The XAS Experiment at Synchrotron Radiation Facilities

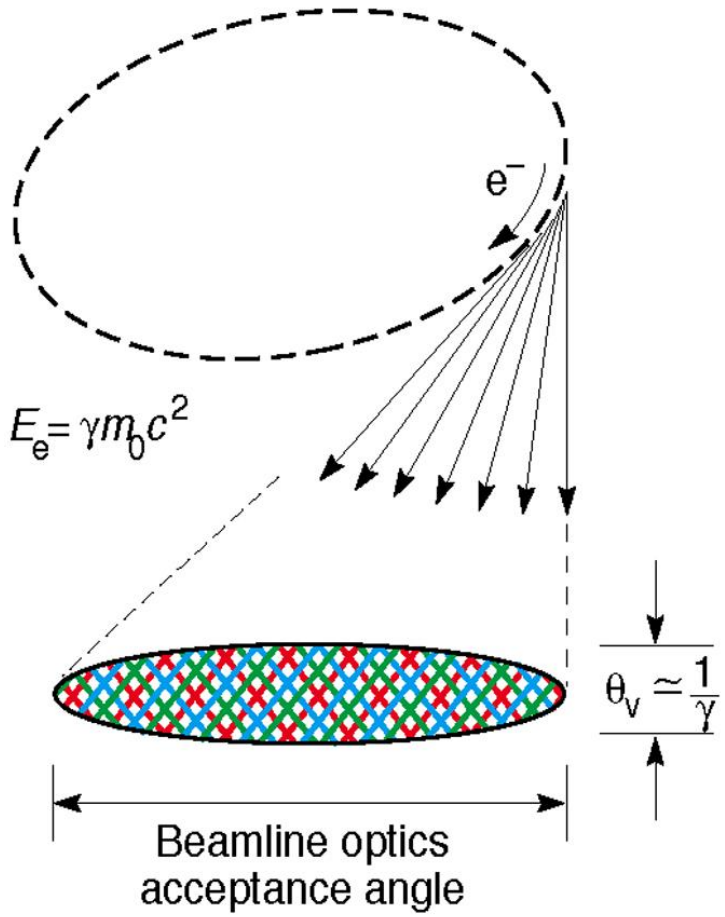
- Basics of synchrotron radiation
- X-ray optics as they apply to EXAFS experiments
- Detectors
- Other experimental considerations

Disclaimer: will primarily consider hard (>2 keV) x-rays

Important properties of Synchrotron Radiation

- Tunability
- High flux
- Collimation
- Polarization
- Time structure

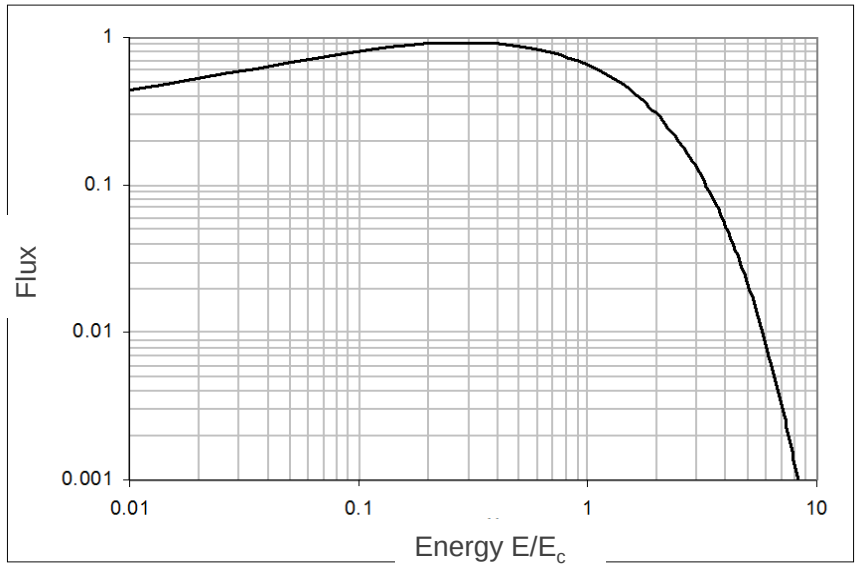
Bending magnet radiation



From relativistic affects, vertical emission limited to angle range $1/\gamma$.

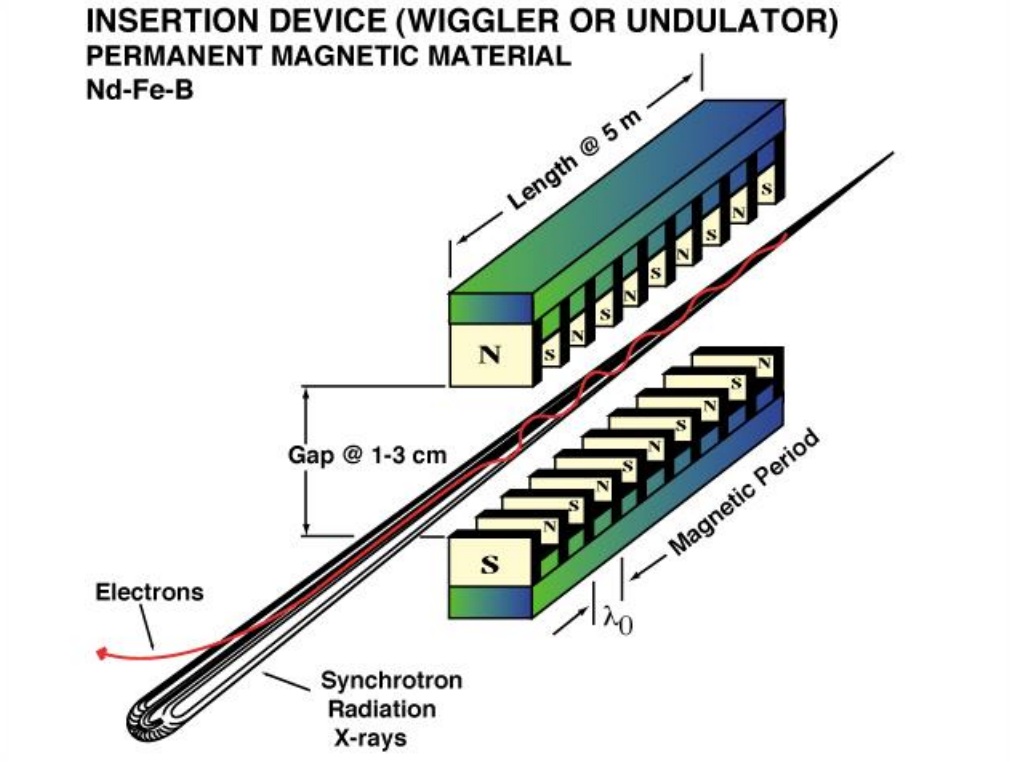
$\gamma = 1957E(GeV)$

Flux fairly flat up to a critical energy that depends on magnetic field



Insertion device

Many bends to increase flux over single bend in bending magnet



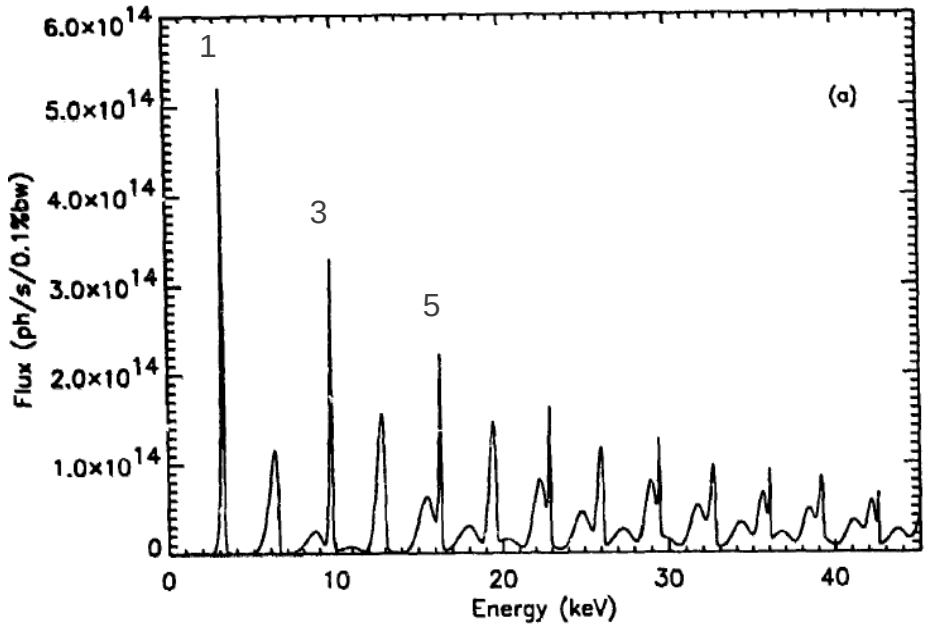
Wiggler: oscillations > $1/\gamma$
(N bending magnets)

Undulator: oscillations ≤ $1/\gamma$
(Interference of individual sources)

Example: APS Undulator A

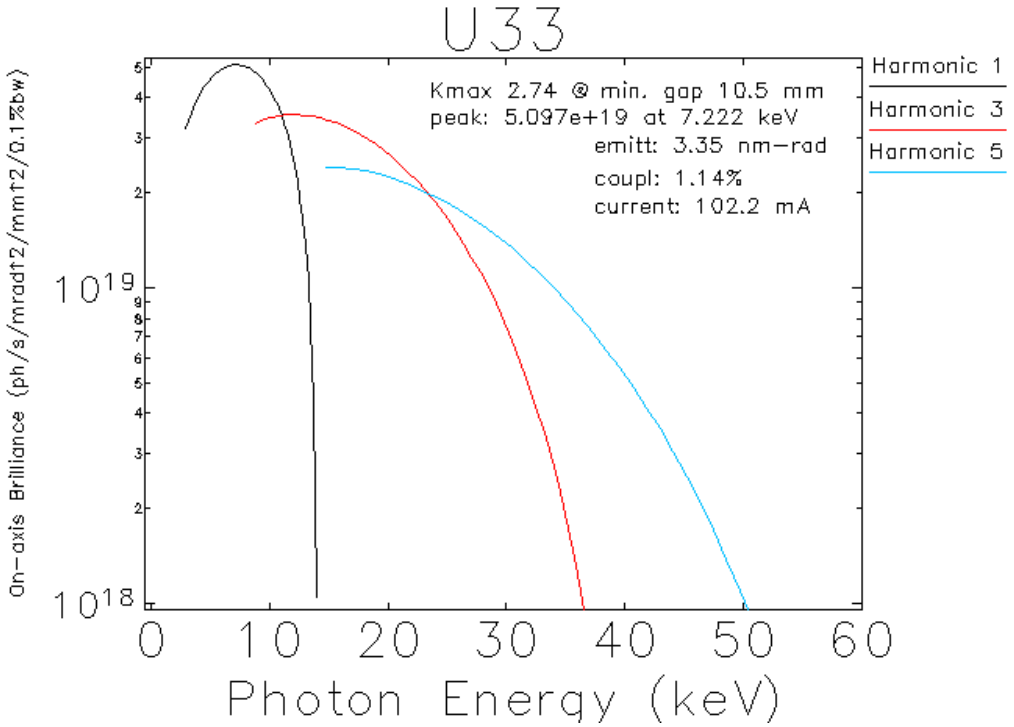
Undulator tuning curve

Typical undulator spectrum



Vary gap

Each curve follows one of the harmonics as K (gap) is varied



Source characterization

Flux – photons/sec/bandwidth
Bandwidth usually chosen as 0.1%
Most XAFS applications use 0.01-0.02%

Spectral Brilliance - flux/source size/source divergence
Photons/sec/0.1% bandwidth/mm^2/mrad^2

Liouville's theorem – brilliance is conserved
Optics can't improve brilliance of source
(smaller focus results in more divergence)

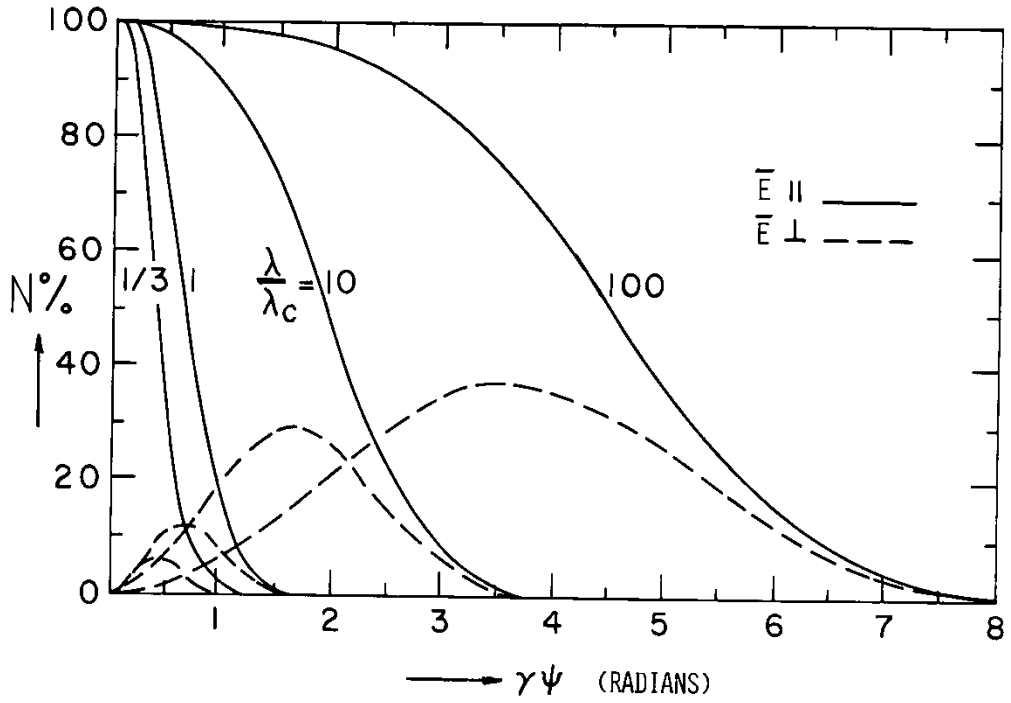
Higher Brilliance implies more flux on small samples

Polarization

Both BM and standard ID's primarily polarized in the horizontal
Fully polarized on axis
→orientation dependent XAFS for oriented samples

Special undulators can provide other polarizations, e.g. circular

BM polarization



VERTICAL ANGULAR DISTRIBUTION OF PARALLEL AND PERPENDICULAR POLARIZATION COMPONENTS

Time structure

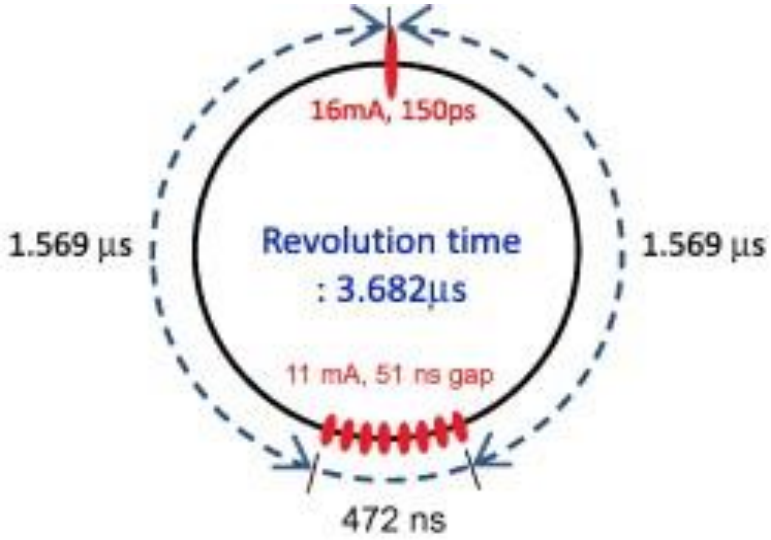
Storage rings store charge in discreet bunches

- Short pulses (100psec)
- Many patterns possible (24, 324, 1296 bunches, hybrid fill with an isolated bunch)
- Generally not important for standard experiments, but can affect the deadtime of fast detectors

Current gradually decays

- Close shutters to refill
- Topoff : refill with shutters open, nearly constant current

Example of fill pattern for timing experiments



X-ray Optics

- Mirror Optics
  - Focusing and collimation (energy resolution)
  - Harmonic rejection
- Perfect crystals
  - Monochromatization
- Typical beamline setups

Mirror optics

Glancing angle optics needed for x-rays

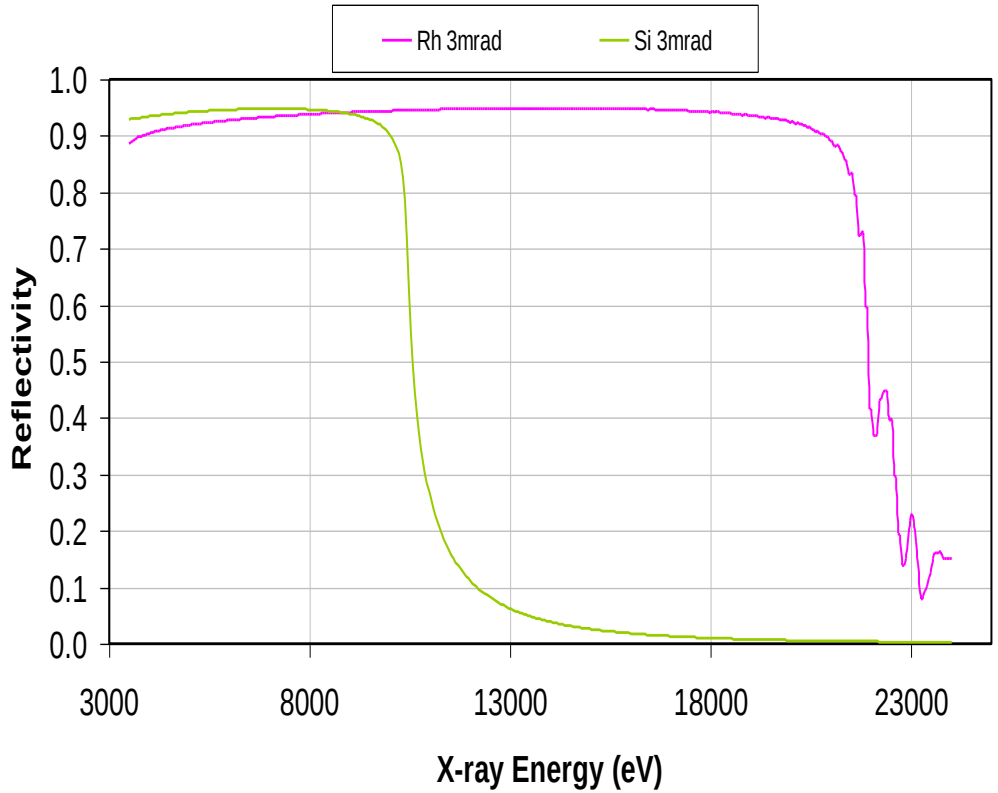
- For small enough angles reflectivity nearly 100%
- Achromatic for energies less than critical energy
- Ultra-smooth surfaces needed (<0.5 nm roughness)
- Critical energy approximately linearly related to angle

  For example, for Rh,

  $E_c(\text{keV}) = 67/\text{angle(mrad)}$

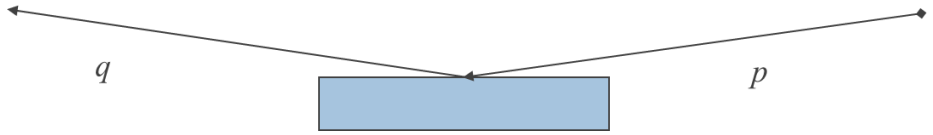
- Small angles mean mirrors need to be long

Sharp cutoff useful for harmonic rejection



Mirror Applications

Focusing



Ellipsoid or toroidal approximation

Magnification M=q/p

Collimation

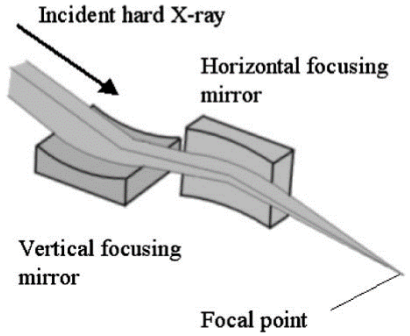
Allows large entrance slits without reducing energy resolution by making parallel beam

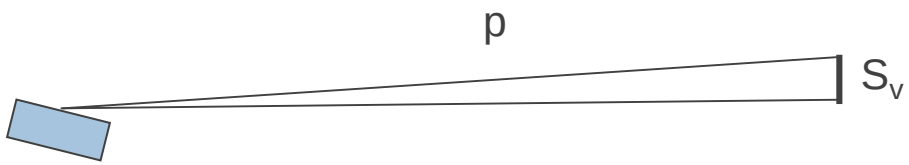
Need parabolic shape

Collimation limited by vertical source size:

$\Delta\theta = S_v/p$

Kirkpatrick-Baez (KB) mirrors for small beams





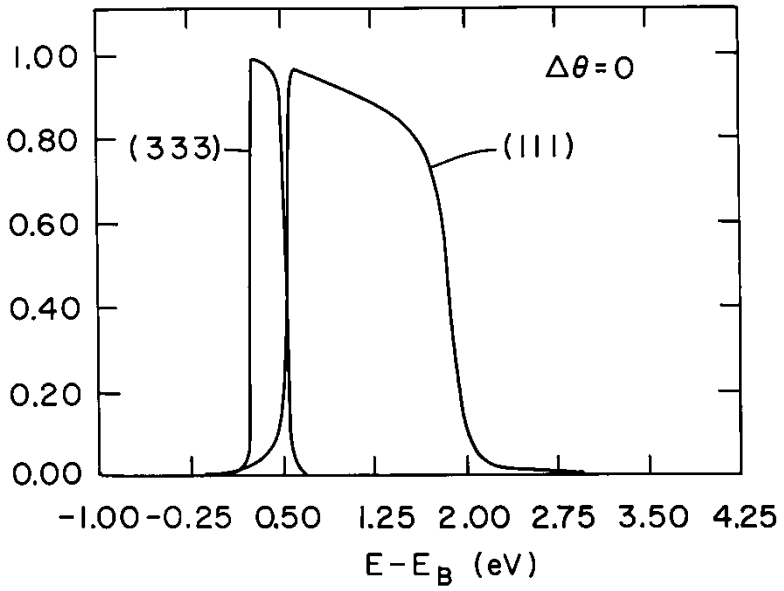
X-ray Optics – perfect crystals

- Bragg reflection and energy resolution
- Monochromators
- Detuning

Bragg reflection basics

- Bragg equation
  - Bragg equation $2d\sin(\theta) = n\lambda$, $\lambda = 12.4/E(keV)$
  - Perfect crystal Si or diamond – reflectivity nearly 1 over finite range $\Delta E/E$

Si 111 10 keV



Intrinsic Resolution of some common reflections

Reflection	ΔE/E
Si 111	1.3×10^{-4}
Si 220	5.6×10^{-5}
Si 311	2.7×10^{-5}
Diamond 111	6.0×10^{-5}

Energy Resolution

Depends on both divergence and intrinsic resolution

From derivative of Bragg equation, divergence $\Delta\theta$ results in:

$$\Delta E/E = \cot(\theta)\Delta\theta$$

$\Delta\theta$ determined by slits or collimating mirror if present

Example: 1mm slit 30 m from source at 10 keV with Si 111

$\Delta\theta = 1/30000 = 3.3\text{x}10^{-5}$, θ=11.4 or $\cot(\theta) = 4.9$

From divergence: $\Delta E/E = 3.3\text{x}10^{-5}(4.9) = 1.6 \text{ x } 10^{-4}$

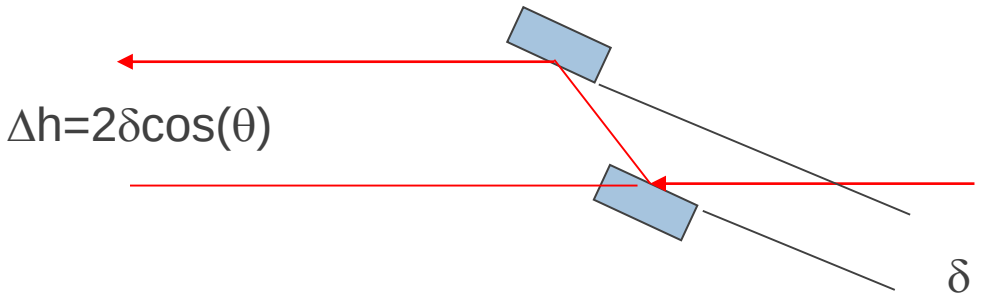
Add divergence term and intrinsic term in quadrature to get the approximate final resolution:

$$\Delta E / E = \sqrt{(1.6x10^{-4})^2 + (1.3x10^{-4})^2} = 2.1x10^{-4} \qquad (2.1 \text{ eV})$$

From divergence From crystal

Double Crystal Monochromator

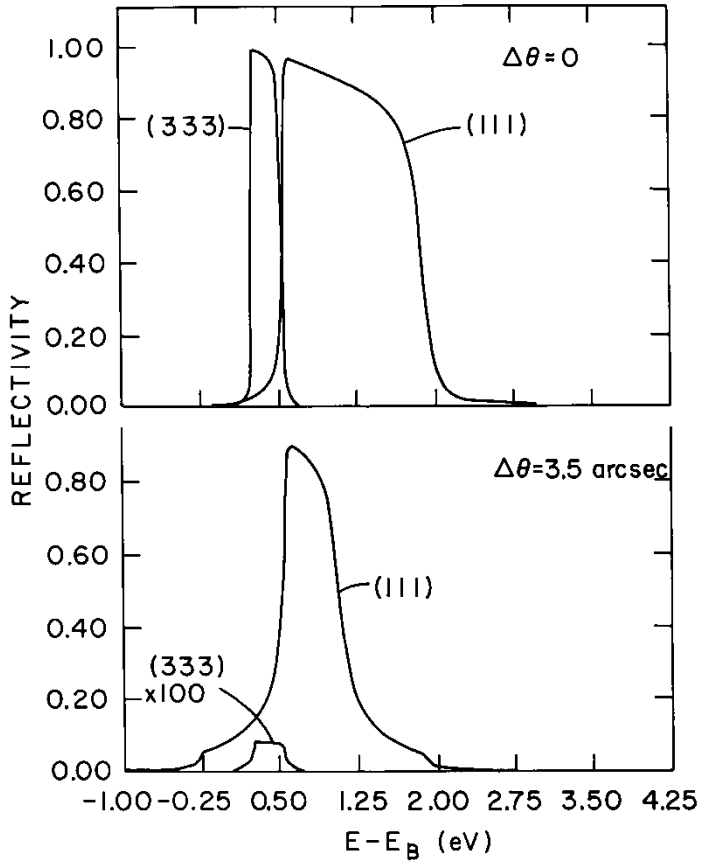
Use two crystals to minimize beam movement with angle change



For true fixed exit height need to change δ as angle changes

Detuning

Detuning can be used to reduce the relative amount of harmonics in the beam



Note: detuning can also affect energy resolution

Some typical beamline layouts

- Monochromator only
  - Good for undulator, small beam size and divergence from source
- Monochromator with focusing/harmonic rejection mirror(s)
  - Toroidal mirror: 100’s of microns, KB mirrors: ~1 micron
- Collimating mirror – monochromator – focusing/HR mirror(s)
  - Typical setup for BM line
- Collimating mirror – sagittal focusing mono – vertical focusing mirror
  - Can provide best flux from BM, may be difficult to optimize for spectroscopy

Detection of XAFS

- Signal to noise requirements
- Transmission measurements
- Fluorescence measurements
- Detectors
  - Ion chambers
  - Multielement and deadtime issues
  - Filters and slits
  - Diffraction based detectors

S/N requirements

$$S / N = \sqrt{\text{detected counts}}$$

3 measurement regimes:

- Detection of element (imaging)
  - –S/N > 10
  - –10^4 data points → >10^6 total counts
- Near edge measurements
  - –S/N > 100
  - –50-100 data points → >10^6 total counts
- Extended fine structure (EXAFS)
  - –S/N > 1000
  - –100-300 data points → >10^8 total counts

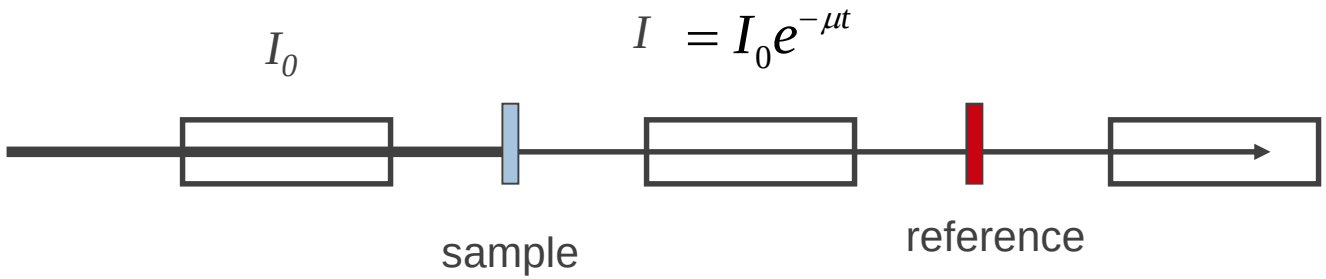
Background degrades the signal to noise:

$$\sqrt{N + N_b} = \sqrt{N}\sqrt{1 + {}^{N_b}/_{N}}$$

Need detectors that eliminate the background

See: J. Synchrotron Rad. 22 (2), 436-445 (2015). DOI: 10.1107/S1600577515001320

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 non-statistical noise starts to dominate

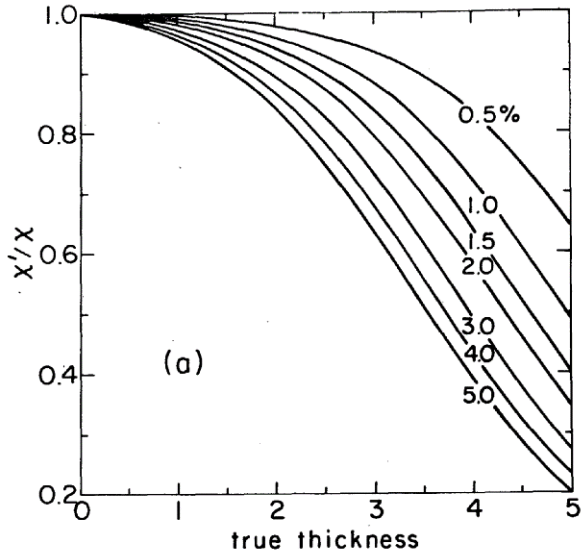
Typical ion chamber becomes non-linear at 10-20 namp/cm

Thickness effects

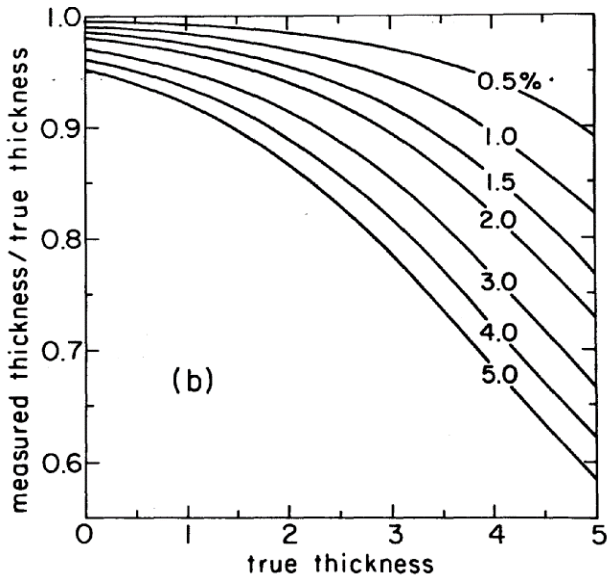
Transmission signal can be distorted by leakage of beam past or through the sample:

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

EXAFS

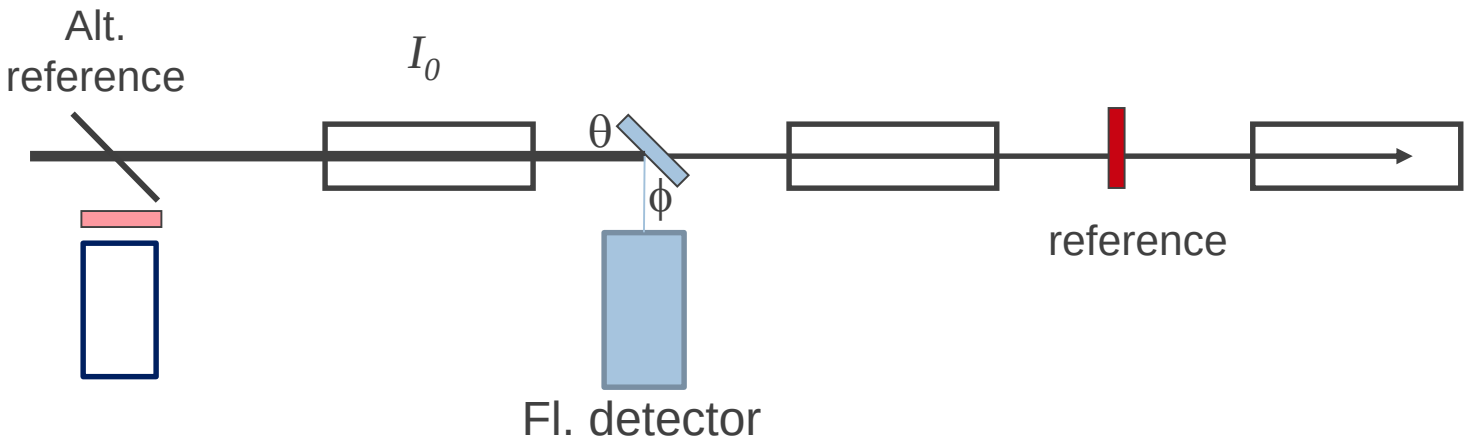


XANES



If thickness effects suspected should measure sample with two different thicknesses

Fluorescence Detection



For thick sample

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

If dilute →

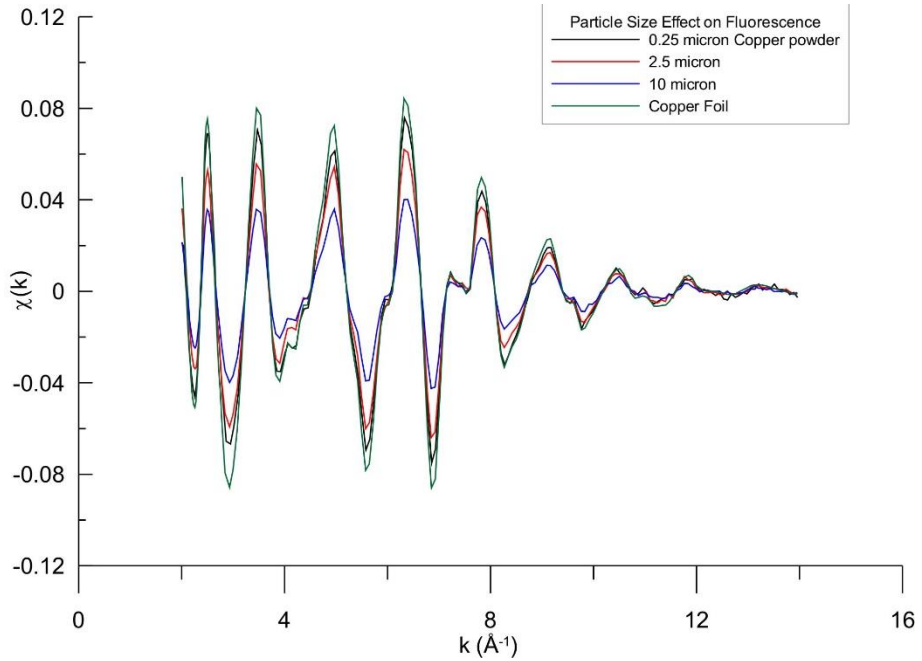
$$\frac{I_f}{I_0} = \frac{\mu(E)}{\mu_{matrix}(E) + \mu_{matrix}(E_f)}$$

(proportional to *μ(E)*)

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

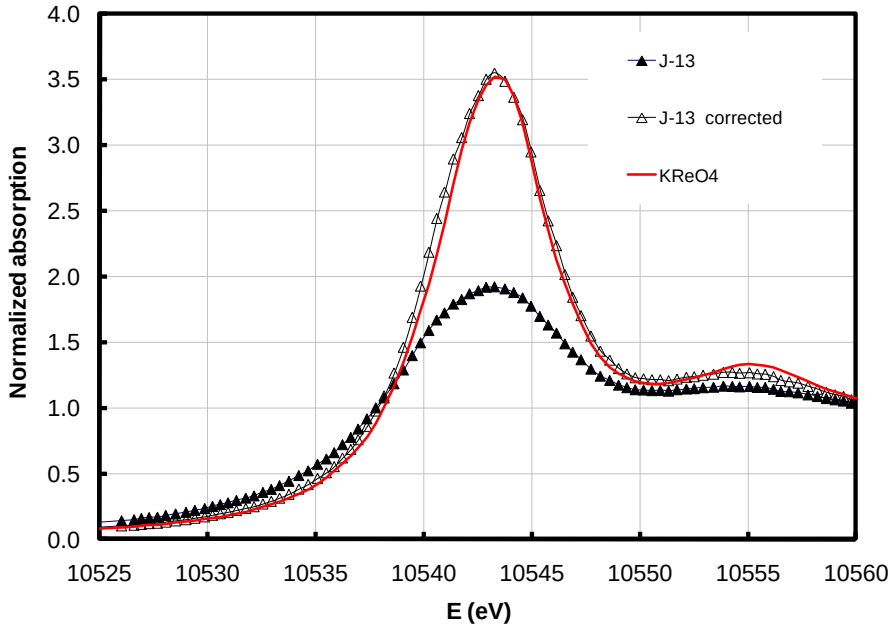
Concentrated samples - Self absorption

Cu metal



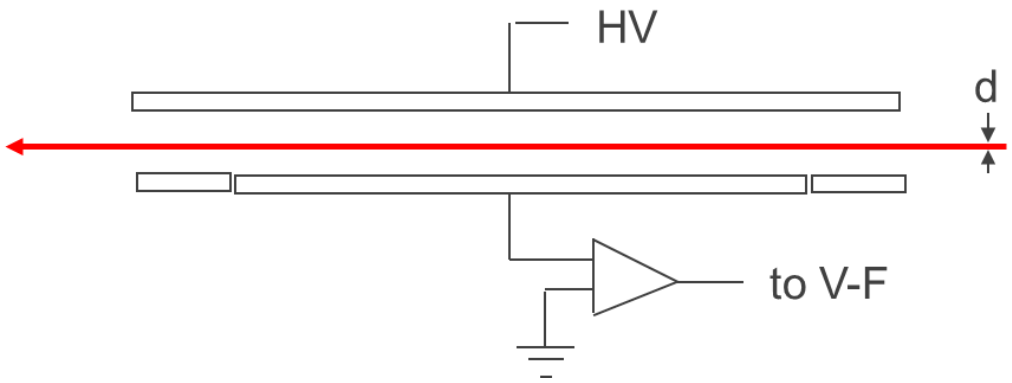
Data from R. Gordon

Re near edge

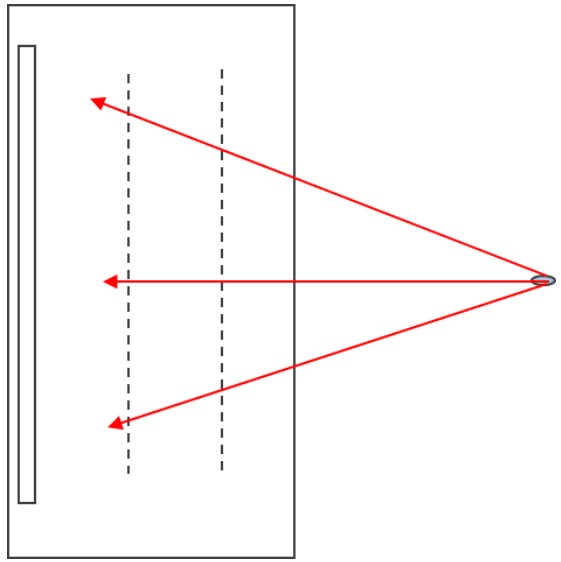


Ion chambers

transmission



Large area (fluorescence)



Collection efficiency:

$$f = \frac{1}{1 + E^2/6}$$

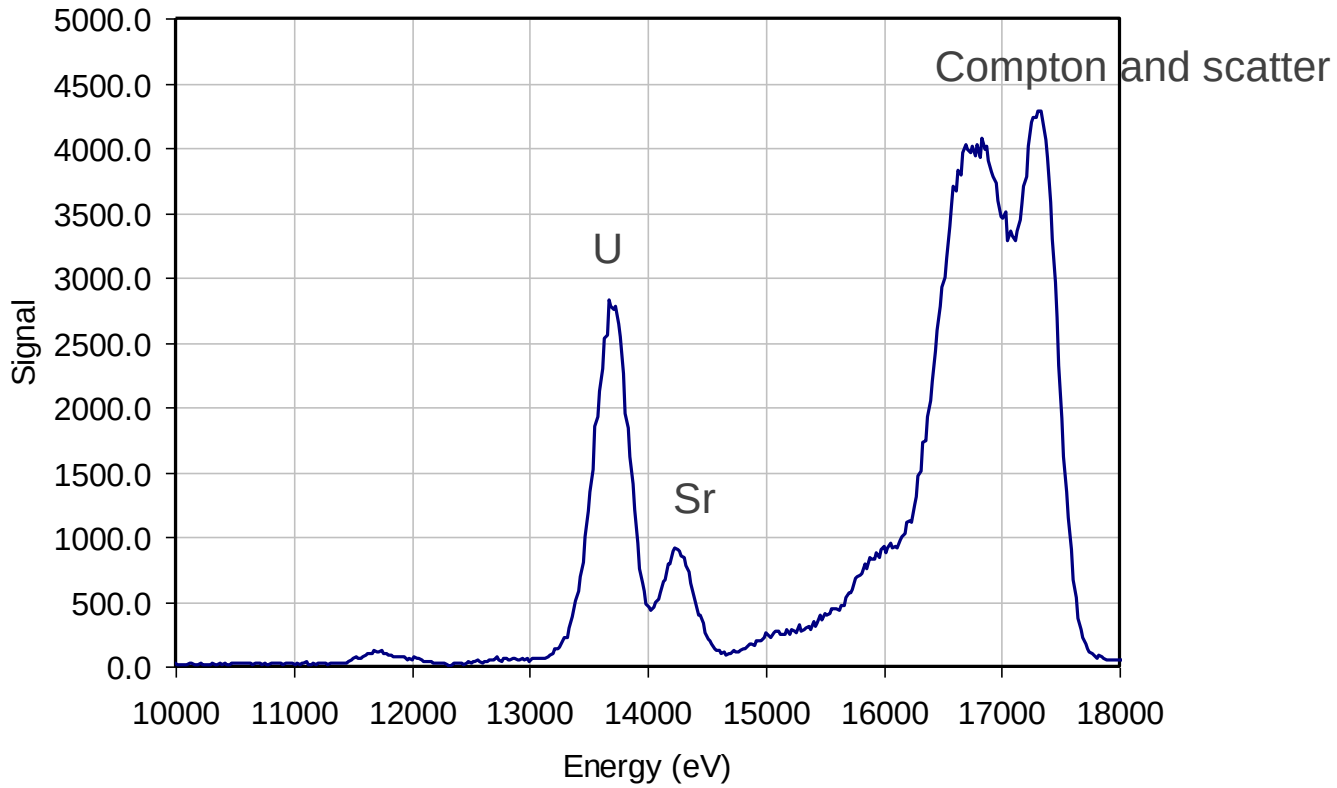
$$E = m\frac{d^2\sqrt{q}}{V}$$

m~30-40, V is volt/cm

q is charge/cm^3

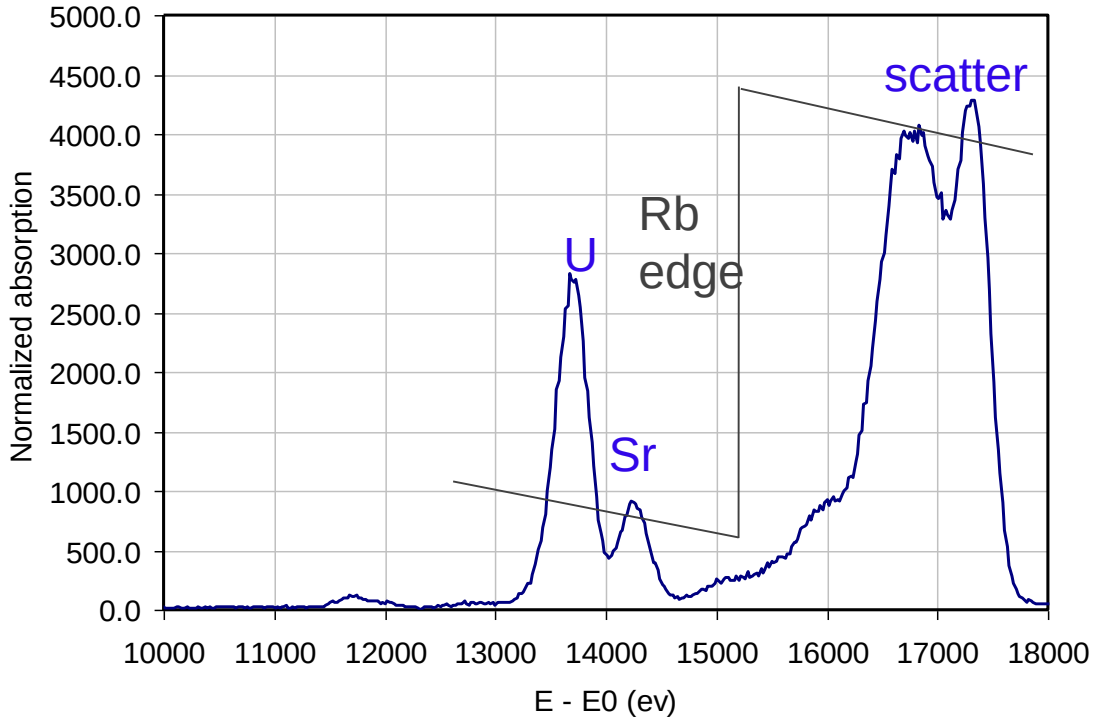
For linearity want E small: V large and q small
→ Minimizes recombination

Typical fluorescence spectrum- U contaminated Sediment



Filter can reduce the background in a fluorescence measurement

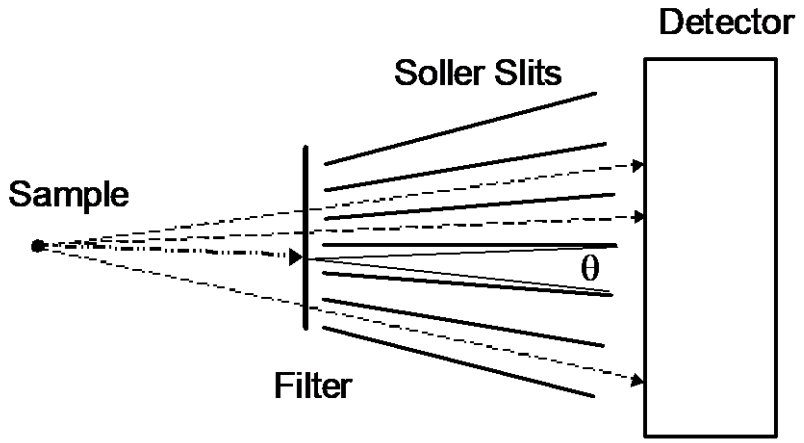
High absorption above edge reduces scatter reaching the detector

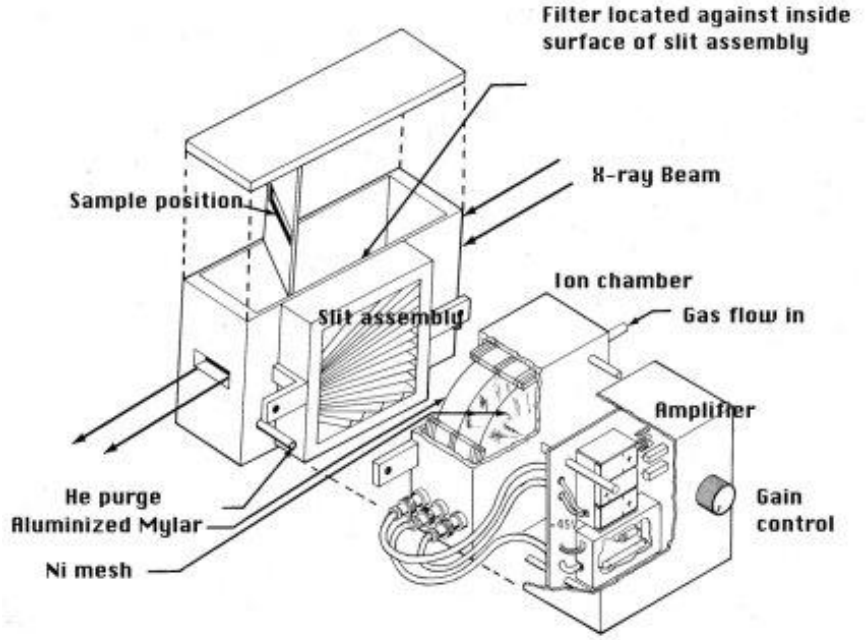


Problem: Rb fluorescence can enter the detector

Filter-slits (Stern-Heald or Lytle detector)

see Stern and Heald, RSI 50, 1579 (1979)





- Large solid angle (large N_f)
- Unlimited count rate
- Moderate reduction in background – N_b still problem
- Little rejection of lower energy fluorescence lines
- Near practical limits
- Works best for K edges above 4 keV

For very dilute samples need better background rejection

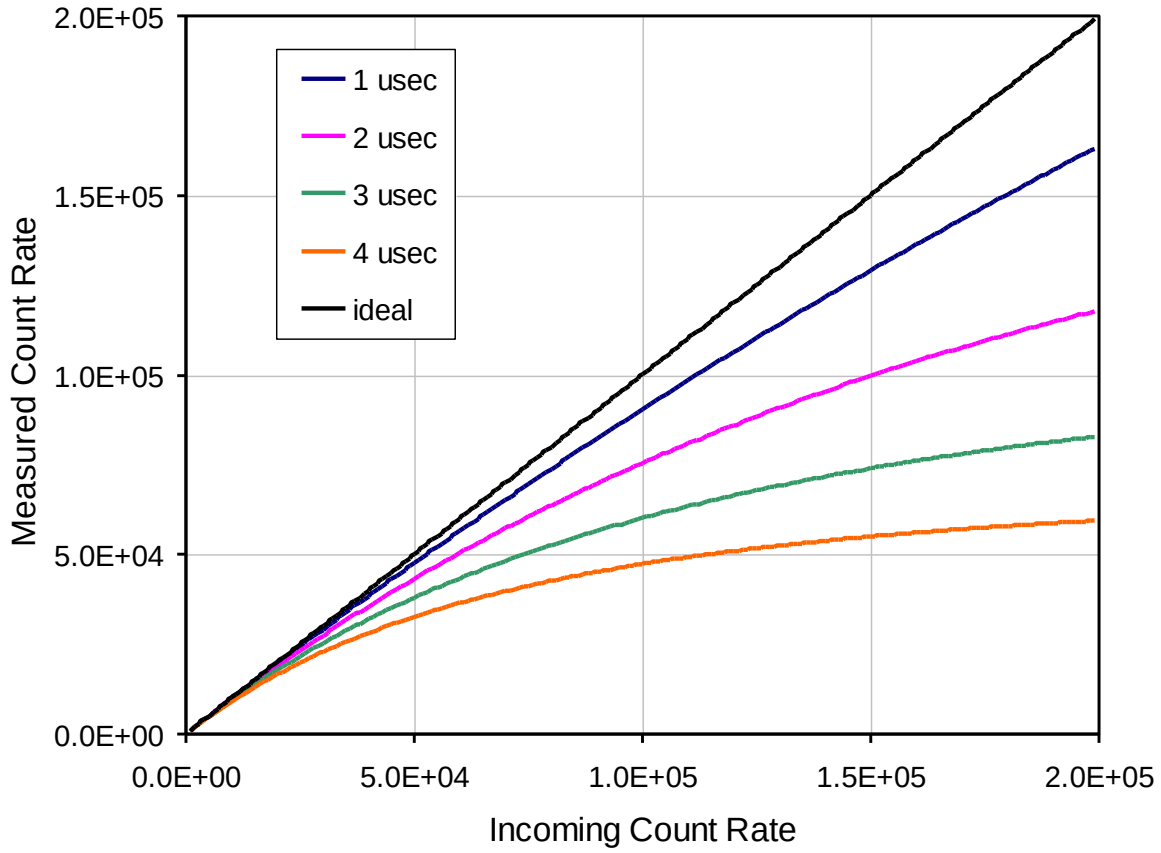
Multi-element solid state

- Resolution (fwhm) Ge: 200-300 eV, Si drift: 150-200 eV
- Individual element limited to few x 10^5
- Background or lower energy fluorescence lines can saturate countrate
- Standard arrays limited to about 30 elements (100 possible in monolithic arrays)

Dead time correction

Simple model:

MCR = ICR*Exp(-ICR*DT)



Diffraction based detectors

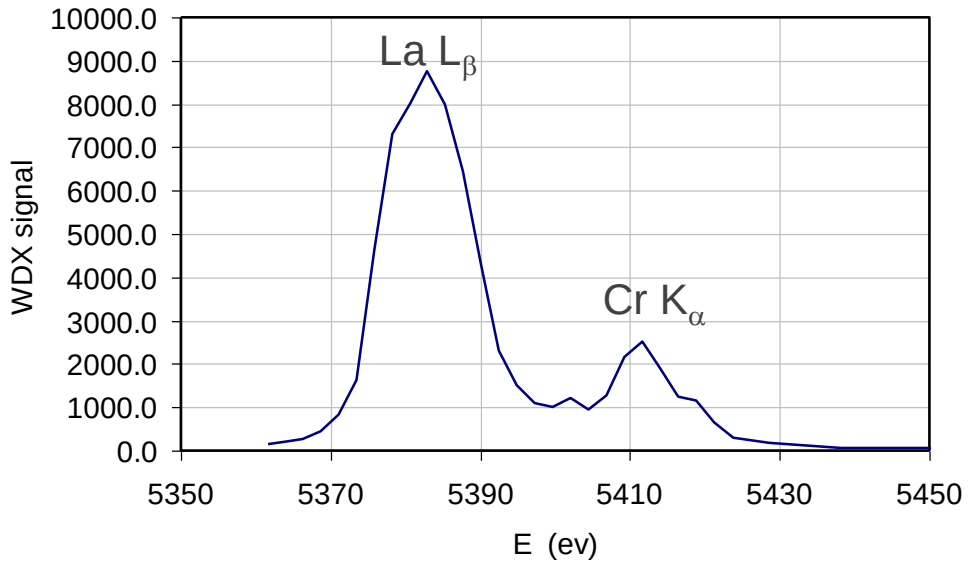
- Rowland circle, log-spiral (Bragg and Laue), multilayers
- Can have excellent resolution and background discrimination
- Unlimited count rates if integrating detectors used
- Difficult to collect large solid angles
- Usually require focused beam (0.1 mm)

WDX detector (Rowland circle)

Very good energy resolution and background discrimination

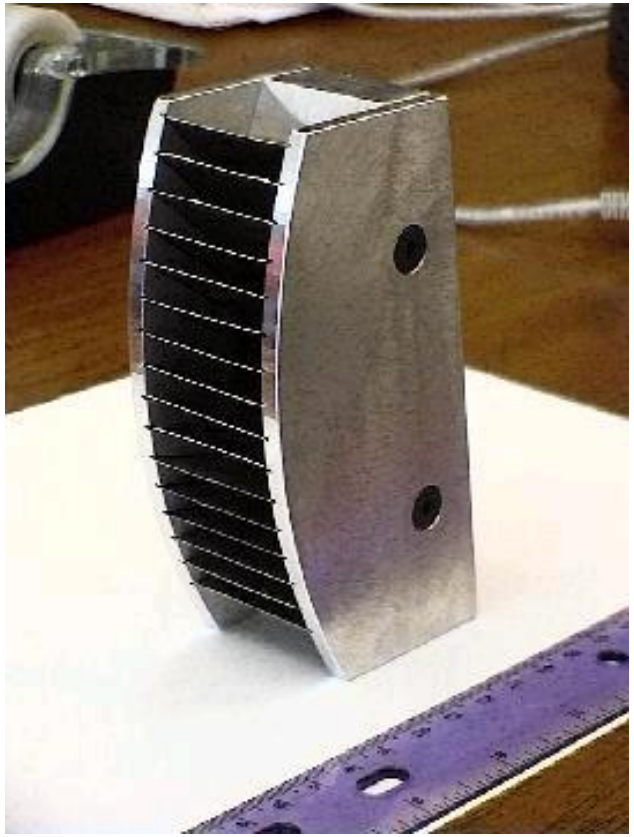
Poor collection efficiency (<0.1%)

20 nm Cr doped TiO_2 on $LaAlO_3$



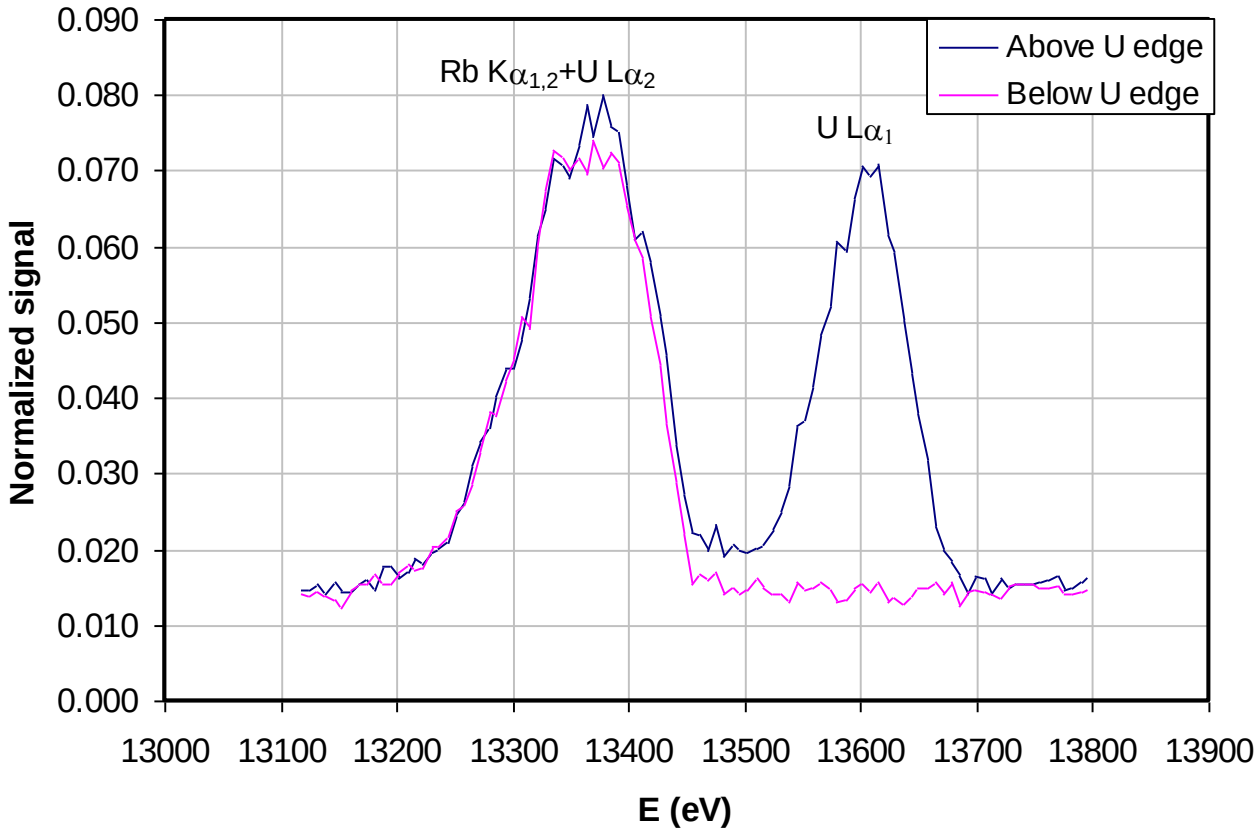
Bent Laue Log spiral detector

- Log spiral makes equal angles from point source
- No focusing so large area detector needed
- Slits block straight thru x-rays



See: C. Karanfil, Z. Zhong, L.D. Chapman, R. Fischetti,G.B. Bunker, C.U. Segre, and B.A. Bunker, *SynchrotronRadiation Instrumentation, Eleventh U.S. NationalConference*, edited by P. Pianetta et al., Vol. **521**, pp. 178-182 (American Institute of Physics 2000).

Performance for detection of U



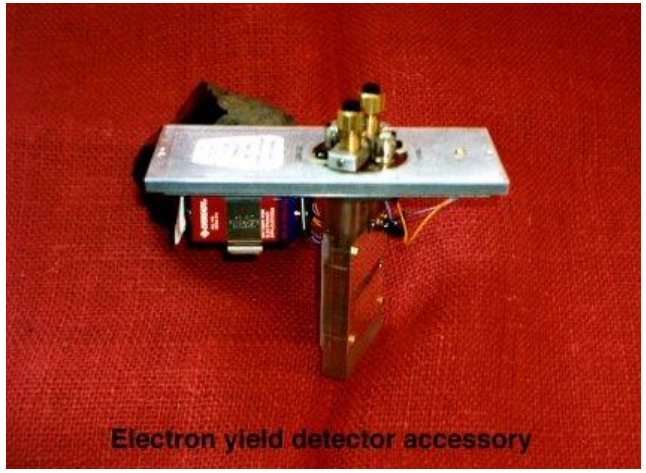
Other measurement techniques - electron yield

Electron yield – Common method for soft x-rays for samples in vacuum

Surface sensitive – total yield 10-100 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



Making samples

Most important to have uniformity – many methods

Other 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

Common methods for powders - Pressed pellets or powder on tape

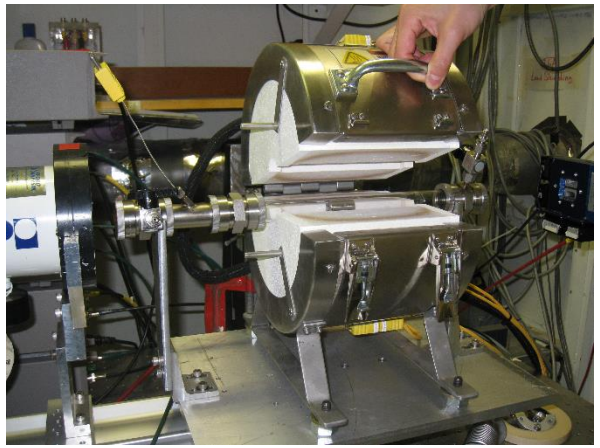
Pellets: Mix measured amounts of sample and binder
Can calculate the amount of material from pellet area

Common binders: graphite, BN or other low absorption materials

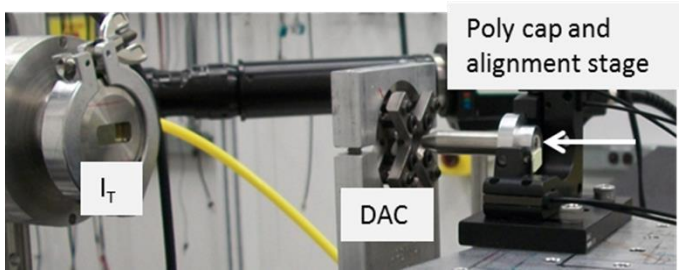
Powder on tape: Place fine powder on sticky tape and **rub vigorously** for even distribution
Scotch magic or kapton (acrylic adhesive) are good choices
Stack multiple layers for proper thickness and uniform sample

Penetrating x-rays allow for complex sample environments

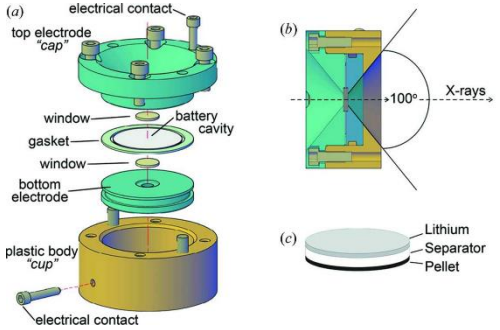
Operating catalysts



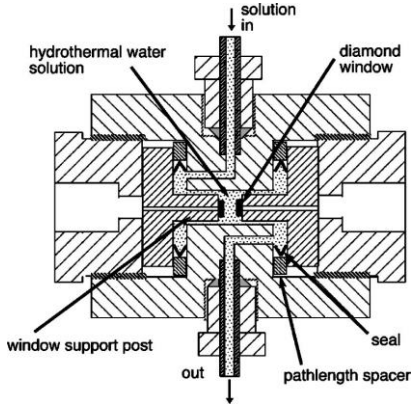
Diamond anvil cell for High pressure



Electrochemisty - batteries



Supercritical solutions



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.