

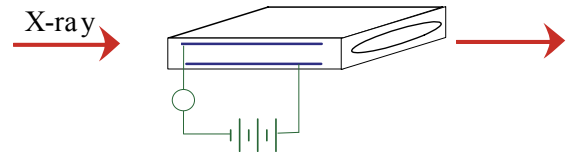
Lecture 2.

Practical Aspects of X-ray Absorption

- Measurement of absorption
- Energy selection
- Artifacts (how **NOT** to measure the right signal)
- Radiation damage

Detection of x-rays

X-rays are ionizing radiation – need to collect (and count) ionizations



Transmission measurements

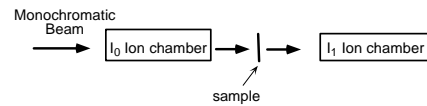
Beer-Lambert law I_0 =incident, I_t =transmitted

$$I_t = I_0 10^{-\varepsilon Cl} \quad I_t = I_0 e^{-\mu t}$$

$$I_t = I_0 e^{-\mu_m \rho t}$$

- t sample thickness (cm)
- μ absorption coefficient (cm^{-1})
- μ_m mass absorption coefficient (cm^2g^{-1})
- ρ Density (g cm^{-3})

Absorbance



$$A = \varepsilon Cl = \log\left(\frac{I_0}{I_t}\right) \quad A = \mu t = \ln\left(\frac{I_0}{I_t}\right)$$

X-ray absorption coefficients

<http://csri.iit.edu/periodic-table.html>

<http://physics.nist.gov/PhysRefData/XrayMassCoef/cover.html>

<http://csri.iit.edu/periodic-table.html>

Periodic Table

Click on any button with element name to get its x-ray properties. If you give an energy value in the box at the top of the table then you also get x-ray cross-sections at that energy. The original subroutine (masal.f or masal.c) used to calculate x-ray cross-sections is available from [here](http://www.slac.stanford.edu/periodic-table.html).

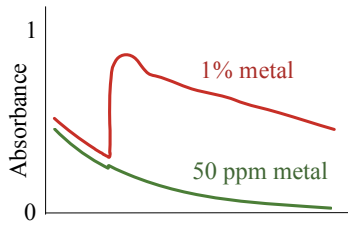
Energy: 7.2 keV

1	2																
H	He																
3	4																
Li	Be																
5	6	7	8	9	10												
B	C	N	O	F	Ne												
11	12																
Na	Mg																
13	14	15	16	17	18												
Al	Si	P	S	Cl	Ar												
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe

Element	Edge Energies (keV)	Edge jumps	Fluorescence yield
Symbol	Fe	K 7.11199999	K 0.0714798
Z	26	L1 0.342000008	L1 0.0100000005
Atomic Weight	55.8499985	L2 0.719900012	L2 0.0999999968
Density	7.86000013	L3 0.706799984	L3 6.40299998
M	0.0939999968		
K-alpha	6.40299998		
K-beta	7.05700016		
L-alpha	0		
L-beta	0		

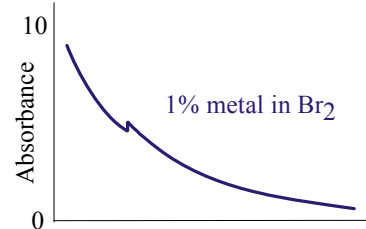
Cross-sections at E = 7.19999981 keV (cm ² /gm)	
Photoelectric	393.506775
Coherent	1.797014
Incoherent	0.0686381012
Total	395.372406
Conversion factor (C) (Barns/Atom) = C * (cm ² /gm)	92.7399979
Absorption coefficient	3107.6272 1/cm
1/lambda (element)	3.21789807 microns

Absorbance is great for concentrated samples,



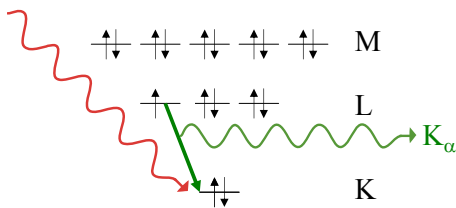
but not for dilute samples.

Transmission is also sensitive to background absorption

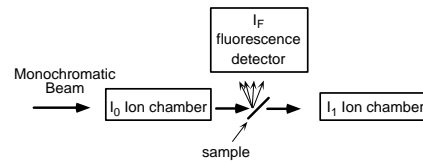


Fluorescence

(what goes up must come down)



Fluorescence excitation spectra

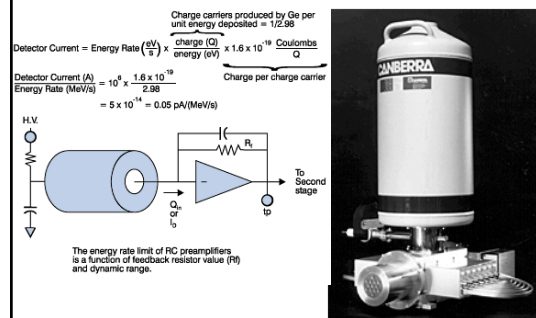


Measure fluorescence intensity as excitation energy is scanned

Fluorescence Detectors

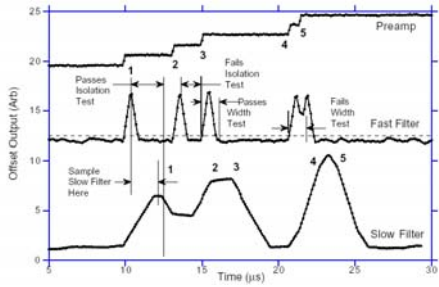
- Energy resolving
 - Energy dispersive – Ge or Si(Li)
 - Wavelength dispersive
 - Exotic
- Non-energy resolving
 - Ion chamber
 - PIN diode

Energy-dispersive detectors



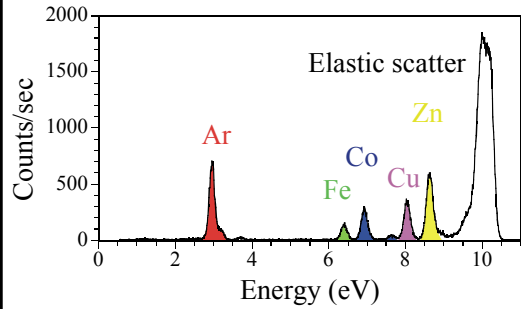
<http://www.canberra.com/products/491.asp>

Solid-state detectors have relatively low maximum count rates



http://www.xia.com/AppNotes/DXP_Pile.pdf

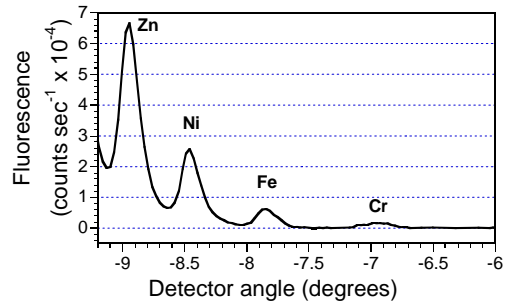
Energy-dispersive detectors typically have high resolution



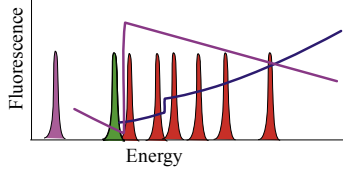
Wavelength-dispersive detectors



Reasonable solid angle results in low resolution, but unlimited count rate

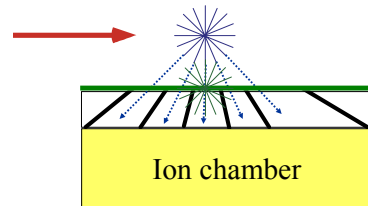


Non-energy resolving detectors
Z-1 element functions as low-pass filter, but filter fluorescences



Fluorescence Excitation

Soller slits + Z-1 filter improve fluorescence



Self-absorption

$$I_F = I_0 \frac{\Omega}{4\pi} \epsilon \frac{\mu_X(E)}{\mu_T(E) + \mu_T(E_{fl})} \left(1 - e^{-[\mu_T(E) + \mu_T(E_{fl})]l}\right)$$

$$\mu_T = \mu_X + \mu_B$$

Reduces to $I_F \propto \mu_X$ if $\mu l \ll 1$ (thin)

If $\mu l \gg 1$ (thick)

$$I_F \approx \frac{\mu_X(E)}{\mu_T(E) + \mu_T(E_{fl})} = \frac{\mu_X(E)}{\mu_X(E) + \mu_B(E) + \mu_T(E_{fl})}$$

Goulon J, et al. "On Experimental Attenuation Factors Of The Amplitude Of The EXAFS Oscillations In Absorption, Reflectivity And Luminescence Measurements", *J de Physique* **43**, 539-548 1982

Self-absorption continued

$$\frac{\mu_X(E)}{\mu_X(E) + \mu_B(E) + \mu_T(E_{fl})} \approx \mu_X(E)$$

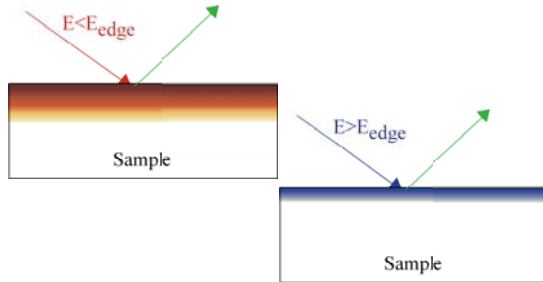
Only if $\mu_X \ll \mu_B$ (dilute)

Fluorescence excitation spectra only give accurate μ_X if samples are thin or dilute.

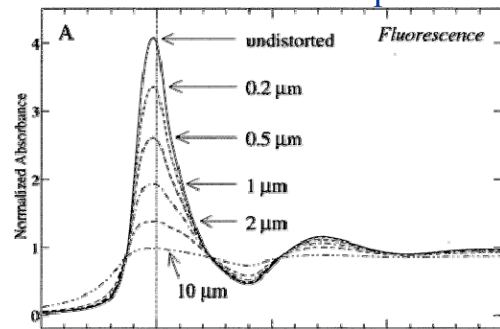
Otherwise, need to correct.

Waldo GS, Carlson RMK, Moldovan JM, Peters KE, Penner-Hahn JE "Sulfur Speciation In Heavy Petroleums - Information From X-ray Absorption Near-edge Structure" *Geochim Cosmochim Acta* **55** 801-814 (1991)

If samples are not either thin or dilute, will have self-absorption



Effect of self-absorption



Pickering IJ, et al. "Analysis of sulfur biochemistry of sulfur bacteria using X-ray absorption spectroscopy" *Biochemistry* **40** 8138-8145 (2001)

Self-absorption

If a sample gives a reasonable transmission signal, it is too concentrated to measure by fluorescence (unless sample is very thin)

Signal/Noise concerns in XAS

Counting statistics – uncertainty $\sim (\text{counts})^{1/2}$

If there is no background, $S/N = (\text{counts})^{1/2}$

Typical fluorescence 10^4 sec^{-1} to 10^5 sec^{-1}

Transmission ion-chambers – typical currents $\geq 10 \text{ nA} \sim 10^{10}$ electrons/s
Negligible noise from counting statistics.

Important noise sources: electronic, microphonic, beam problems (below)

Sensitivity

EXAFS amplitude falls of $\approx 1/k^3$
10% effect at $k=2 \text{ \AA}^{-1}$; 0.03% at $k=14 \text{ \AA}^{-1}$
For EXAFS $S/N=3$ at 14 \AA^{-1} need
absorption $S/N=3/0.0003=10^4$
Therefore need 10^8 counts at $k=14 \text{ \AA}^{-1}$

What is required to have 10^8 fluorescent photons

Incident flux $\approx 2 \cdot 10^{13} \text{ sec}^{-1}$ in 10^{-8} m^2
Fluorescence yield $\approx 0.5 \rightarrow$ need
absorbance of 10^{-5} to give 10^8 fluorescent
photons in 1 second
Absorbance = $3 \cdot 10^4$ barns/atom
 $= 3 \cdot 10^{-16} \cdot N$
Need $N \approx 3 \cdot 10^{10}$
50 fmole, 50 μM if sample is $(100 \mu\text{m})^3$

Reality

Detected solid angle is 1-5% (i.e., 10^6 sec^{-1})
but – count times of 100 sec/pt are realistic \rightarrow
total measurement time ~ 6 hrs (vs. 3 minutes)

However

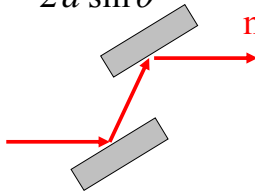
Effective count rate is often detector-limited:
if scatter:fluorescence is 100:1, $N_{\text{max}} \sim 10^4$
(10^2 -fold lower than optimum).

- Solids
 - If absorbance of element of interest $>$ background absorbance use transmission
 - If absorbance of element of interest \ll background absorbance use fluorescence
 - Samples need to be optically thin – often requires dilution
- Solutions
 - If concentrated, treat like a solid
 - If dilute (negligible edge jump) use fluorescence
 - Typical limits
 - $\sim 100 \mu\text{M}$ Zn in $50 \mu\text{L}$ aqueous solution (5 nmole)
 - $\sim 1.0 \text{ mM}$ V in $10 \mu\text{L}$ aqueous solution (10 nmole)
 - $10 \mu\text{M}$ Mo in $200 \mu\text{L}$ aqueous solution (2 nmole)

Bragg's Law

$$n\lambda = 2d \sin \theta; E = hc/\lambda$$

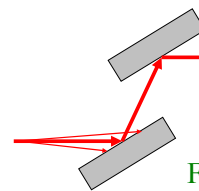
$$E = \frac{nhc}{2d \sin \theta}$$



Double-crystal
monochromator

Energy resolution

$$n\lambda = 2d \sin \theta$$



Angular divergence gives
spread in energy. Vertical
slits decrease $\Delta\theta$, and thus
 ΔE .

For many 3rd generation sources,
angular divergence of beam is
small compared to intrinsic
width of reflection

Energy calibration

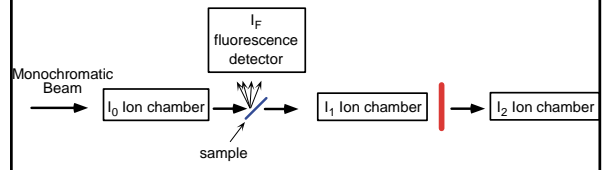
$$n\lambda = 2d \sin \theta$$

Want to know E to ~0.1 eV (1 part in 10⁵)
 Accurate absolute energy determination is hard. Typically, settle for precise relative energy.

For absolute calibration, see:

Pettifer RF, Hermes C "Absolute energy calibration of x-ray-radiation from synchrotron sources" *J Appl Crystallogr* **18**, 404-412 (1985)

Internal energy calibration



$$A_{sample} = \ln\left(\frac{I_0}{I_1}\right) \quad A_{foil} = \ln\left(\frac{I_1}{I_2}\right)$$

Harmonic contamination

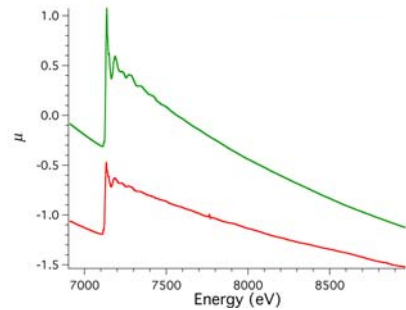
$$n\lambda = 2d \sin \theta$$

$$I_0 = I_0 + \beta I_{0,2E}$$

$$I_t = e^{-\mu t} I_0 + \beta I_{0,2E}$$

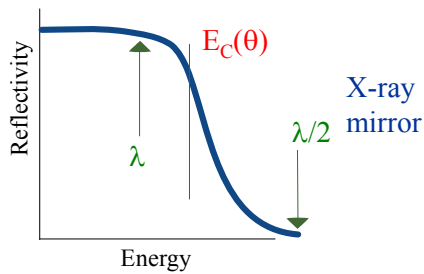
$$A = \ln\left(\frac{I_0}{I_1}\right) = \ln\left(\frac{I_0 + \beta I_{0,2E}}{e^{-\mu t} I_0 + \beta I_{0,2E}}\right)$$

Experimental consequence of harmonic contamination

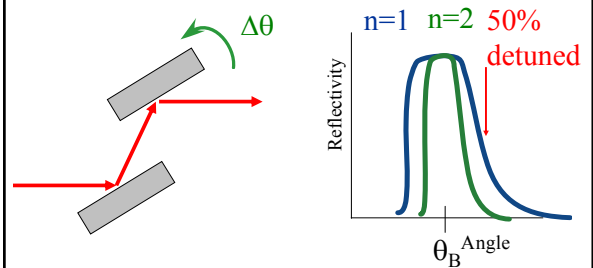


pinholes and self-absorption cause similar effect – amplitudes are too small

Harmonic rejection mirror

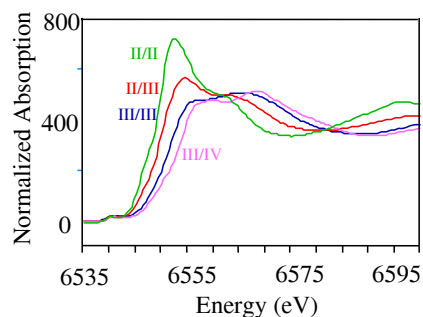


“Detuning” monochromator



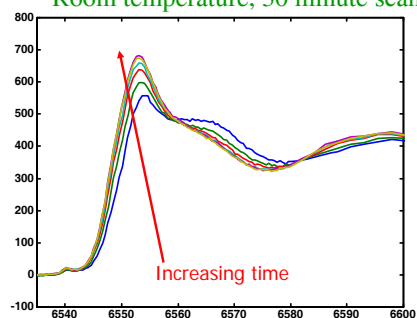
Radiation damage

Dependence of XANES on Oxidation State

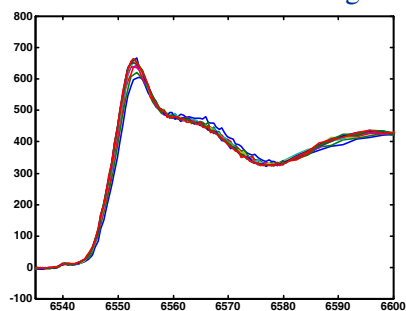


Mn(III) shows significant radiation damage

Room temperature, 30 minute scans



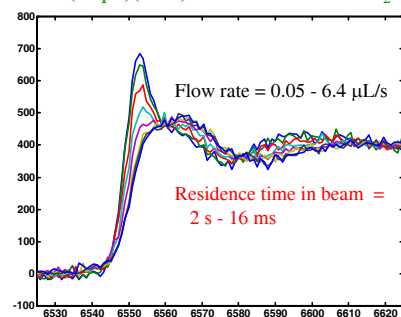
Low temperature (4K) reduces *but does not eliminate* radiation damage



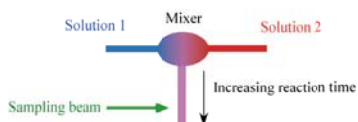
Low temperature can't be used if thermochromic

Flowing fluid samples *can* prevent radiation damage

Mn³⁺(salpn)(acac) in Acetone + 15% H₂O



Flow system can be used for time resolved measurements

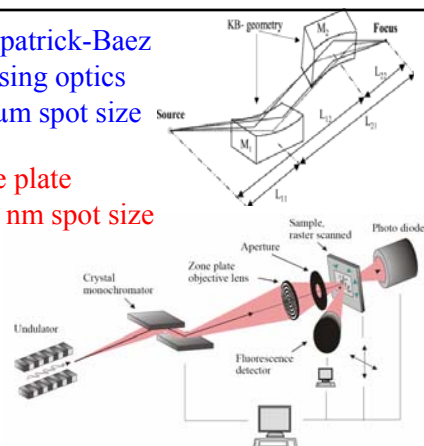


Requirements (for reasonable sample volumes):

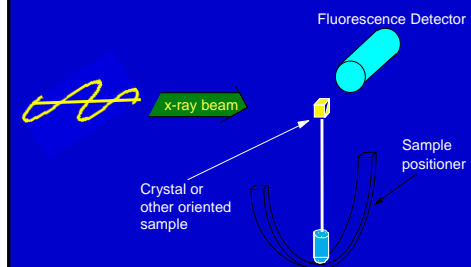
- Rapid scanning
- Small sample (i.e., small beam)

Kirkpatrick-Baez focusing optics
~ 1 μ m spot size

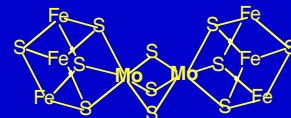
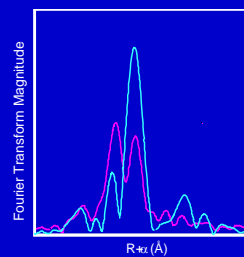
Zone plate
~ 30 nm spot size



Polarized XAS



Polarized XAFS of Mo/Fe/S clusters



Flank, Weinger, Mortenson, &
Cramer, *J. Am. Chem. Soc.*, **108**,
1049.