Designing and Executing an XAFS Experiment

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Steps in a successful experiment

- Initial considerations:
  - Is XAFS the right choice?
  - Is the experiment feasible?
- What is the best measurement method?
- Making samples
- Taking data – recognizing problems
- Analyzing and interpreting the data

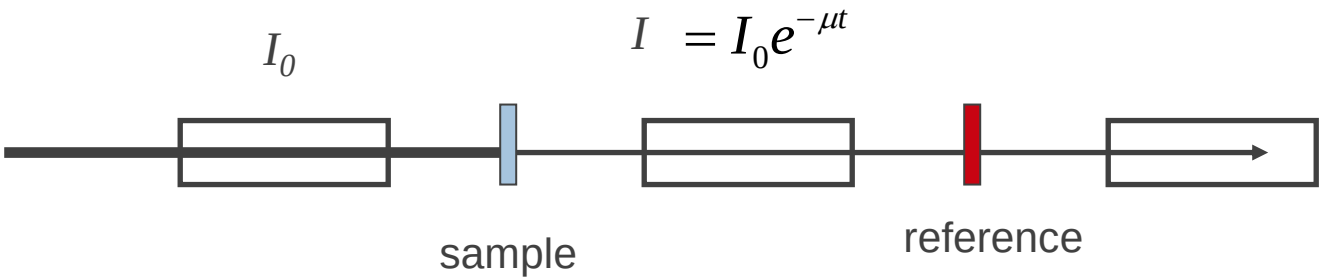
S/N requirements

3 typical measurement regimes: $S/N = \sqrt{\text{detected counts}}$

- Detection of element (imaging)
  - S/N > 10 (>100 counts per point (pixel))
  - 10^4 data points
- Near edge measurements
  - S/N > 100 (>10,000 counts per point)
  - 50-100 data points
- Extended fine structure (EXAFS)
  - S/N > 1000 (>10^6 counts per point)
  - 100-300 data points

Any background will increase the needed counts since signal now only a fraction of the total counts

Transmission measurements



$$\mu t = -\ln(I / I_0) = \ln(I_0 / I)$$

Optimum for measuring changes in μt from statistics:

μt = 2.6 I_0 has 24% absorption

Practical optimum

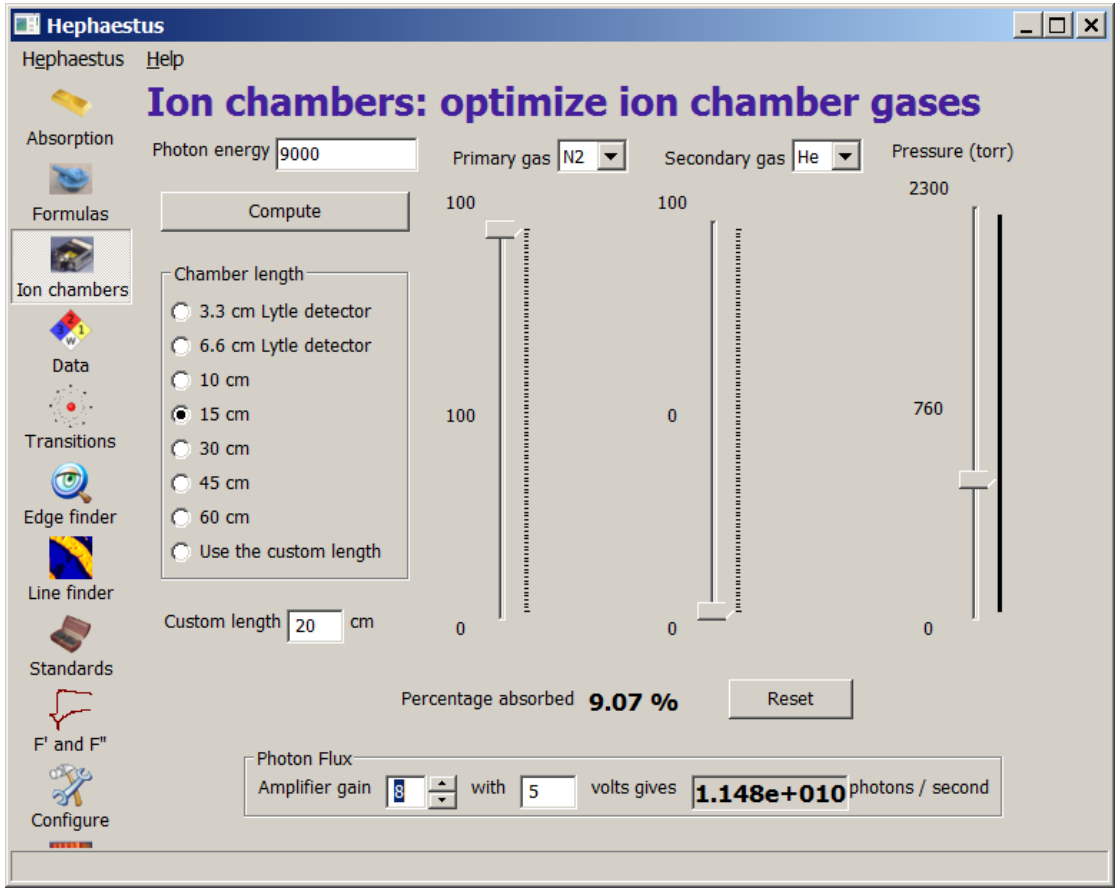
μt = ~1.5 (concentrated samples), I_0 absorption 10-30%

Signal to noise limit ~10^4 , limited by electronics

Once ion chamber signals > few namps electronic noise starts to dominate

Typical ion chamber becomes non-linear at 10-20 namp/cm

Hephaestus to optimize ion chambers



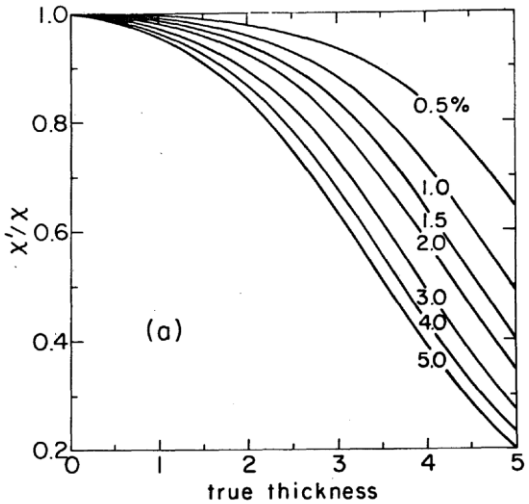
Can also use it to calculate the beam flux

Thickness effects

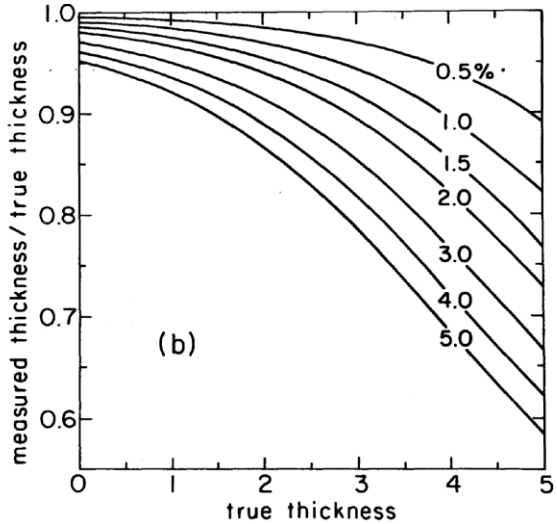
Transmission signal can be distorted by leakage of beam past or through the sample

- Pinholes
- Harmonics in the beam
- Part of beam missing the sample

EXAFS



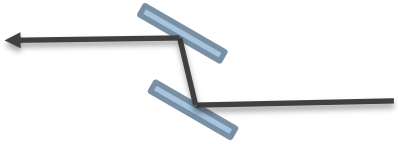
XANES

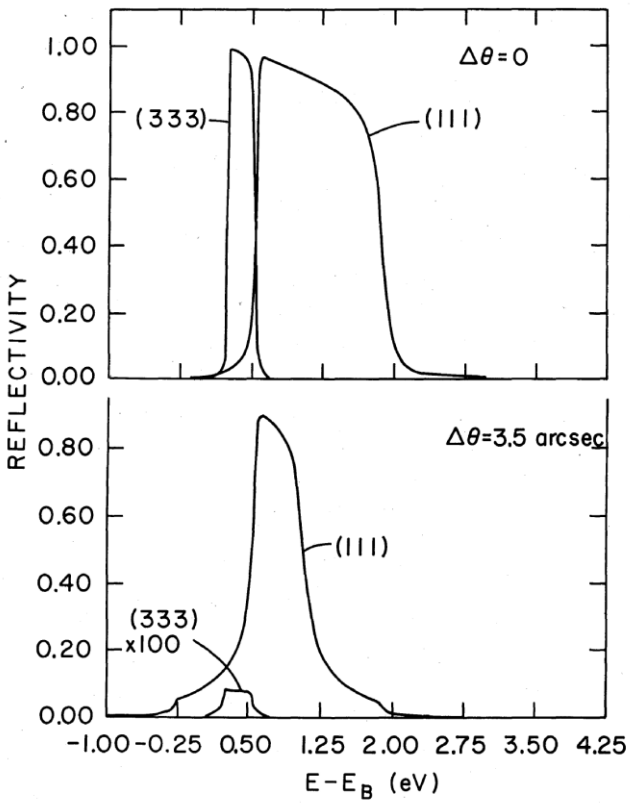


If thickness effects suspected should measure sample with two different thicknesses

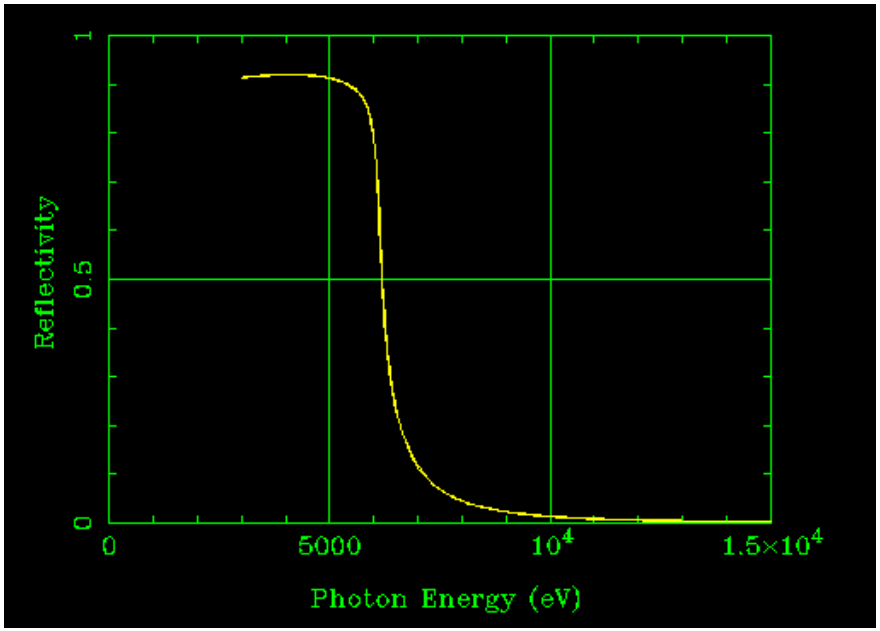
Harmonics

Harmonics are a common form of leakage, especially when the sample is thick. They can be reduced by detuning or a harmonic rejecting mirror.





SiO_2 5 mrad



$E_c \approx 67(\text{keV})/\theta(\text{mrad})$ Rh

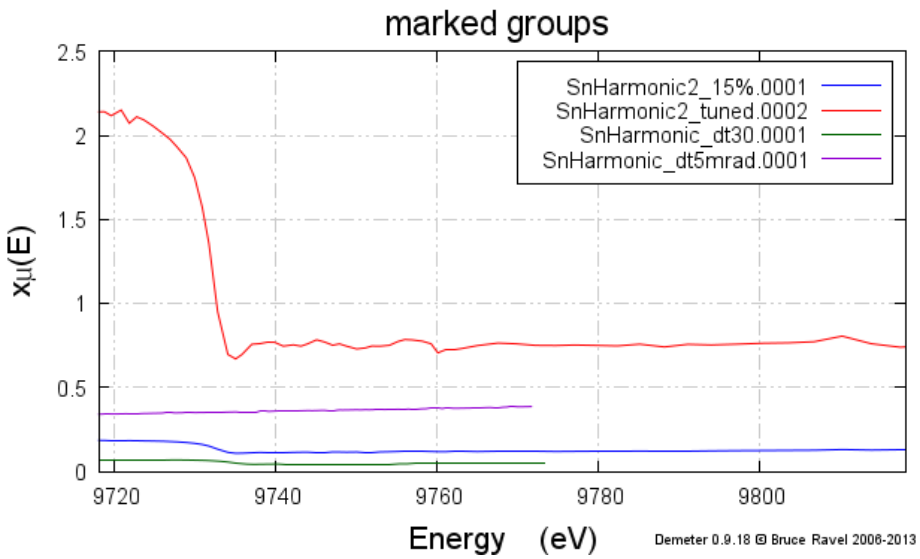
$\approx 84/\theta$ Pt

$\approx 32/\theta$ Si

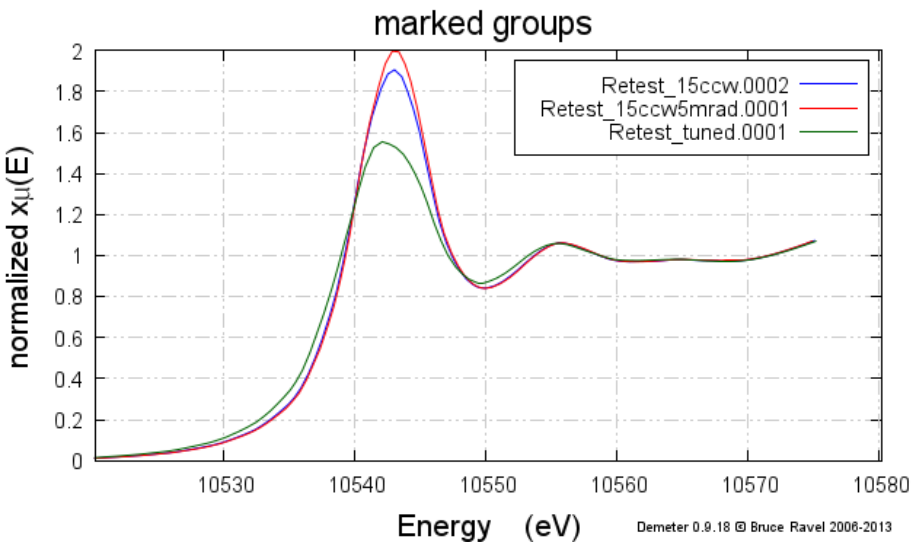
See http://henke.lbl.gov/optical_constants/

Harmonics at the APS

Sn foil (edge energy 29200 eV)

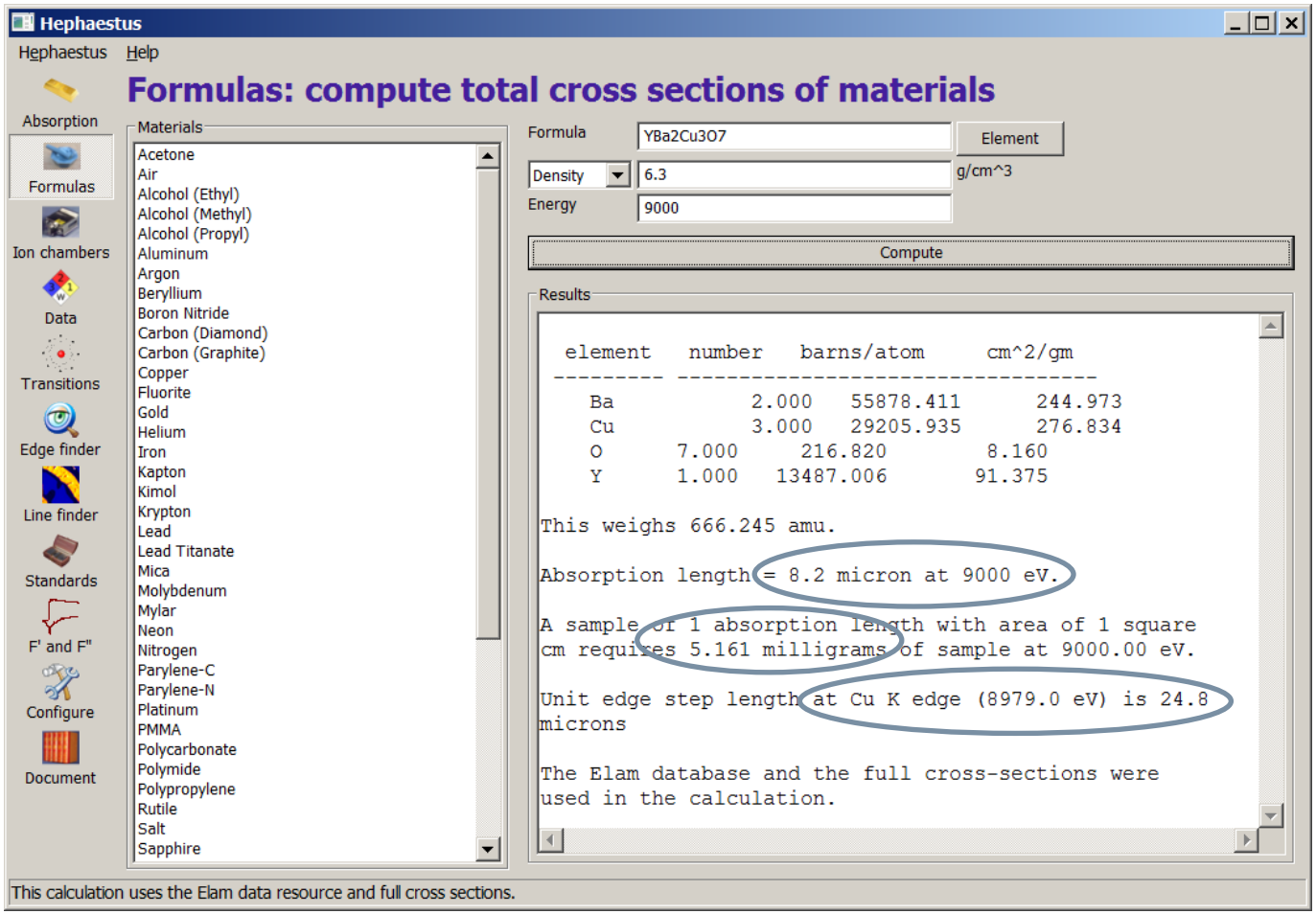


Rhenium sample – edge step ~1.5



3rd Harmonic ~5% of fundamental at 10 keV when mono tuned

Calculating sample thickness - Hephaestus



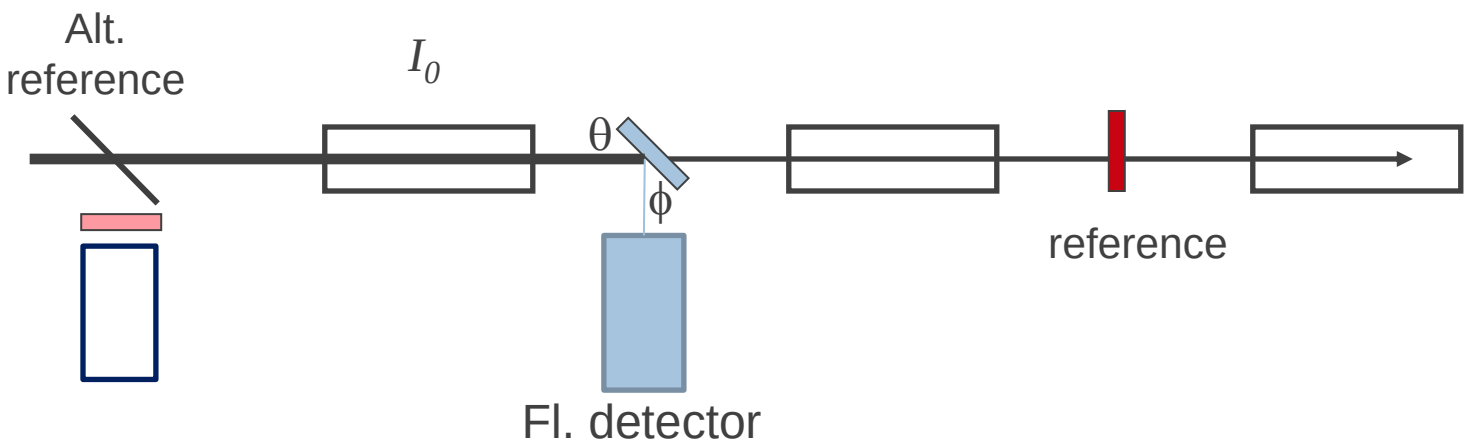
Total absorption

Amount of sample per cm^2

Absorption at Cu edge

In this case choosing $\Delta\mu t = 1$ at Cu edge would result in a thick sample, $\mu_t = 3$

Fluorescence Detection



For thick sample

$$\mu'(E) = \frac{I_f}{I_0} = \frac{\mu(E)\sin(\theta)}{\mu_t(E)/\sin\theta + u_t(E_f)/\sin\varphi}$$

μ_t - total absorption of sample ($\mu + \mu_{matrix}$)

Fluorescence detection - cont.

Typical case $\sin\theta = \sin\phi = 45$

Dilute sample: $\mu \ll \mu_{matrix}$

$$\frac{I_f}{I_0} = \frac{\mu(E)}{\mu_{matrix}(E) + \mu_{matrix}(E_f)}$$

Denominator almost constant

Concentrated sample: $\mu \sim \mu_{matrix}$

(self absorption)

$$\frac{I_f}{I_0} = \frac{\mu(E)}{\mu(E) + \mu(E_f)}$$

For K edge: $\mu(E_f) \approx \mu(E)/8$

Thin concentrated sample: absorption of x-rays entering and exiting sample are negligible

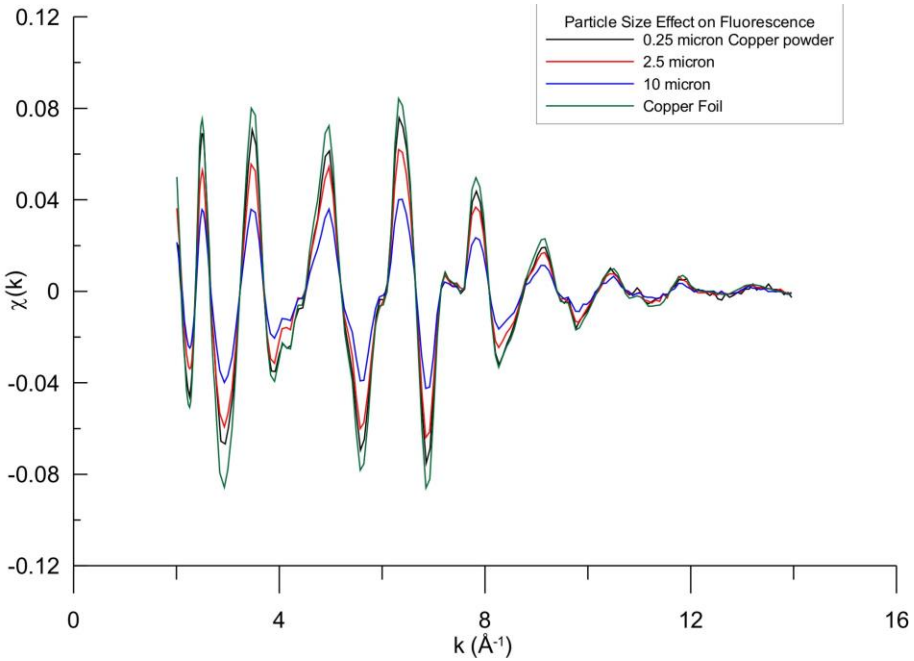
$$\frac{I_f}{I_0} \approx \mu(E)$$

Glancing exit angle: $\sin\phi \ll 1$

$$\frac{I_f}{I_0} \propto \frac{\mu(E)}{\mu_{matrix}(E_f)}$$

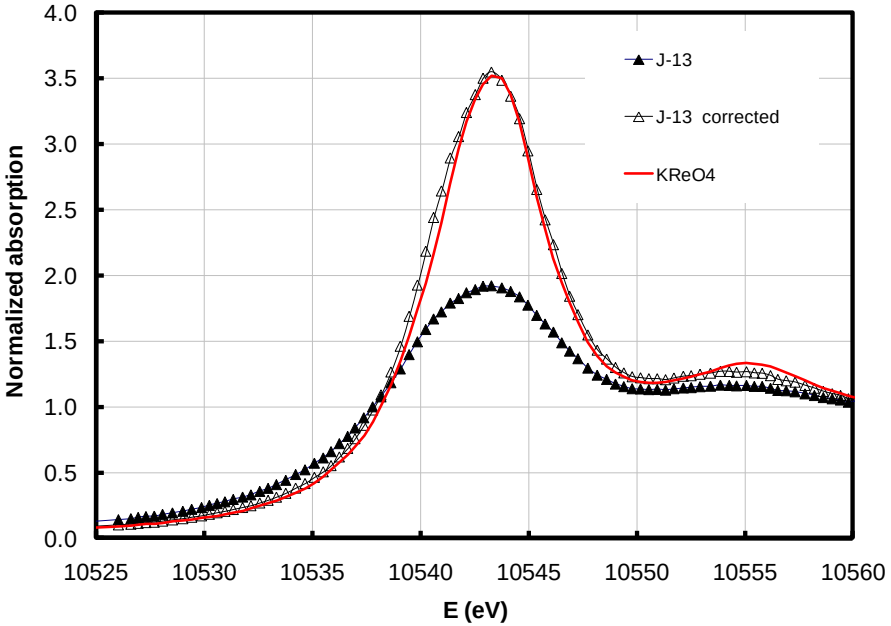
Self absorption

Cu metal



Data from R. Gordon

Re near edge



Fluorescence Detection - effective counting rate

For dilute samples fluorescence count rate, *N*, is accompanied by large background, N_b

With no background discrimination the noise becomes, $\sqrt{N + N_b} = \sqrt{N}\sqrt{1 + {N_b}/{N}}$

which is $\sqrt{1 + {N_b}/{N}}$ larger.

Typical case: 1mmol Fe in solution - N_b ~ 20*N

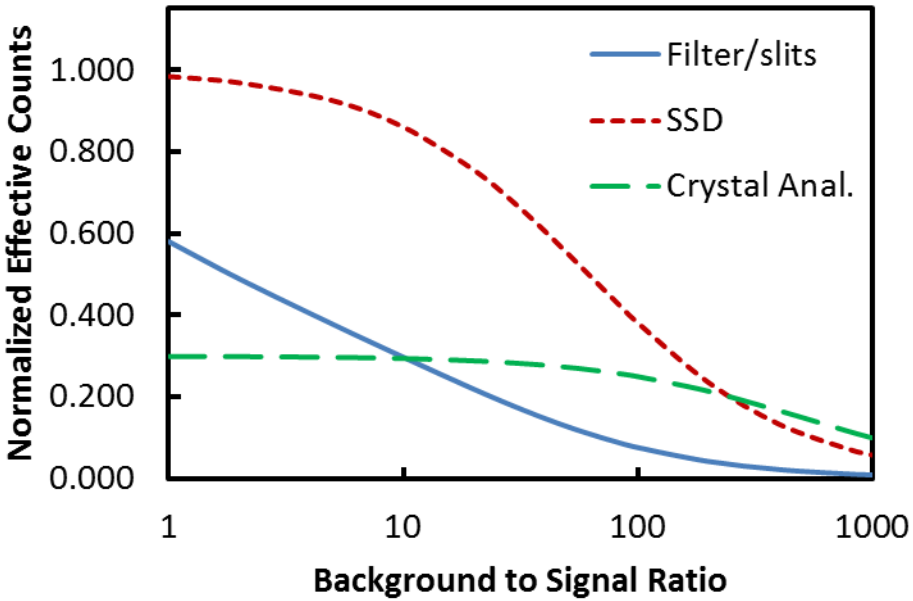
Some detectors (ie solid state) have good background discrimination but limited count rates

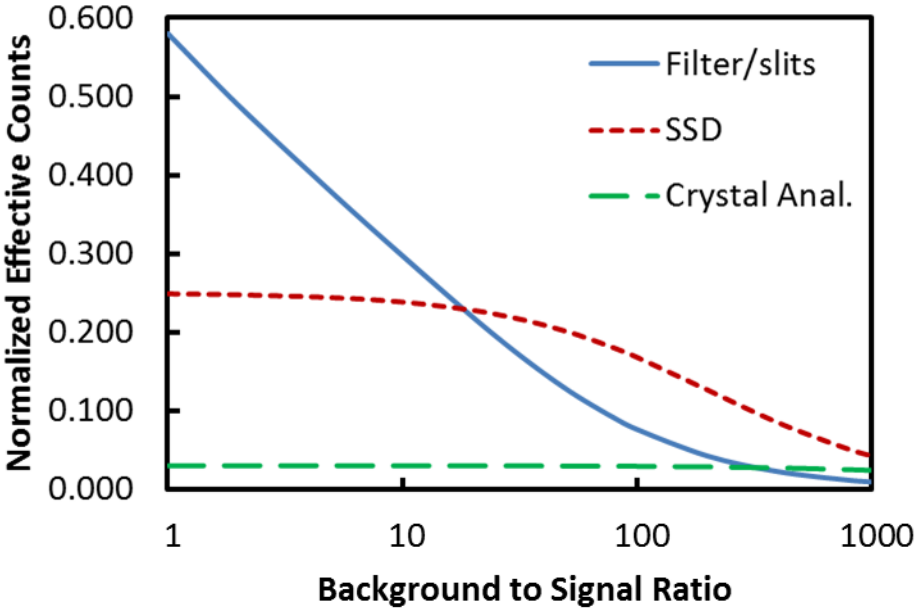
Other detectors (ie filter-slit) have large collection efficiency but poorer background elimination

Comparison of detectors using the effective counting rate

Equal solid angles with typical background discrimination and crystal efficiency of 30%

Filter with 5x solid angle of SSD and 10X of crystal analyzer.





Normalized counts are **effective counting rates/N** for largest solid angle

Fluorescence or transmission?

From statistics – $\Delta\mu x < 0.05 – 0.1$ fluorescence generally better

Many factors can influence this

- monochromator glitches
- sample uniformity
- other fluorescence lines
- difficulty in making thin sample

Often can measure both simultaneously and choose the best one

Other measurement techniques - electron yield

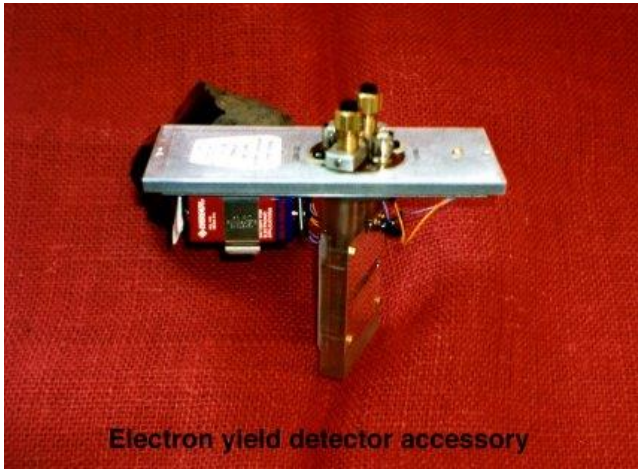
Electron yield – typically measure the total electron yield either in vacuum or using a conversion gas such as He

Surface sensitive – typically 100 nm

electron mean free path very small
similar to having $\mu(E_f)$ very large in fluor.

$$\frac{I_e}{I_0} \propto \frac{\mu(E)}{\mu_e}$$

Conversion gas can give a large gain (50-100x) in current



Electron yield - applications

Excellent choice for concentrated samples difficult to measure by transmission

Thick substrates

Low energies such as S K edge (2.47 keV)

Thin films – especially transition metal L edges or 1st row elements

Surface layers

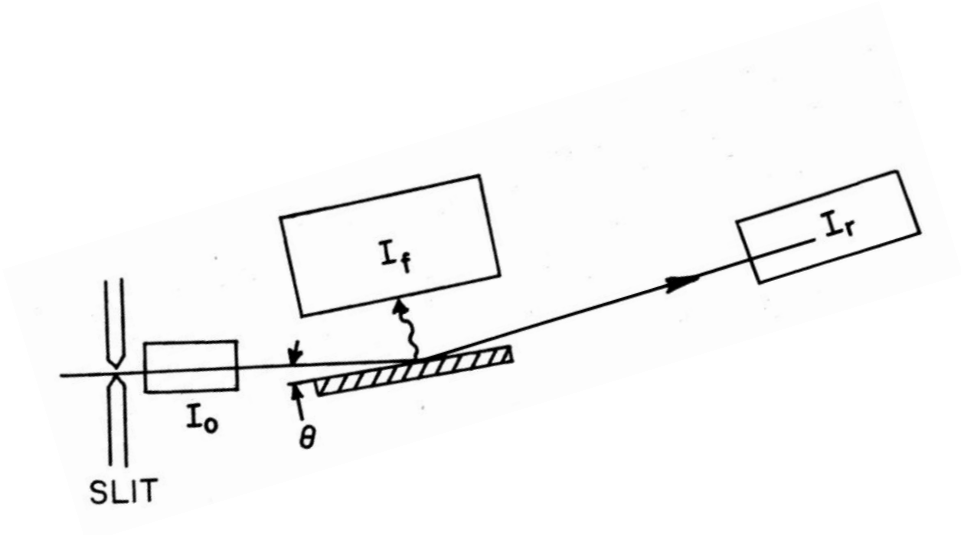
Not a good choice for dilute samples since no background discrimination

Glancing angle detection

Small angles can enhance signal from thin film – signal increased by 1/sin(θ)

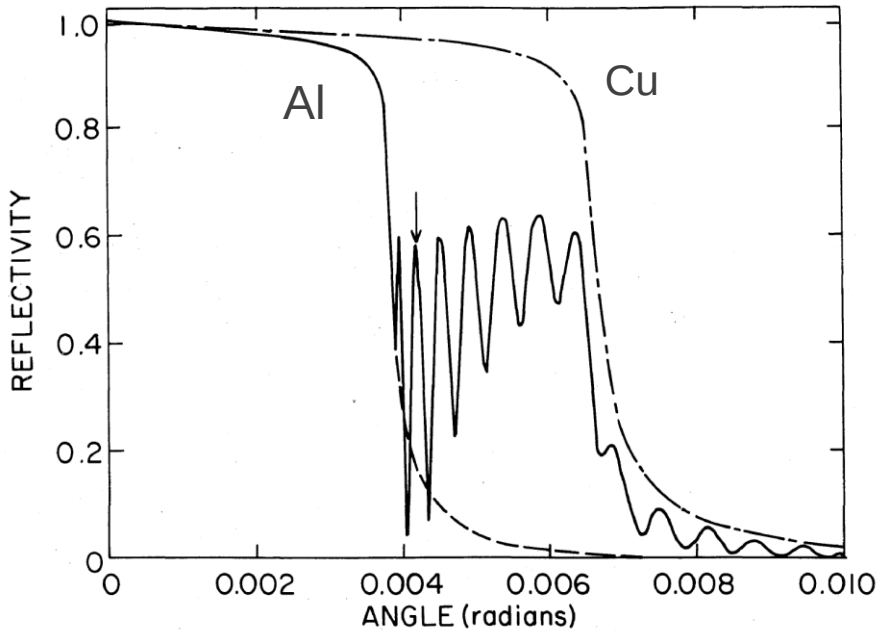
Need large sample and/or small beam

In total reflection mode can limit x-ray penetration to surface or interface region

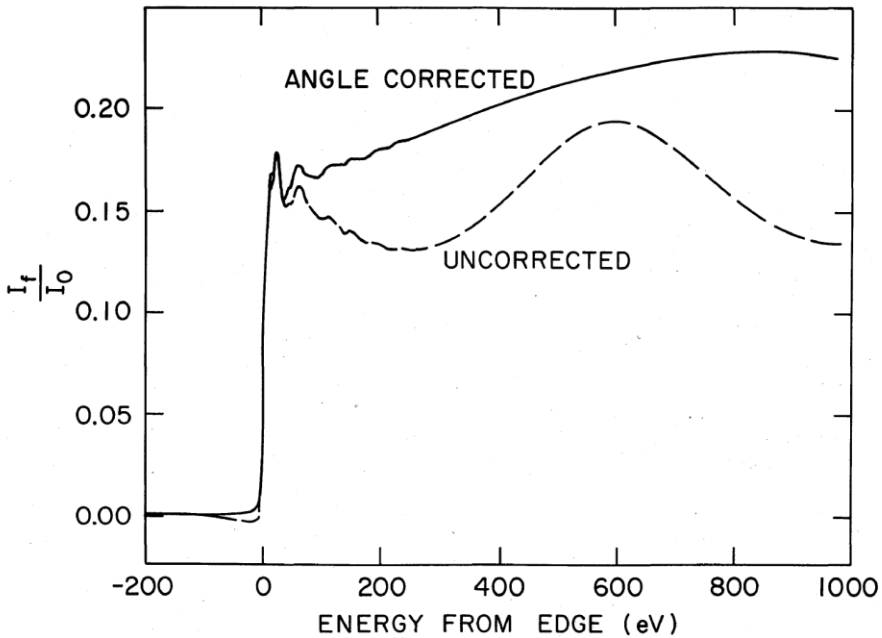


Application to buried interfaces

100 nm Al on Cu

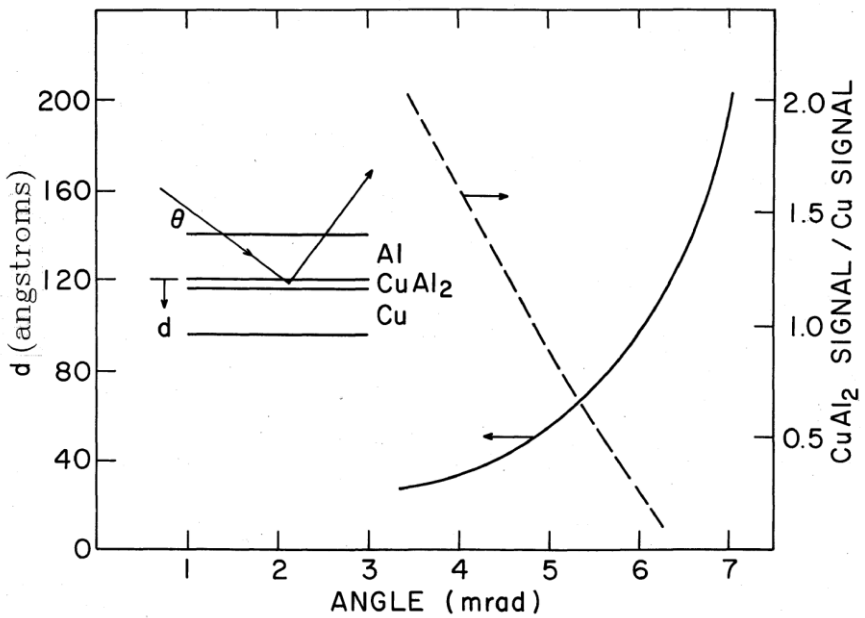


EXAFS from interface

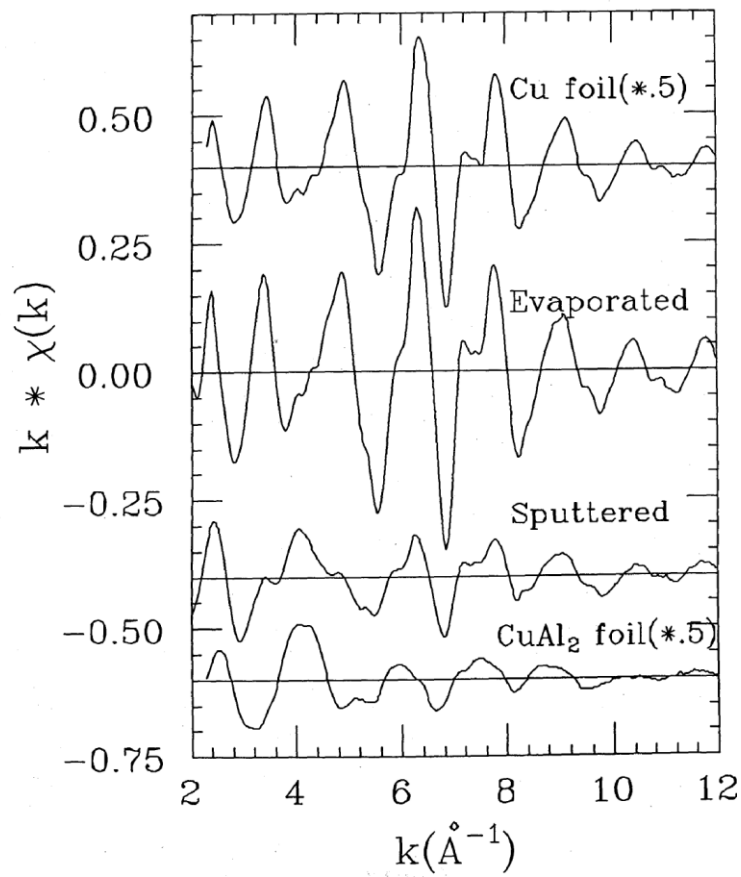


$CuAl_2$ formed at interface

Sensitivity to 5 nm $CuAl_2$



EXAFS from interface



Making samples - initial considerations

Concentration – transmission or fluorescence?

Low or high temperature

Other conditions – anaerobic?

Hazard level – is containment necessary?

Note: containment will increase background absorption

Typical particle sizes

	$\mu x=1$
FeS_2 (pyrite)	1.3 microns (S edge)
Fe_2O_3	0.3 (O edge)
Fe_2O_3	6.7 (Fe edge)
GeO_2	20
U_3O_8	13

Need a fraction of these sizes for a uniform sample

Difficult to get much ground powder through less than 400 mesh

Often fine particles will stick together

Sieve sizes

Mesh	Micron	Inches
4	4760	0.185
6	3360	0.131
8	2380	0.093
12	1680	0.065
16	1190	0.046
20	840	0.0328
30	590	0.0232
40	420	0.0164
50	297	0.0116
60	250	0.0097
70	210	0.0082
80	177	0.0069
100	149	0.0058
140	105	0.0041
200	74	0.0029
230	62	0.0023
270	53	0.0021
325	44	0.0017
400	37	0.0015
625	20	0.0008
1250	10	0.0004
2500	5	0.0002

Fine powders from sedimentation

Can further refine sieved powders by sedimentation methods

Suspend powders in suitable liquid and allow them to settle out

The coarse particles will settle first and the fine particles can be captured by drawing off the liquid before they settle out

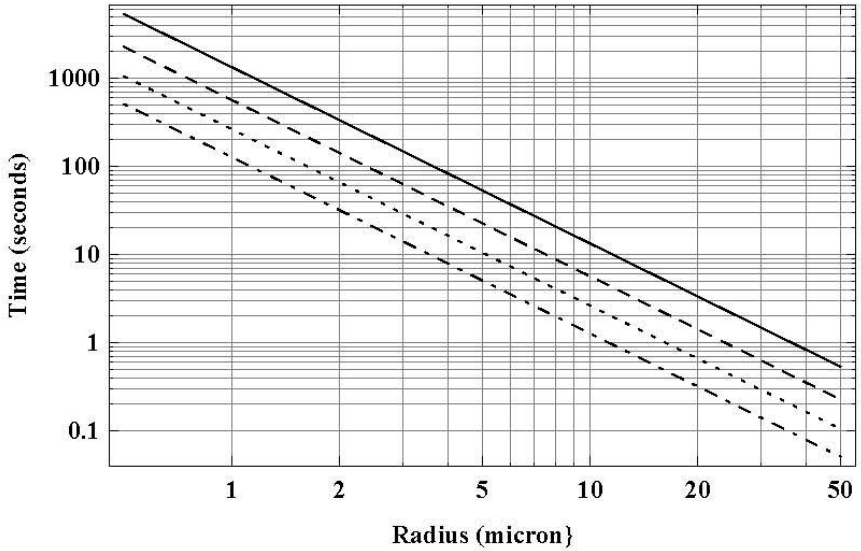


Fig. 3.28. Sedimentation time in acetone at 20° C vs radius and particle density, 5 cm drop height. Solid line: $\rho = 3\text{g/cm}^3$; Dashed line: $\rho = 6\text{g/cm}^3$; Dotted line: $\rho = 12\text{g/cm}^3$; Dot-Dashed line: $\rho = 24\text{g/cm}^3$.

From Grant's book

Making samples – powder on tape

Place fine powder on sticky tape and **rub vigorously** for even distribution
Scotch magic or kapton (acrylic adhesive) are good choices

Advantages

- Simple
- Rubbing breaks up particle clumps and selects finer particles (400 mesh may be good enough)
- Using several tape layers results in homogeneous final sample

Disadvantages

- Single layer may be too thick or thin – one or two layers may not be uniform enough or if too many layers needed the tape absorption may be excessive
- Not good for lower energies where tape absorption excessive
- Tape can have impurities (e.g. Ti in Scotch magic)

Making samples - pressed pellets

Mix measured amounts of sample and binder

Can calculate the amount of material from pellet area

Common binders: graphite, BN or other low absorption materials

Can use ball mill to ensure even mixing

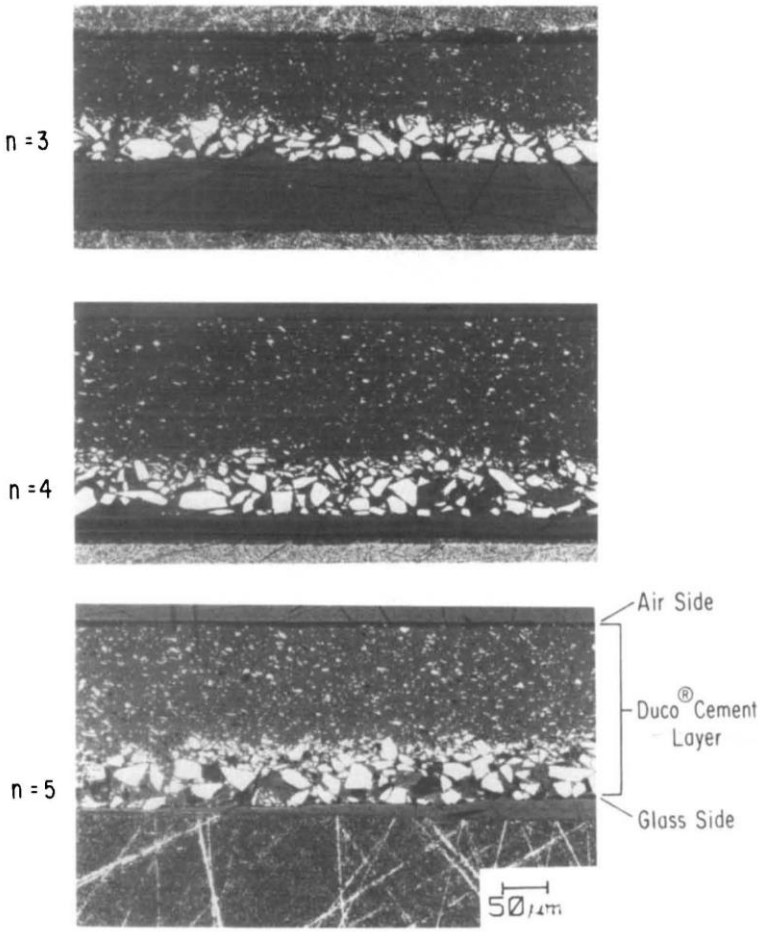
Press into self supporting pellet

Need well dispersed fine powders – often find $\Delta\mu x$ is less than expected

Making samples – other methods

Cast in epoxy or Duco cement
need to check chemical compatibility

Capture on filter paper
good for very fine particles suspended in liquid



Wong, NIM 224, 303 (1984)

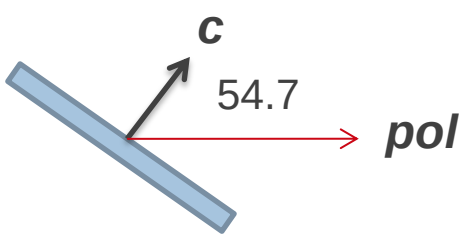
Sample orientation

Samples can be oriented unintentionally if particles are asymmetric such as platelets

Rubbing on tape or pressing pellets can partially orient them making analysis difficult – what is the amount of orientation?

Good test is to measure sample with different orientations – since this generally changes sample thickness it is also a good test for thickness effects

Typical case c-axis aligned



signal proportional to $\cos^2\theta$

Want $\cos^2\theta = 1/3$ or $\theta = 54.7$

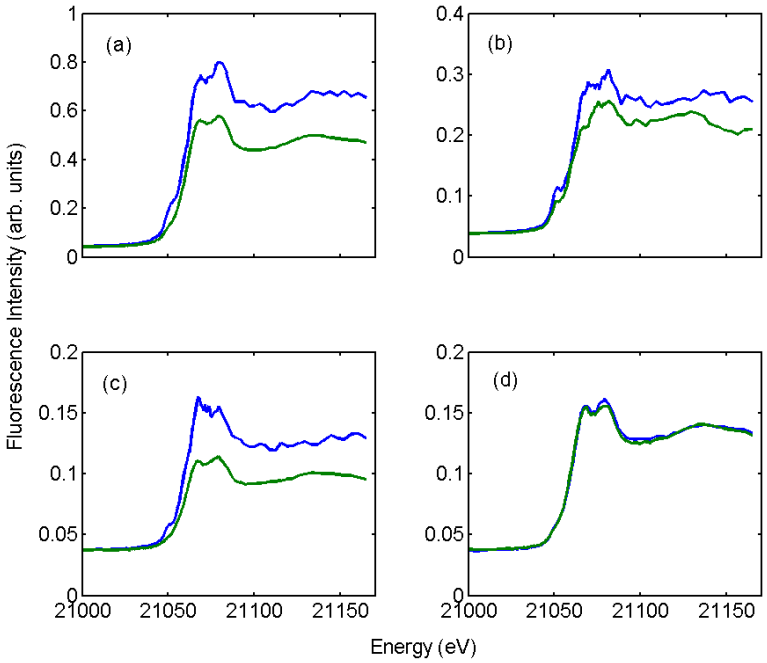
If suspect ***a*** and ***b*** axes also aligned, can spin sample

Radiation damage

Beam can change the sample – especially for wet samples

- Low temperatures
- Flowing solutions
- Fast scans of different regions
- Sample spinner

MicroXAFS of Tc containing particles



Blue first scan
Green last scan

Pertechnetate tends to leave beam spot

Micro-XAFS samples

Thin sections preferred

beam can penetrate degrading resolution

beam can see parts of the samples not visible optically

Be careful of substrate – glass has many impurities

Radiation damage enhanced by concentrated beam

For EXAFS measurements search for uniform regions

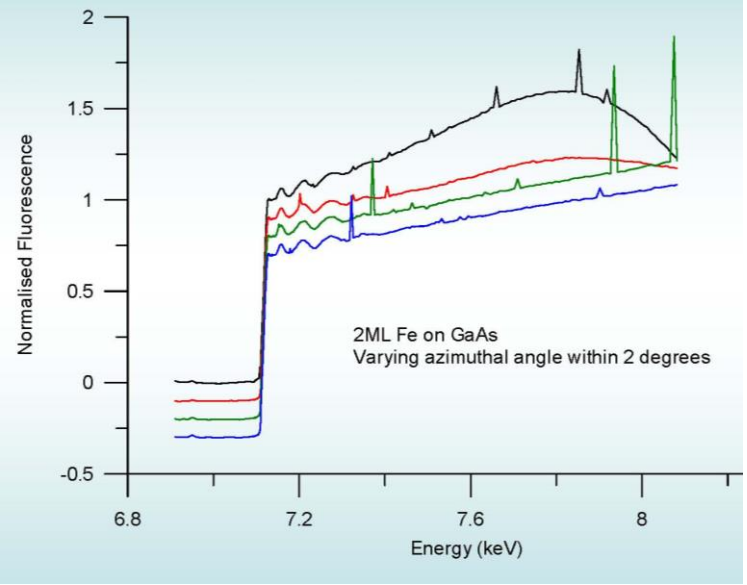
A 2 μm beam on a 2 μm particle generally requires unobtainable beam stability (10^{-3} implies 2nm)

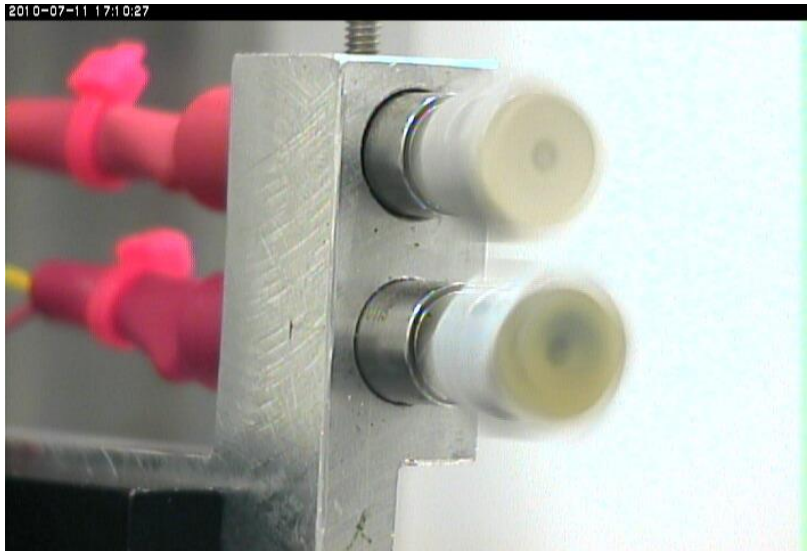
Single crystal samples

Bragg peaks!

Can search for best orientation or try to splice different orientations together

Spinning sample can help -
If combine with energy dispersive detector can effectively remove peaks





Data from Robert Gordon

Some final thoughts

Good sample preparation essential for success

- Plan ahead
- Simple calculations can be very instructive

Generally better to collect good data on fewer samples then rushing through many samples

XAFS amplitudes most likely to show distortions

- Thickness effects in near edge and EXAFS
- If amplitudes important (ie accurate coordination numbers) some simple checks should be run.