Anatomy of an XAFS Measurement

Matt Newville
Consortium for Advanced Radiation Sources
University of Chicago

Experiment Design

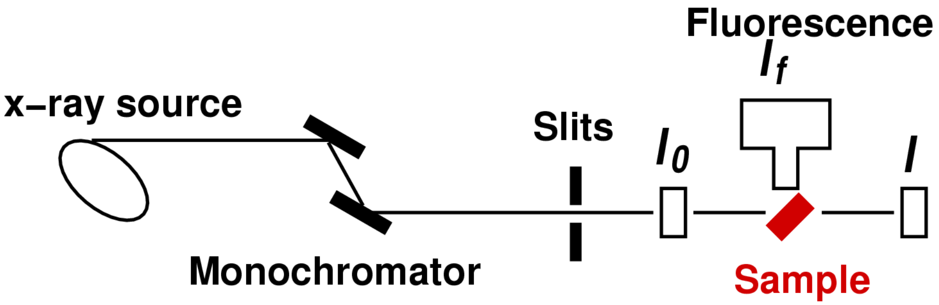
- **Transmission v. Fluorescence modes**
- **X-ray detectors**
- **Data Collection Strategies**

Sample Preparation

Problems to Avoid

(version 1.1.1, 21-June-2004)

X-ray Absorption Measurements



XAS measures the energy dependence of the x-ray absorption coefficient $\mu(\mathbf{E})$ at and above the absorption edge of a selected element. $\mu(\mathbf{E})$ can be measured in two ways:

Transmission: The absorption is measured directly by measuring what is transmitted through the sample:

$$\begin{aligned} I &= I_0 e^{-\mu(E)t} \\ \mu(E)t &= -\ln(I/I_0) \end{aligned}$$

Fluorescence: The re-filling the deep core hole is detected. Typically the fluorescent x-ray is measured, but sometimes emitted electrons are measured. Either way,

$$\mu(E) \propto I_f/I_0$$

X-ray Absorption Measurements: Experimental Design

Important items for an XAFS measurement:

Monochromatic x-rays: **Need x-rays with a small energy spread or bandwidth: $\Delta E \approx 1$ eV at 10keV.**

Linear Detectors: **The XAFS $\chi(k) \sim 10^{-2}$ or smaller, so we need a lot of photons and detectors that are very linear in x-ray intensity (ion chambers). These usually means using a synchrotron source.**

Well-aligned Beam: **The x-ray beam hitting the detectors has to be the same beam hitting the sample.**

Homogeneous sample: **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.**

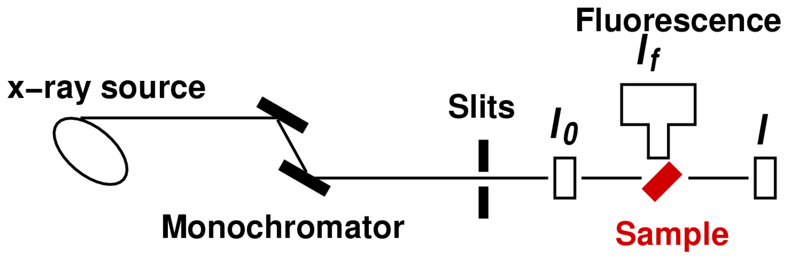
Counting Statistics: **For good data $\mu(E)$ should have a noise level of about 10^{-3}. That means we need to collect at least 10^6 photons.**

Transmission: **Fluxes at synchrotrons are $> 10^8$ photons$/$sec. Count rate is not much of an issue.**

Fluorescence: **May be a concern, especially when concentrations are very low.**

An X-ray Beamline: Synchrotron and Monochromator

The synchrotron produces *white radiation* – x-rays of all energies. A monochromator selects a single energy.



A monochromator is typically a pair of parallel, highly perfect silicon crystals that use Bragg diffraction

$$n\lambda = n\frac{hc}{E} = 2d\sin\theta$$

to select an energy E by selecting angle θ. The lattice spacing d is set by the "cut" of the crystal: Si(111), Si(220), and Si(311) are common.

Important characteristics of monochromators are:

Angle/Energy Range: **sets what edges can be accessed.**

Angle/Energy Calibration: **how accurate and reproducible is the energy?**

Energy Resolution: **typically, $\Delta E \sim 10^{-4}E$ or so (1 eV at 10 keV).**

Harmonics: **At angle θ, energy E, $2E$, $3E$, etc can be passed (some cuts don't pass $2E$). These *harmonics* needed to be removed from the "monochromatic" beam before the experiment.**

Monochromator: Harmonic Rejection

It is important to remove the *harmonics* (energies of $2E$, $3E$, . . .) from the x-ray beam before it gets to the experiment.

Two ways of to reject harmonics:

Detuning: **The angular width of a Bragg reflection is finite (a few μrad), and *decreases with increasing energy*: the harmonics have a narrower angular width than the fundamental energy.**

> **Making the two crystals slightly non-parallel rejects most of the harmonics, an preserves most of the fundamental.**

A piezo-electric crystal on the second crystal adjusts the parallelness, and so intensity, and harmonic content. *Rule of thumb*:

> **Adjust the piezo until the total intensity is about half the maximum intensity.**

Harmonic Rejection Mirror: **An x-ray mirror will not pass energies above a *critical energy* set by the pitch of the mirror (in mrad). This works very effectively for harmonic rejection.**

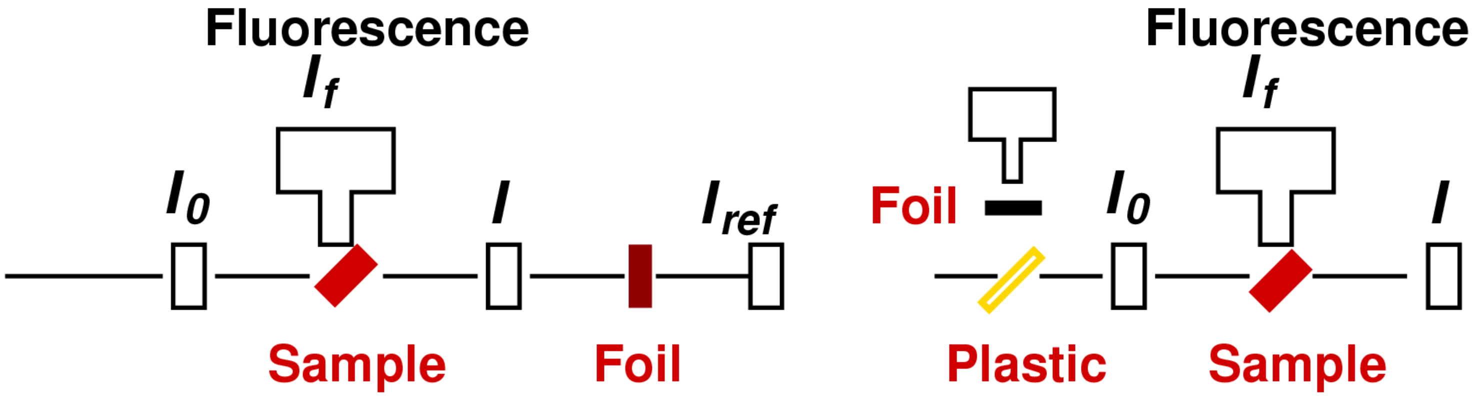
Use one or both of these methods!

Monochromator: Energy Calibration and Reproducibility

The absolute monochromator angle is usually not known to great precision (relative changes are much more precise).

We need to *calibrate* the energy for a particular edge. Typically, a metal foil is used and an arbitrary position on the edge (say, maximum of $d\mu/dE$) is set to the tabulated edge energy.

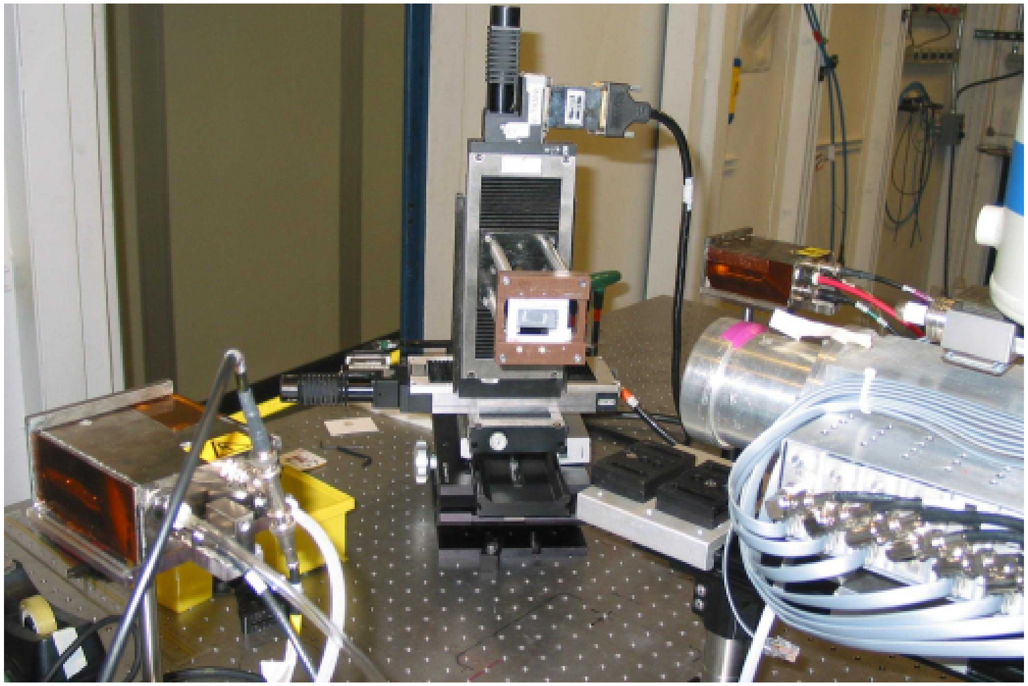
Many monochromators drift in angle from scan to scan (or over time). It's good to measure a *energy reference sample*, such as a metal foil. The energy reference can be measured periodically or, in some cases, at the same time as the sample:



Either of these approaches can be used to calibrate the edge energy during a normal XAFS scan.

An XAFS Beamline End Station

A typical XAFS station for Transmission and Fluorescence XAFS:



Slits: **To define beam size (just out of the picture).**

I_0 ***Ion Chamber:*** **To measure of the incident x-ray intensity**

I ***Ion Chamber:*** **To measure of the transmitted x-ray intensity**

Fluorescence Detector: **To measure fluorescence signal.**

Motorized Sample Stage: **To move sample into beam.**

Ion Chamber: measure x-ray intensities

X-rays enter a chamber filled with an inert gas (e.g., N_2). A gas molecules absorbs an x-ray, ejecting an electron and a charged ion, which ionizes more gas molecules. For most gases used, each x-ray of energy E generates

$$N_{\textbf{electrons}} \approx E/(32\,\textbf{eV})$$

(a 10keV x-ray generates 312 electrons!). A *voltage* applied across the chamber sweeps out the electrons, giving a current. Each absorbed x-ray generates electrons, and the total current is amplified to a voltage (I-to-V amplifier):

$$V = 1.6 \times 10^{-19}\,\textbf{coul} \times \frac{E\,\textbf{G}_{\textbf{amp}}\,N_{\textbf{photons}/\textbf{sec}}}{32}$$

for E in eV, V in Volts, and $\textbf{G}_{\textbf{amp}}$ the amplifier gain in Volts/Amps.
The x-ray flux absorbed in the chamber is then:

$$N_{\textbf{photons}/\textbf{sec}} = \frac{2 \times 10^{20} V}{E\,\textbf{G}_{\textbf{amp}}}$$

Typical values:

At $E =$ 10 keV, and $\textbf{G}_{\textbf{amp}} = 10^8$ Volts/Amp, measuring 1 V means 2×10^8 photons /sec.

Ion Chambers: . . . continued

The I_0 chamber should not absorb *all* the x-rays – $\sim\ 10\%$ is about right. For transmission measurements, the I chamber should absorb most of the x-rays. The fraction of x-rays absorbed can be changed with:

- **The length of the chamber**
- **The gas in the chamber (He, N_2, Ar, Kr, . . .), including mixing gases.**
- **The gas pressure.**

Of course the I_0 intensity hitting the sample is *not* the $N_{\text{photons}/\text{sec}}$ absorbed in the ion chamber. With I_0' *before* the ion chamber and I_0 *after* the ion chamber:

$$\begin{aligned} I_0 &= I_0' \exp[-\mu_{\text{gas}} t_{\text{chamber}}] \\ I_{\text{chamber}} &= I_0'(1 - \exp[-\mu_{\text{gas}} t_{\text{chamber}}]) \\ I_0 &= I_{\text{chamber}} \exp[-\mu_{\text{gas}} t_{\text{chamber}}]/(1 - \exp[-\mu_{\text{gas}} t_{\text{chamber}}]) \end{aligned}$$

Usually we're not that picky and use the measured I_{chamber} in place of I_0: This is off only by a simple scale factor that changes slowly (E^{-3}) with energy, and neglects the absorption by windows and air anyway.

Values for μ_{gas} are tabulated many places, and in the program HEPHAESTUS**.**

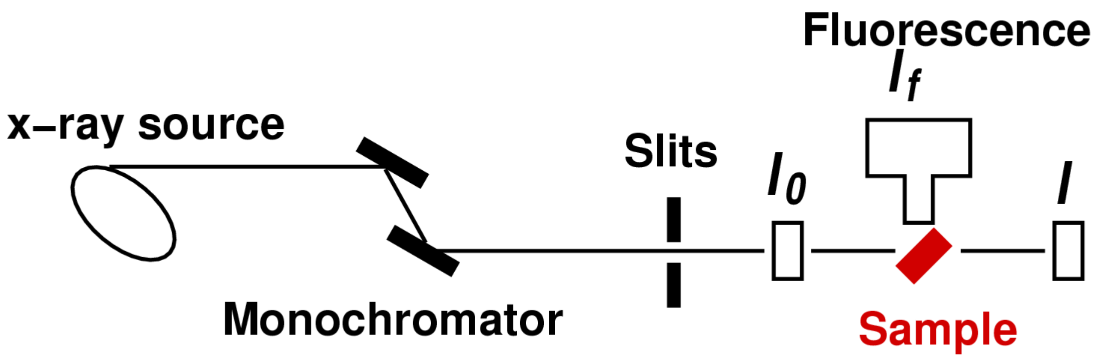
X-ray Absorption Measurements: The Experiment

Energy Scanning **The monochromator gives an energy-tunable x-ray source, so we can scan energy across the absorption edge. We'll scan from ~ 200 eV below to ~ 800 eV above the selected edge energy E_0, like this:**

Region	Starting Energy (eV)	Ending Energy (eV)	Step Size (eV)
Pre-edge	$E_0 - 200$	$E_0 - 20$	**5.0 – 10**
XANES	$E_0 - 20$	$E_0 + 30$	**0.25 – 1.0**
EXAFS	$E_0 + 30$	$E_0 + \sim 800$	**0.05 Å^{-1}**

- **In the EXAFS region, it's common to step in *k* rather than energy.**
- **Typical count times are 1 to 15 seconds per point, so that a spectrum is collected in 10 minutes to several hours (dilute samples take longer than concentrated samples!). Multiple sweeps is common.**
- **Very fast measurements (1 second for the whole spectra) can be made at specialized beamlines.**

X-ray Absorption Measurements: Transmission



For concentrated samples, XAFS is best measured in transmission.

But we need enough transmission through the sample to get a decent signal for I. The sample thickness t should be chosen so that $\mu(E)t \approx 2.5$ above the absorption edge and/or the edge step $\Delta\mu(E)t \approx 1$.

The sample must be uniform, and free of pinholes. For a powder, the grain size should not be bigger that an absorption length.

If a transmission measurement can be made, it is easy and gives excellent data. It's usually appropriate for compounds with element concentrations $>$ 10%.

X-ray Transmission Thicknesses

Typical X-ray Absorption Thicknesses (to give $t\Delta\mu = 1$):

material	edge	$1/\Delta\mu$ (μm)
Fe foil	Fe K	3.6
Fe_2O_3	Fe K	6.8
Pb foil	Pb L_{III}	5.5

An absorption length is very small. We need a uniform sample of these thicknesses, and free of pinholes. This is not always easy!

Calculating absorption lengths:

Absorption cross-sections $\sigma(E)$ are tabulated in the McMaster tables (online or book form) in barns/atom (1barn = 10^{-24}cm^2). From a material's chemical formula and density ρ (in gr/cm^3), an absorption length (in cm) is given by:

$$t = 1/\mu = \frac{1.66 \sum_i n_i M_i}{\rho \sum_i n_i \sigma_i(E)}$$

sums are over the elements i in the chemical formula, n_i the elemental stoichiometry , M_i is the atomic mass (in amu), and $\sigma_i(E)$ the cross-section.

Getting both $t\Delta\mu > 0.1$ and $t\mu < 4$ are important!

Calculating Absorption Lengths: Example

The thickness to give $t\Delta\mu = 1$ is

$$t = 1/\Delta\mu = \frac{1.66 \sum_i n_i M_i}{\rho \sum_i n_i [\sigma_i(E_+) - \sigma_i(E_-)]}$$

where E_+ and E_- are just above and below the edge energy.

Example: Fe_2O_3 at Fe K-edge (7112 eV).

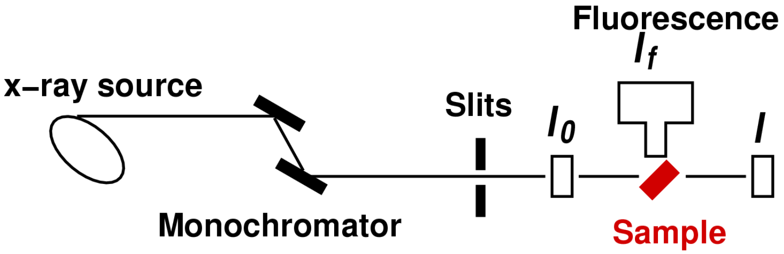
$M_{\text{Fe}} = 55.85$ amu, $M_{\text{O}} = 16.00$ amu, and $\rho = 6.00\,\text{gr}/\text{cm}^3$.

E (eV)	σ_{Fe} (barns/atom)	σ_{O} (barns/atom)
7150	37325	434
7100	4956	443
$\Delta\sigma$	32369	-9

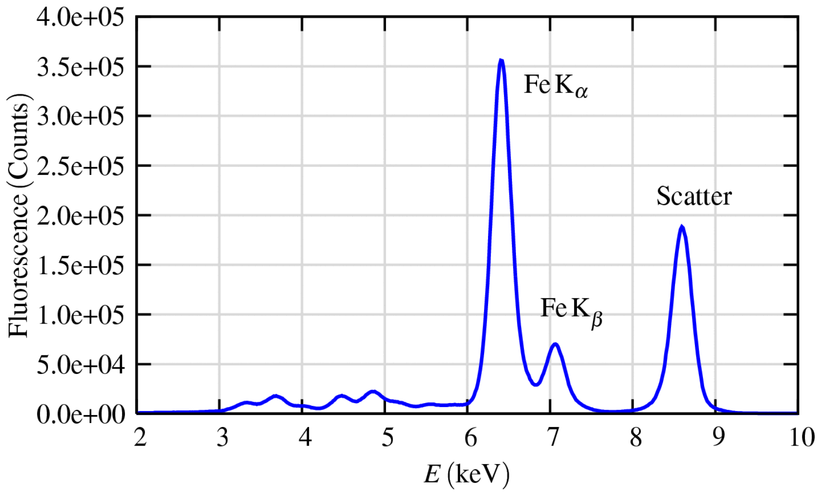
$$t = \frac{1.66(2 \cdot 55.85 + 3 \cdot 16)}{6.00(2 \cdot 32369 + 3 \cdot -9)}\,\text{cm} = 6.8 \times 10^{-4}\,\text{cm} = 6.8\mu\text{m}$$

These calculations can be done with the program HEPHAESTUS.

X-ray Absorption Measurements: Fluorescence



For low concentrations (10 wt. % to a few ppm), fluorescence is the preferred measurement mode.



X-rays emitted from the sample will include the fluorescence line of interest (here, both Fe K_α and Fe K_β) as well as *scattered* x-rays, and other fluorescence lines (here, Ca, Ti, and V).

Scattered x-rays include both *elastic* (at the same energy as the incident beam) and *inelastic* (e.g., Compton scattering) processes

For dilute samples, the fluorescence peaks of interest are much smaller than the scatter peak.

Fluorescence Measurement Considerations

There are two main considerations for fluorescence measurements:

Energy Discrimination either physically or electronically filter the unwanted portions of the fluorescence/scatter spectra.

Solid Angle fluorescence is emitted isotropically in all directions, so we collect as much of the solid angle as possible.

Fluorescence measurements are better when the samples are:

Uniform not as stringent as for transmission, but a uniform sample gives better data.

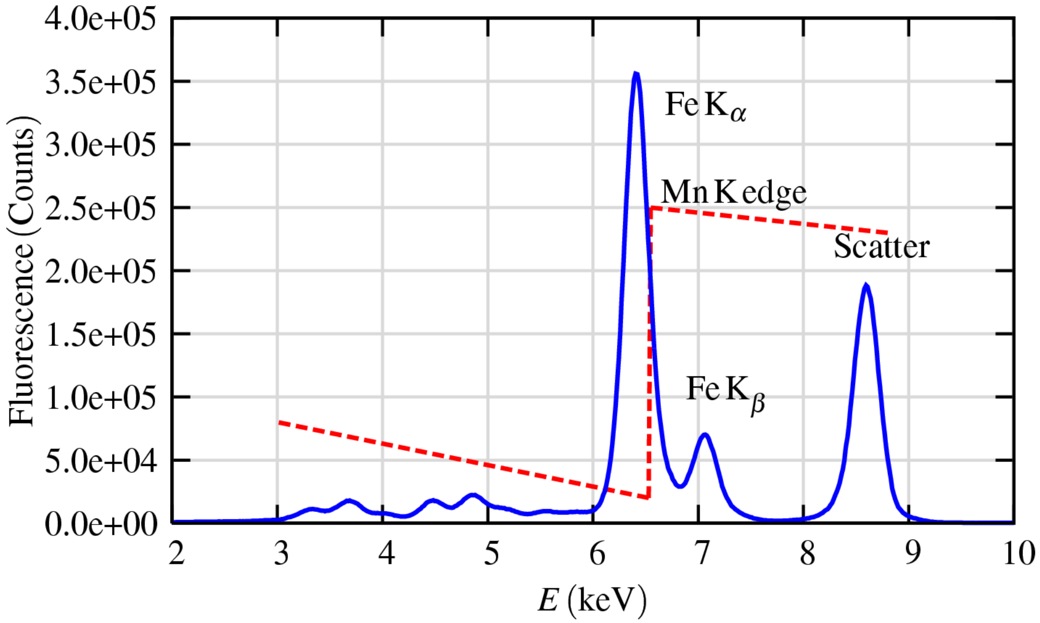
Thick, Dilute Samples The element of interest should be below $\sim$ 10 wt. % of the sample. Measurements are possible for more concentrated samples, but the data may need corrections.

Very Thin Sample Alternatively, the sample can be much thinner than one absorption length.

> The x-rays from a synchrotron are polarized in the horizontal plane. This means the elastic scattering is zero at 90° to the incident beam and in the horizontal plane. Putting the fluorescence detector there minimizes the "scatter peak".

Fluorescence Measurements: Z-1 Filter

A simple method of energy discrimination uses a *filter* of "Z-1" from the element of interest. For Fe, a Mn filter absorbs the scatter and Fe K_β line while passing the Fe K_α line.



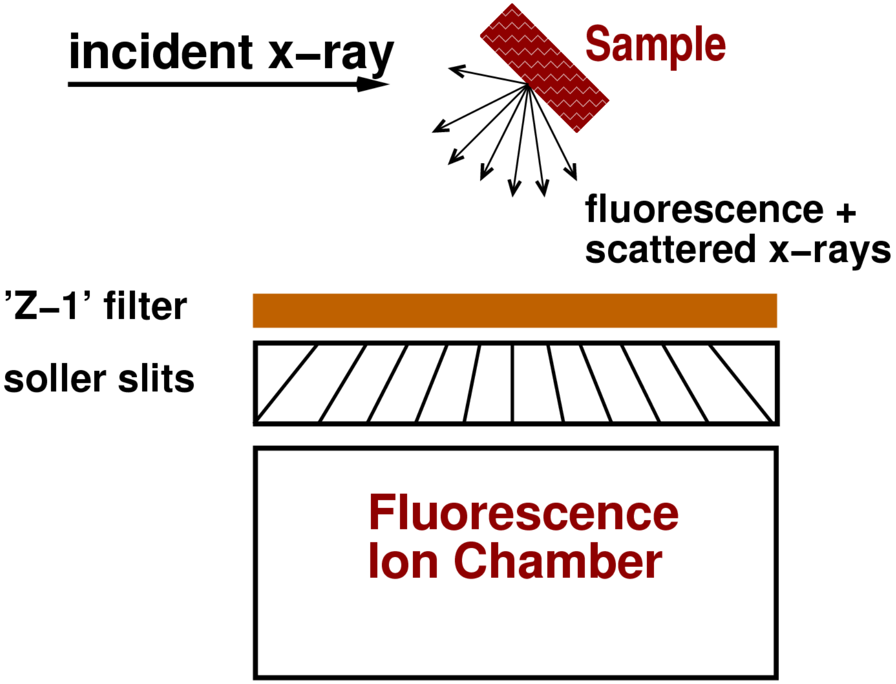
This method can be used with a detector without any energy resolution, such as a fluorescence ion chamber (aka Stern-Heald chamber or Lytle chamber).

Edge / Line	**Energy (eV)**	**Edge/Line**	**Energy (eV)**
Fe K_α	**6405**	**Fe K_β**	**7059**
Mn K edge	**6539**	**Fe K edge**	**7112**

Fluorescence Ion Chamber, Z-1 Filters, Soller Slits

A typical setup with a 'Z-1' filter uses an ion chamber which has no energy resolution, but high count rate and linearity.

Because the filter absorbs the scattered beam, it can itself re-radiate!!



A set of *Soller slits* can be used to see the sample, but absorb most of the re-radiate scatter from the filter.

This arrangement can be very effective especially when the signal is dominated by *scatter*, and when the concentration is at per cent levels.

Fluorescence Measurements: Solid-State Detectors

Another common fluorescence detector is a ***solid-state detector*** which uses Ge or Si as the x-ray absorber.

This works much like an ion chamber, but more current is created per x-ray, and the current moves quickly enough that each x-ray pulse can be detected individually (usually!).

This allows an electronic energy measurement of each x-ray, so that the ***XRF Spectra*** can be measured, which is useful for identifying other elements in the sample.

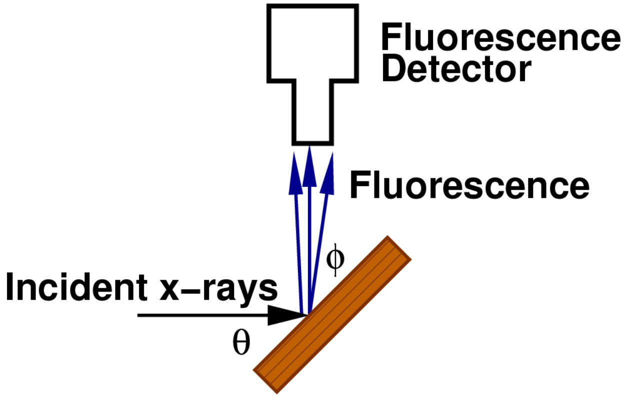
This can be used for XAFS measurements with concentrations down to 10's of ppm. This has many advantages, and a few drawbacks:

Dead time The electronic discrimination of energy saturates at $\sim 10^5$ Hz or so. Ten (or more) detectors are often used in parallel, but XAFS measurements are still often limited by these detectors.

Complicated Maintaining, setting up, and using one of these is more work than an ion chamber.

Fluorescence Measurements

The incident x-ray has to get in the sample, and the fluorescent x-ray has to get out of the sample. The measured fluorescence intensity goes as:



$$I_f = I_0 \frac{\epsilon \Delta\Omega}{4\pi} \, \frac{\mu_\chi(E)\left\{1 - e^{-[\mu_{\text{tot}}(E)/\sin\theta + \mu_{\text{tot}}(E_f)/\sin\phi]t}\right\}}{\mu_{\text{tot}}(E)/\sin\theta + \mu_{\text{tot}}(E_f)/\sin\phi}$$

for

ϵ	**fluorescence efficiency.**
$\Delta\Omega$	**solid angle of the detector.**
E_f	**energy of the fluorescent x-ray.**
$\mu_\chi(E)$	**absorption from the element of interest. (this is what we want!)**
$\mu_{\text{tot}}(E)$	***total* absorption in the sample:** $\mu_{\text{tot}}(E) = \mu_\chi(E) + \mu_{\text{other}}(E)$
θ	**incident angle (between incident x-ray and sample surface)**
ϕ	**exit angle (between fluoresced x-ray and sample surface)**

Fluorescence Measurements

$$I_f = I_0 \frac{\epsilon \Delta\Omega}{4\pi} \frac{\mu_\chi(E)\{1 - e^{-[\mu_{\text{tot}}(E)/\sin\theta + \mu_{\text{tot}}(E_f)/\sin\phi]t}\}}{\mu_{\text{tot}}(E)/\sin\theta + \mu_{\text{tot}}(E_f)/\sin\phi}$$

Thin Sample Limit: **($\mu t \ll 1$).**
The $1 - e^{-\mu t}$ term becomes $\approx [\mu_{\text{tot}}(E)/\sin\theta + \mu_{\text{tot}}(E_f)/\sin\phi]\, t$ (by a Taylor series expansion), which cancels the denominator, so that

$$I_f \approx I_0 \frac{\epsilon \Delta\Omega}{4\pi} \mu_\chi(E) t$$

Thick Sample Limit: **($\mu t \gg 1$), the exponential term goes to 0, and**

$$I_f = I_0 \frac{\epsilon \Delta\Omega}{4\pi} \frac{\mu_\chi(E)}{\mu_{\text{tot}}(E)/\sin\theta + \mu_{\text{tot}}(E_f)/\sin\phi}$$

Thick, Dilute Limit: **($\mu_\chi \ll \mu_{\text{other}}$, $\mu_\chi \ll \mu_{\text{tot}}$), and we can then also ignore the energy dependence of μ_{tot}, so that**

$$I_f \sim I_0 \mu_\chi(E)$$

These two limits (very thin or thick, dilute samples) are the best cases for fluorescence measurements.

Fluorescence Measurements: Self-Absorption

Thick Sample Limit: **($\mu t \gg 1$):**

$$I_f = I_0 \frac{\epsilon \Delta\Omega}{4\pi} \frac{\mu_\chi(E)}{\mu_{\text{tot}}(E)/\sin\theta + \mu_{\text{tot}}(E_f)/\sin\phi}$$

Thick, Concentrated Limit: **($\mu_\chi \sim \mu_{\text{other}}$, $\mu_\chi \sim \mu_{\text{tot}}$). We *cannot* ignore the energy dependence of μ_{tot}, and must correct for the oscillations in $\mu_{\text{tot}}(E)$.**

This is generally called *self-absorption* can dampen the XAFS – even completely wiping it out for highly concentrated elements.

For very concentrated samples, it's best to avoid this problem and measure transmission. For *moderately concentrated* samples, the self-absorption effects can be corrected.

Grazing Exit Limit: **($\phi \to 0$).**

One way to reduce the self-absorption effects is to rotate the sample so that it is normal to the incident beam.

With ϕ very small, so that $\mu_{\text{tot}}(E_f)/\sin\phi \gg \mu_{\text{tot}}(E)/\sin\theta$, and

$$I_f \approx I_0 \frac{\epsilon \Delta\Omega}{4\pi} \frac{\mu_\chi(E)}{\mu_{\text{tot}}(E_f)/\sin\phi}$$

which gets rid of the energy dependence of the denominator.

Should I measure Transmission or Fluorescence?

The choice of Transmission v. Fluorescence depends solely on the sample, and particularly the concentration of the element of interest.

Transmission Samples **Concentrated samples – element of interest is above $\sim$10 wt. %, and a thin enough sample can be made.**

Sample preparation is more stringent for transmission measurements than fluorescence measurements.

Fluorescence Samples **Dilute samples – element of interest is below $\sim$10 wt. %.**

For concentrated samples that cannot be made thin enough for transmission, use fluorescence, but pay attention to self-absorption effects and consider using grazing-exit geometry.

Also consider Electron Yield: Like fluorescence, but measures electron current emitted from the sample surface. This works best for metallic samples.

Because the electrons are emitted from a few 100Å from the surface, this is very *surface sensitive*, but is always in the *Thin Sample* limit, so there are no self-absorption effects.

Sample Preparation for XAFS

The Good News: **XAFS does not require a good single crystal, carbon coating, a dried sample, a large amount of material, or a particular isotope to work. In principle, it can be done on nearly any system.**

But, as we've just seen, there are *some* requirements for the samples.

Should I be worried that XAFS can't be done on my samples? ***No!***

Fluorescence measurements put very few restrictions on samples:

Fluorescence XAFS can be measured at concentrations of a few ppm to $\sim$ 10 wt. %. More dilute samples are very hard, especially in a heavy matrix. More concentrated samples may suffer self-absorption effects.

Transmission measurements require thin, uniform samples, without pinholes, and without particles that are much thicker than one absorption length.
We saw that Fe_2O_3 should be 6.8 μm thick!

How is this possible?

I'll show two common procedures for making transmission samples for powders.

Why are Pinholes so Bad?

With a typical x-ray beam size of 1 $\times$ 5 mm, why are a few pinholes or a few particles that are much thicker than 1 absorption length so bad?

***Because logarithms don't add*: $\ln(x+y) \neq \ln(x) + \ln(y)$**

The XAFS measurement integrates over the sample and beamsize:

$$\mu_{\textbf{measured}} = \ln\Big[\frac{\int dx dy I_0(x,y)}{\int dx dy I(x,y)}\Big]$$

If some area of the beam sees no sample, then $I(x,y) \approx I_0(x,y)$ for that area, and will have no XAFS oscillations. This reduces the measured variations in absorption, suppressing the XAFS.

Plus: $I_0(x,y)$ is not always spatially uniform, and the heretogeniety in $I_0(x,y)$ can change with energy. This will compound the problems of pinholes and overly-thick portions of the sample.

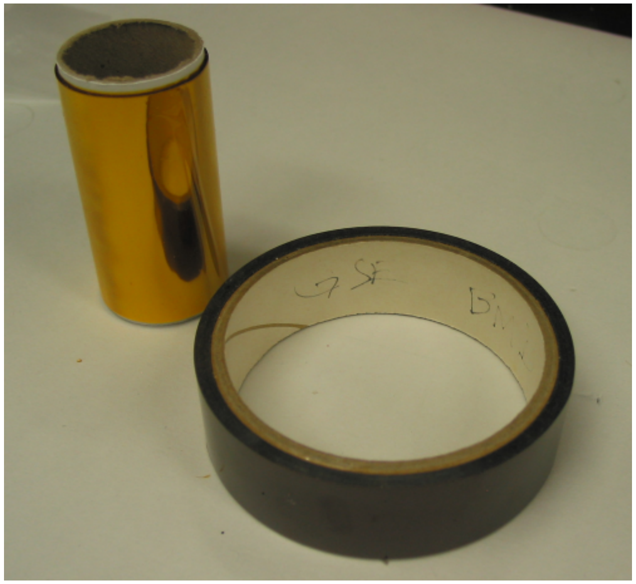
How do I know if I have pinholes?

Use the beamline slits to make a small beam (say 0.5 $\times$ 0.5 mm), and use the beamline sample stage to move the sample through the beam. Pick the are with the most uniform transmitted intensity.

Transmission XAFS Sample Preparation

First, this does not require great laboratory skills, but does require a mortar and pestle and *a lot of tape!*

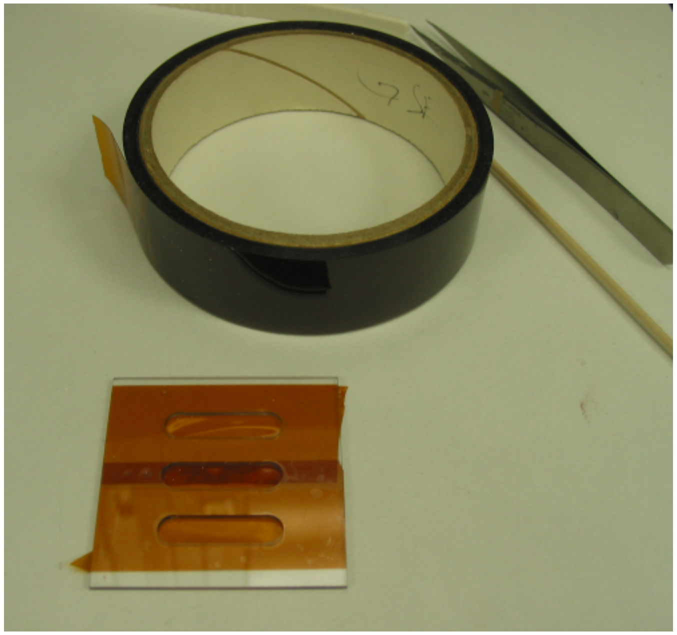
XAFS requires scotch tape, double-sided scotch tape, and Kapton® tape (the "duct tape of the synchrotron").



This plastic (polyimide) is strong and unusually radiation resistant. It comes in plain film (7 μm to 75 μm or thicker) and tape form.

Sample Preparation: Diluted Powder

We start with a blank sample holder with known dimensions, and cover one side with tape.

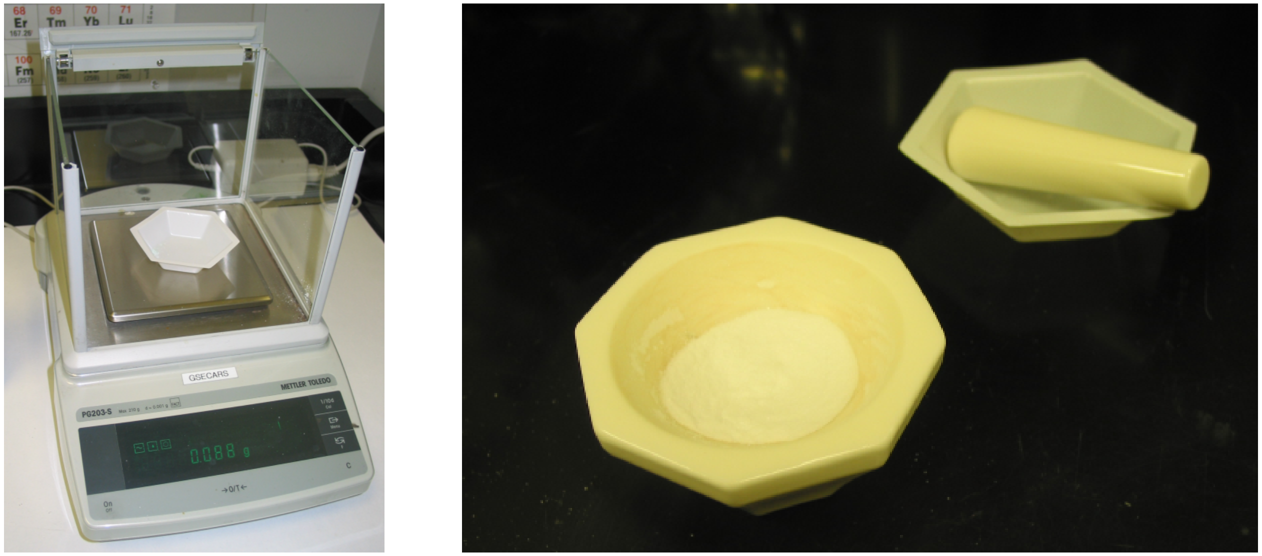


We calculate the necessary mass of material (from absorption thickness, sample holder cross-section, and sample density).

The powder should be ground to give very fine particle size ($< 1/\Delta\mu$!!). Many people use a sieve to separate particle sizes. A 400-mesh sieve has wires $\sim$ 37 μm apart. That's a good start, but not fine enough for most transmission XAFS samples.

Sample Preparation: Diluted Powder

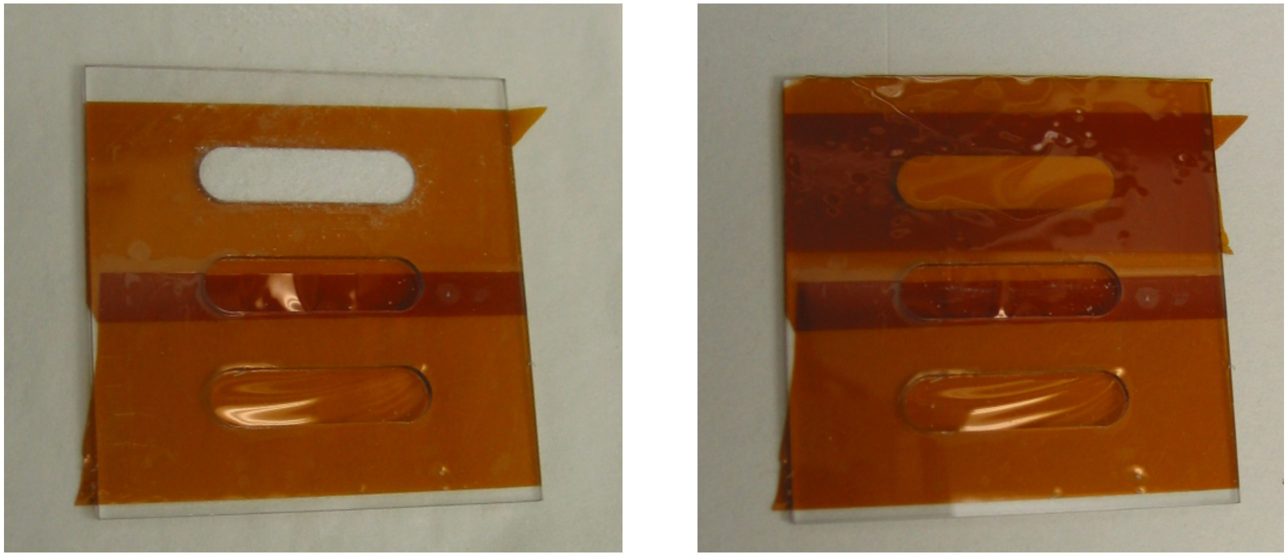
We dilute with a low-Z material (sugar, BN, graphite, $B(OH)_3$, duco cement, . . .) so the remaining volume of the sample holder is filled.



The sample and matrix are then ground together in a mortar and pestle and mixed thoroughly.

Sample Preparation: Diluted Powder

The sample holder is filled with the mixture, and sealed.



Personally, I don't use this method very often:

- **doesn't select fine particles – a very fine sieve might be needed.**
- **requires a very well mixed combination of sample and low-Z material (use color contrast if possible!)**
- **requires mass calculations and weighing, with mass ratios (mg sample :: grams matrix) that are difficult to achieve with good precision.**

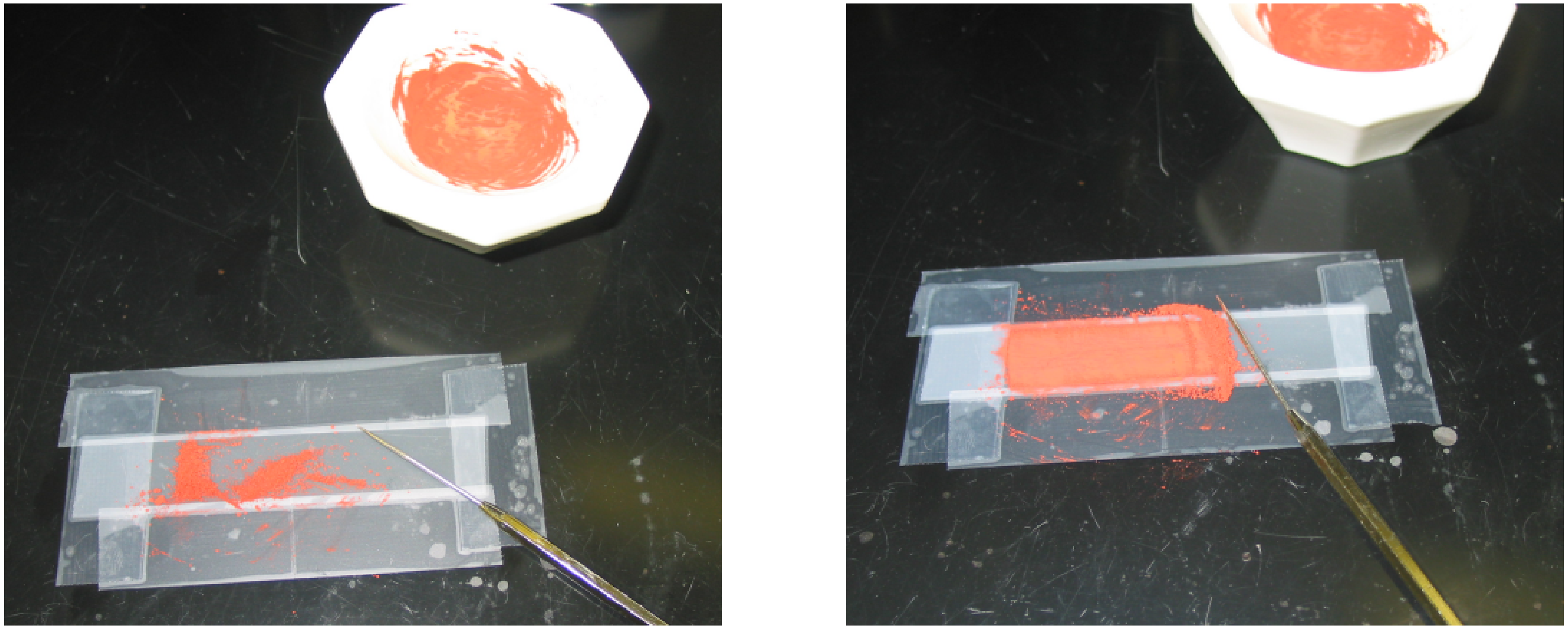
But: the precision doesn't need to be great. $0.2 < \Delta\mu t < 2.0$ **is usually OK, and I've seen some very good data from such samples.**

Sample Preparation: Powder on Tape

Here’s a method that works for me for most metal-oxides:

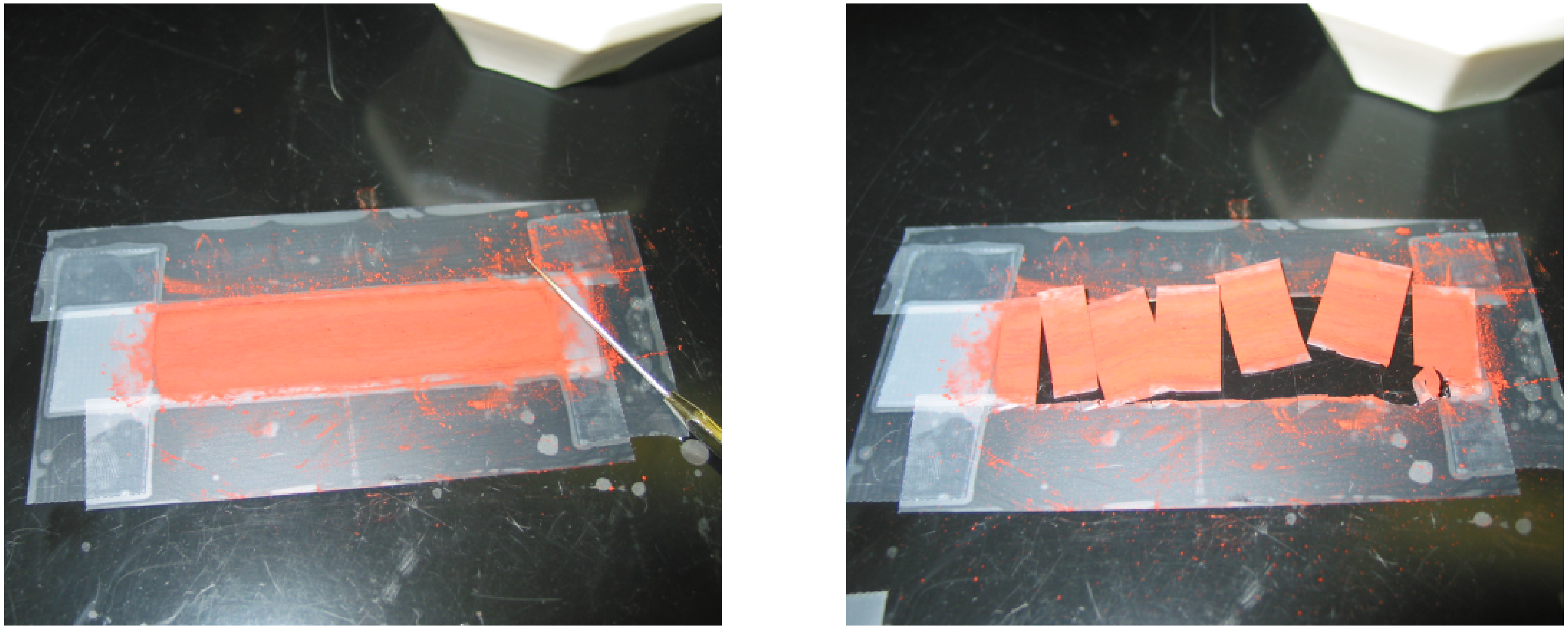
- **Start with powder material**
- **Grind with a mortar and pestle for a few minutes.**

Sample Preparation: Powder on Tape (2)



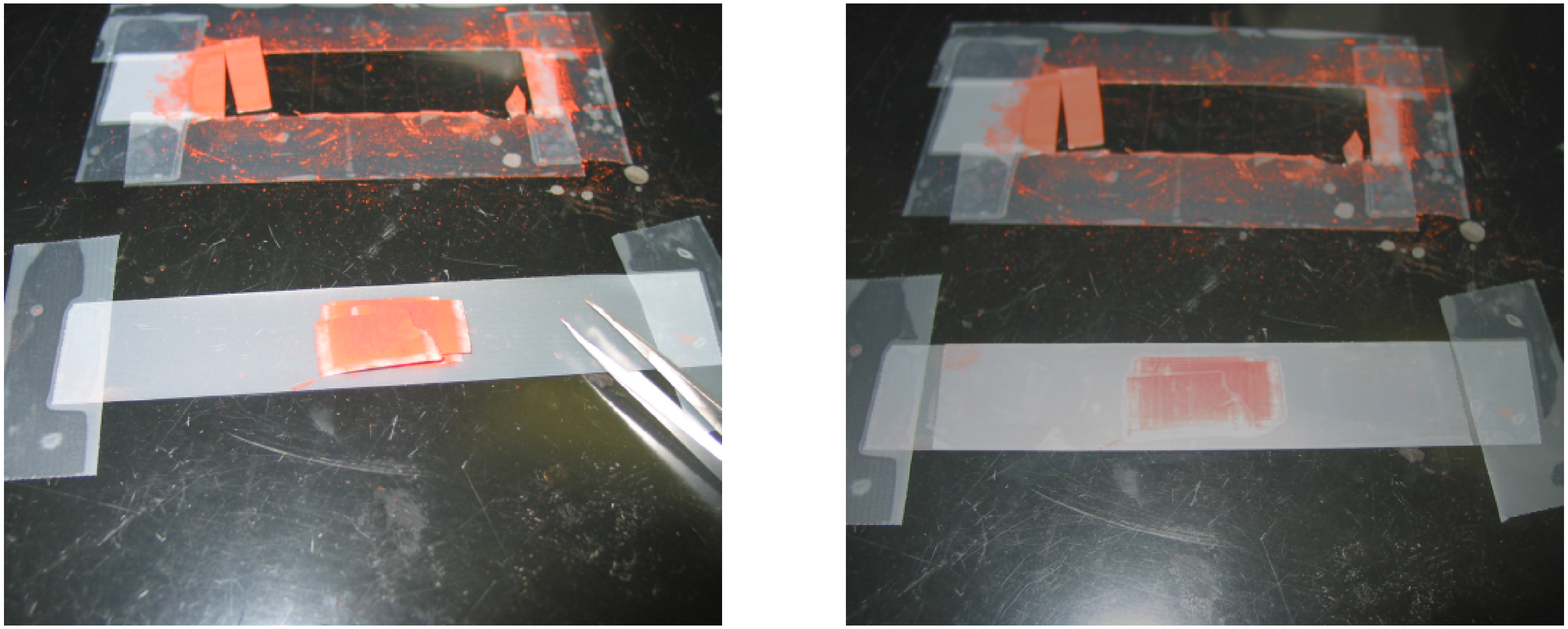
- **Place a piece of Scotch Tape sticky-side up on the bench, and tape it down, covering all four sides of the exposed tape.**
- ***Paint*** **the powder on the sticky tape. The smallest grains will stick to the tape, which is what you want – try to remove as much excess as you can, so that there are few large particles.**

Sample Preparation: Powder on Tape (3)



- **finish painting the sample on the tape**
- **cut tape into small pieces.**

Sample Preparation: Powder on Tape (4)



- **place another piece of tape on the bench, sticky-side up.**
- **move small pieces of painted sample onto tape, stacking 4 to 8 layers.**
- **cover with another piece of tape**

This method works great for metal oxides and other powders needed for EXAFS and XANES standards.
It can be done in a glove box, but samples in scotch tape can still react with air.

Sample Preparation: Other Approaches

Don't be afraid to try new sample preparation techniques, or even none at all! You can usually let your sample dictate the preparation and measurement method.

Aqueous solutions often make great fluorescence samples – uniformity is not an issue!! Here's a standard XRF liquid sample cup used to measure XANES on a $\sim$ 100 ppm Hg in solution:

Other sample preparation techniques include:

- **pressing samples into pellets**
- **mixing with duco cement or epoxy.**
- **using carbon-coated polished samples straight from a TEM.**

XAFS Measurements in Non-Ambient Conditions

Finally, XAFS can be measured in a wide range of sample environments and conditions:

- **at low temperature**
- **at high temperature**
- **at high pressure**
- **in a electro-magnetic field**
- **under ultra-high vacuum**
- **in a wet cell or hydrated environment**
- **in an electrochemical cell or other *in situ* environments.**
- **at shallow *incident angle* to be surface-sensitive.**
- **with a micro-beam**
- **with a timing gate, and laser pump-probe**

Many of these conditions and methods will put more constraints on the sample preparations than EXAFS will by itself.