu t)) \quad (\text{uniform } t \text{ assumed})$$

If the absorption is small...

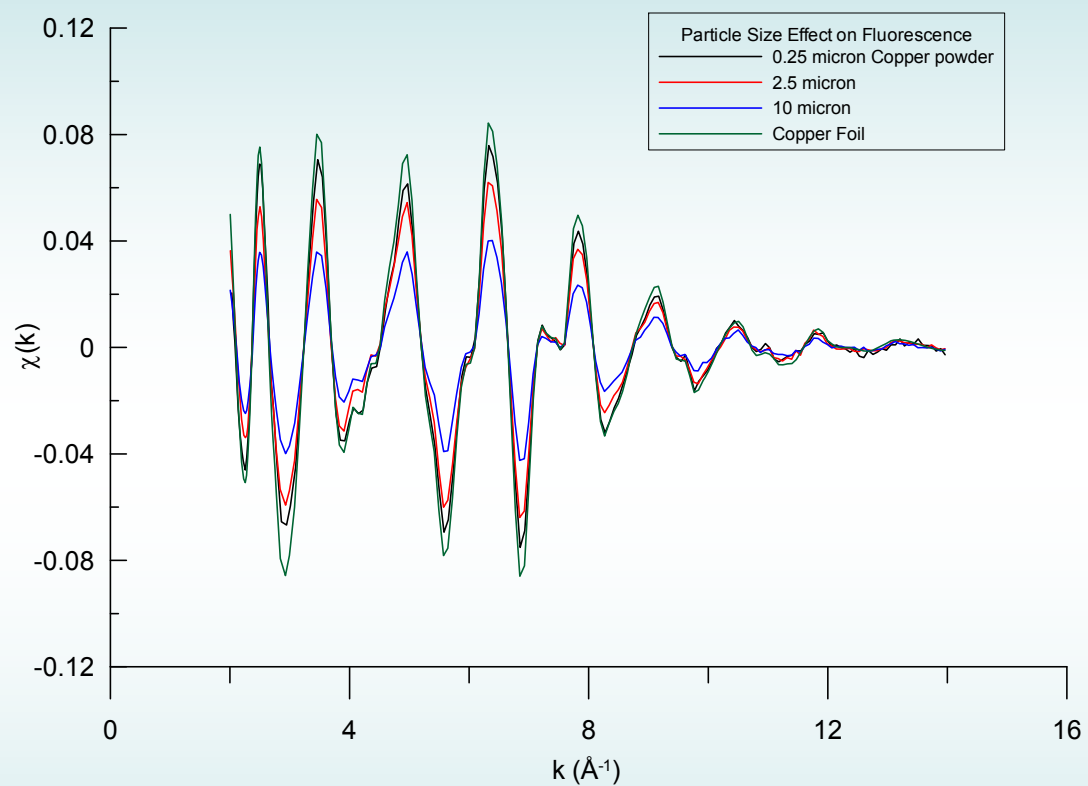
$$\frac{I_f}{I_0} \propto (1 - (1 - \mu t + \frac{(\mu t)^2}{2} - \dots))$$

$$\propto \mu t - \frac{(\mu t)^2}{2} + \dots$$

$\approx \mu t$  IF  $\mu t$  much less than 1...  
i.e. if  $t$  is much less than an absorption length

If not, the FL signal can be attenuated (reduced)  
Leading to SELF ABSORPTION

## EXAMPLE: Copper foil and powder



Particle size, non-uniformity, self-absorption all affect EXAFS amplitude ( $S_0^2$ ) – harder to extract N's



Two most important issues:

Sample uniformity over scale of beam size influences:

- noise (sample vibrations, beam motion, structure in beam)
- XAFS amplitude (pinholes, thickness distribution)

Sample size relative to:

- absorption length of sample (penetration/fluorescence escape)
- absorption length of target element in sample (self-absorption)

TAKE HOME LESSON:

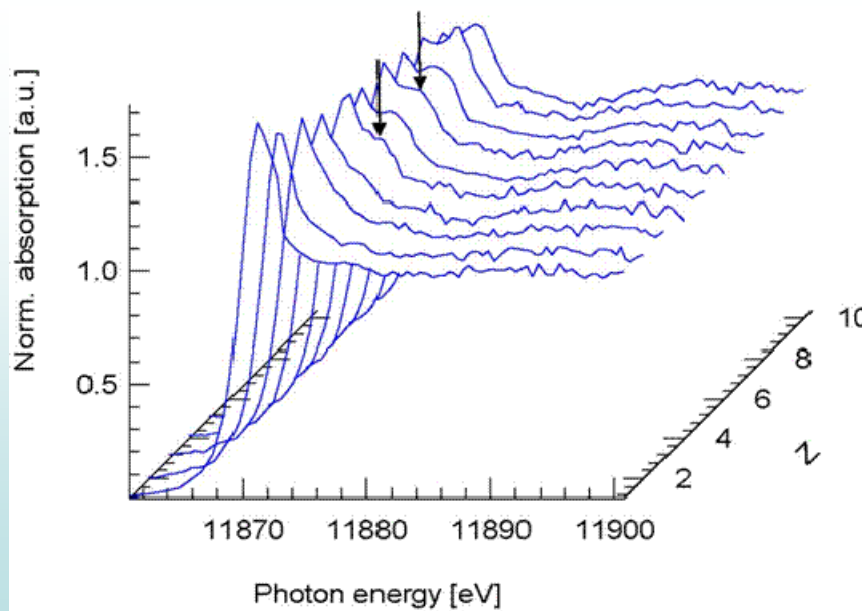
Try to keep your samples as uniform as possible, and if you are working in fluorescence, keep the sample size small compared to the absorption length.

## Beam Damage

sample changes during measurement (and you didn't want it to)  
(detector windows, burn paper etc exhibit this too!!)

Can see changes (oxidation, reduction, migration) be caused by:

sensitivity to intense radiation (burning organics)  
photolysis (water dissociating in the beam, H, O radicals)  
reaction with ozone produced by beam  
coating/stripping due to impurities in air (organics)



**FIG. 3.6:** Oxidation of aqueous  $10 \mu\text{g}\cdot\text{L}^{-1}$  MMA(III) was marked by the growth of a spectral feature (indicated by arrows) at  $11874.2 \text{ eV}$  over successive scans. This new feature has a similar white line position to that of aqueous MMA(V) ( $11874.1 \text{ keV}$ ).  $Z = \text{Scan Number}$ .

P.G. Smith, Thesis, Queen's U. 2007

Preventing beam damage:

Freezing the sample – still happens? Go colder

Work under vacuum or helium

Spinning the sample – have the material spend less time in the beam

Attenuate the beam (slow down the damage, but you may have to integrate longer)

But you may encounter a sample where none of this works...and there is nothing more you can do...

Making samples: Powder

Three methods: tape, pellet, epoxy

Start with fine powder: Grinding,  
Sieving,  
Fluid suspension (big particles sink faster)

Tape: easiest, quickest

- sprinkle fine powder on tape, spread around with finger (GLOVES!) – shifting, circular motion works well – to get uniform distribution
- spreading motion breaks up clumps, brushes away big particles, leaves the smaller ones on the tape
- use multiple layers (folds) of tape to get edge jump ~ 1-2 for transmission or 1 layer (perhaps more if low concentration) for fluorescence

Cautions:

- some materials don't spread well on tape
- tape adds background to absorption – too much is bad (particularly at low energy)
- pinholes (non-uniformity in particle size/distribution)

## Powders (continued)

### Pellet: pressed in die

- combine fine powder with inert binder (e.g. graphite, boron nitride) to get uniform mixture with known amount of target to give 1 – 2 absorption lengths when distributed over area of pellet

### Epoxy: section

- combine fine powder with inert liquid epoxy to give mixture with known concentration of target, then wait for epoxy to set
- using a microtome, one can section the hardened epoxy to a desired thickness based on the concentration

### Cautions:

- binder/epoxy add to the background absorption – can calculate binder absorption as well – keep total absorption less than 3 for transmission
- clumping may occur (pellet), may be difficult to determine if the mixture is not homogeneous (and, “homogeneous” on what length scale)

## Liquid samples

Uniform by default unless beam causes photolysis (bubbles!)

Can do fluorescence or transmission, depending on concentration

keep in mind, solvent adds to background absorption

1mm of H<sub>2</sub>O transmits 60% at 10keV

1mm of H<sub>2</sub>O transmits 9% at 6keV

keep in mind,  $\mu t \ll 1$  for fluorescence

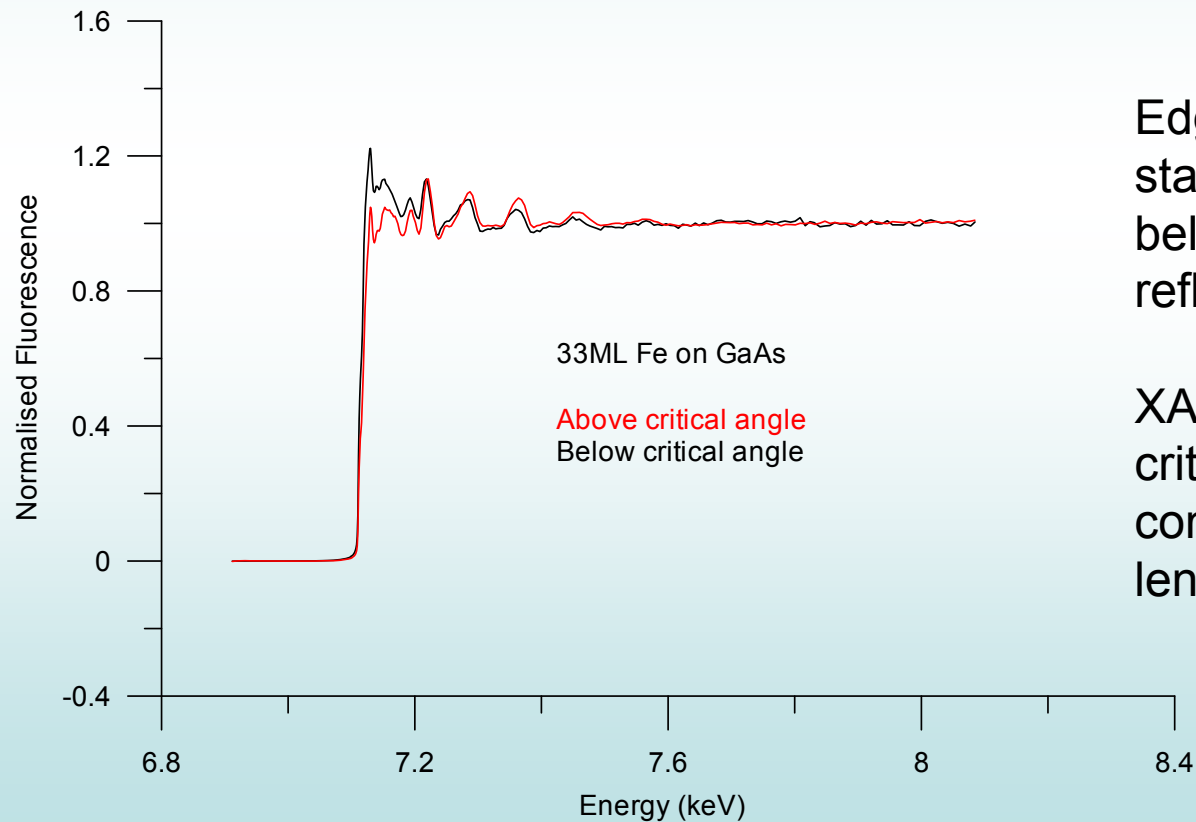
X-ray windows must be compatible with solution (acid/base tolerance)

Thin films (on substrates)

Biggest concerns: uniformity, thickness and crystallinity

Measure in fluorescence: in-situ, ex-situ (under He)

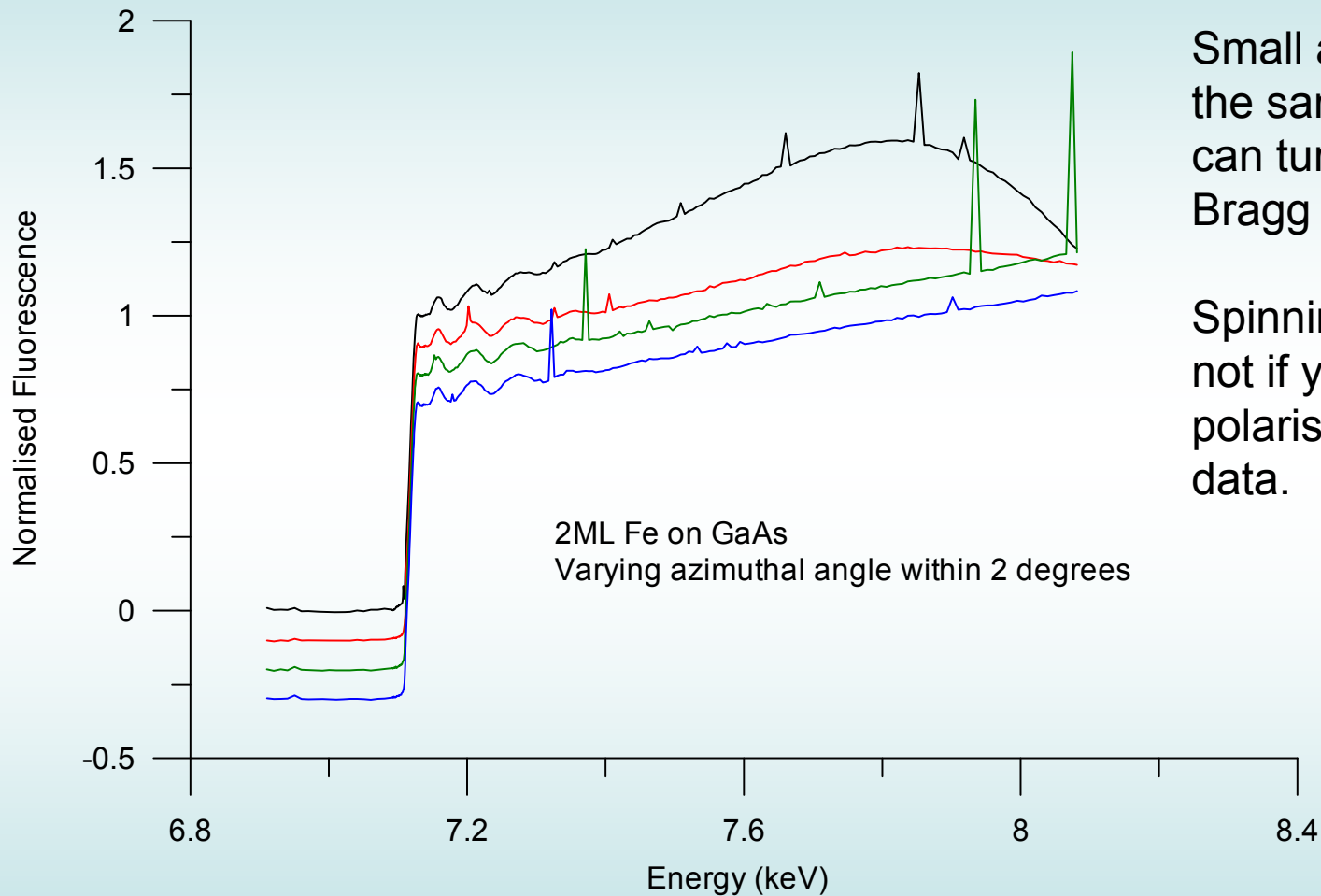
Sensitive to incident angle when near grazing:



Edge enhancement due to standing wave formation below critical angle for total reflection.

XANES distorted below critical angle if film is thick compared to penetration length of x-rays

# Influence of substrate: BRAGG PEAKS!!!



Small angle changes in the sample orientation can turn on/off or shift Bragg peaks.

Spinning might help, but not if you want x-ray polarisation-dependent data.



## Microprobe Samples

### Remember:

uniformity over scale of beam (vibrations lead to noise in signal)

thickness versus concentration of absorber (avoid self-absorption)

thickness versus penetration of x-rays: what lies beneath the surface that you can't see and the x-rays can

be careful with mounting material

impurities (e.g. float glass (Fe, As, Zn, Pb...etc...)) versus pure SiO<sub>2</sub>)

mount thickness can affect transmission ( $\mu$ XAFS,  $\mu$ XRD)

Mounting epoxy (thin section) should be free of detectable impurities

# Thickness Effects: e.g. Lead contamination of hair

Preliminary synchrotron analysis of lead in hair from a lead smelter worker

R.R. Martin, I.M. Kempson, S.J. Naftel, W.M. Skinner  
Chemosphere 58 (2005) 1385–1390

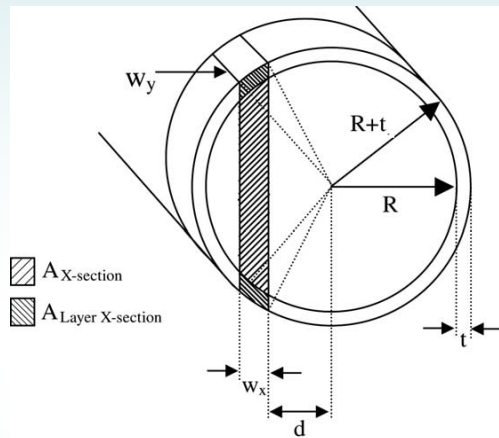


Fig. 4. The model and variables used to represent the analysis of a cylindrical hair shaft.

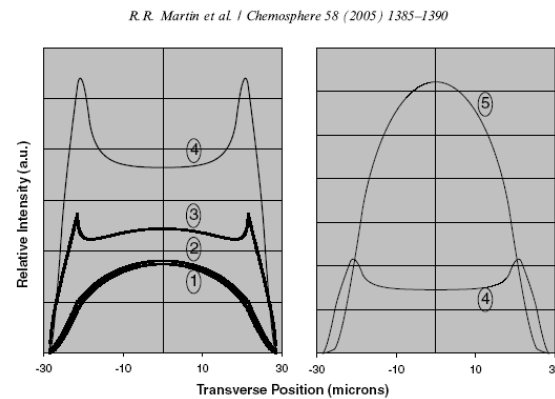
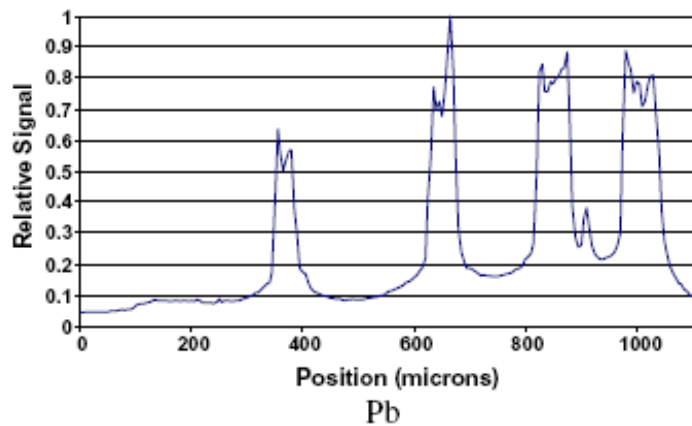


Fig. 5. Predicted X-ray fluorescence intensities as a function of exciting X-ray position ( $d$ ), with different thicknesses ( $t$ ) of outer layers from a hair with a total radius ( $R+t$ ). The relative metal concentrations in the hair surface layer and in the interior are also varied as given in Table 1.



## Epoxy suggestions for microprobe thin sections

**Material Name:** Petropoxy 154 Curing Agent

**Family/Chemical Name:** Liquid BF<sub>3</sub> Based Epoxy Catalyst

“The main trick is to use a slow curing epoxy - the rapid cure catalysts typically contain transition metals. The other material used is Canada Balsam which seems to be pretty clean. Canada Balsam is however water soluble (maybe an advantage for floating specimen off slide) and not as long lived as Epoxy (The geologists like to keep their thin sections forever).

Alberta has for years used a slow cure epoxy - 12 hr at room temp.  
Buehler Epo Thin Epoxy resin (20-8140-032) and Epoxy hardener (20-8142-016).”  
- *R.G.Cavell, March 2007*

*H. Stover*

**TTE**  
(trimethylolpropane  
triglycidyl ether)  
Aldrich: 43026-9

**MMHA**  
(4, 4'-methylenebis  
(2-methylcyclohexylamine))  
Aldrich: 36950-0

**1:1 mole ratio of  
TTE:MMHA  
recommended**

Useful links:

“The Orange Book” <http://xdb.lbl.gov/>

Useful information on edges and fluorescence lines, and so much more  
(pdf version of book available!)

McMaster Tables <http://www.csrri.iit.edu/periodic-table.html>

For calculating cross-sections of atoms

LBNL X-ray Tools <http://www-cxro.lbl.gov/index.php?content=/tools.html>

X-ray interactions with matter:

transmission, attenuation lengths, reflectivity, etc...