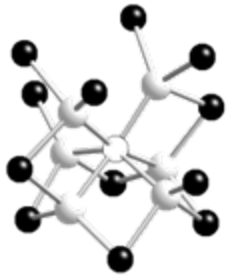
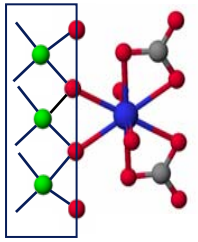
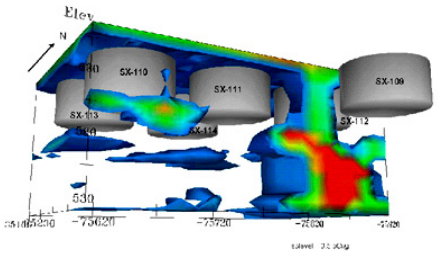
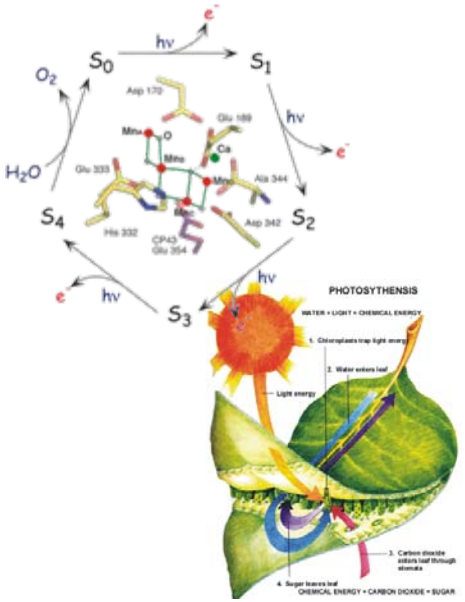
X-Ray Absorption Spectroscopy: Practical Aspects







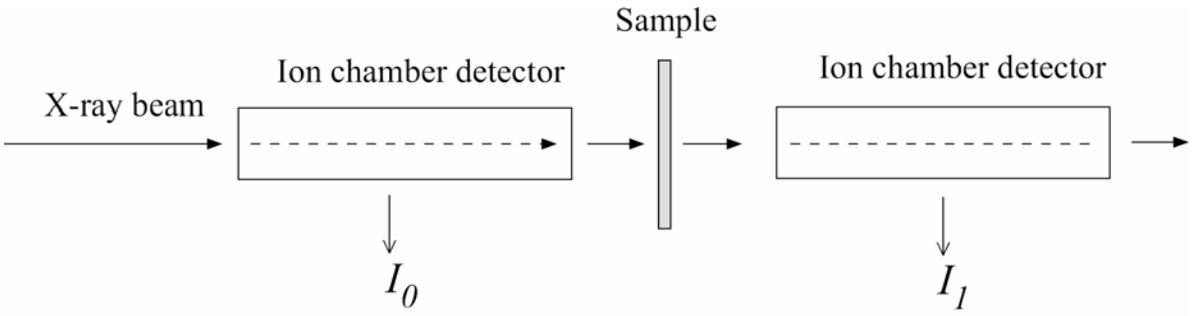


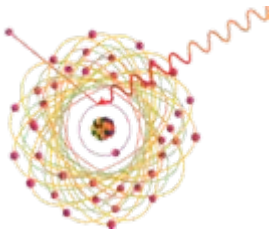
John Bargar, May 20, 2008

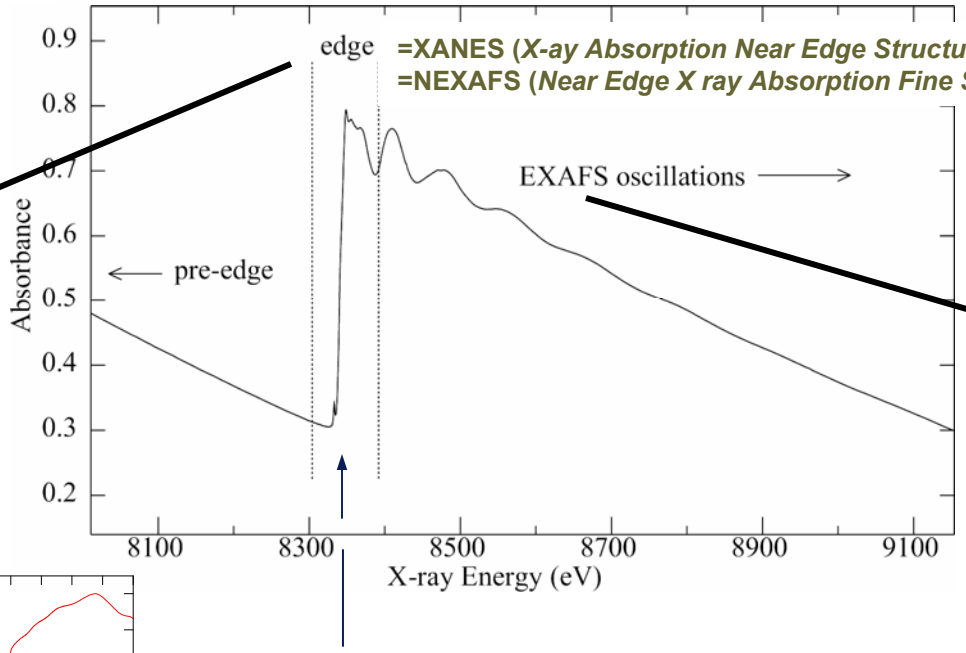
SSRL School on Synchrotron X-ray Absorption Spectroscopy Techniques in Materials and Environmental Sciences: Theory and Application

XAS: What you get out of the measurement:

Basic Experiment :



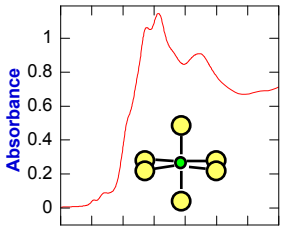




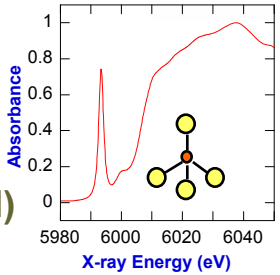
(EXAFS = *Extended X ray Absorption Fine Structure*)

XANES / NEXAFS
Oxidation state,
Molecular structure,
Electronic structure.

EXAFS
Quantitative Local Structure.

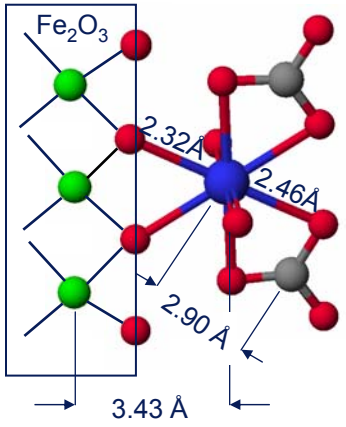


Cr(III)



Cr(VI)

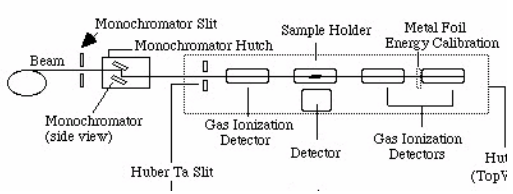
Core electron
binding energy, E_b



Synchrotron-Based Techniques: Key Advantages

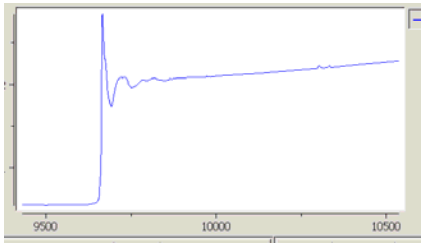
Three Major Categories

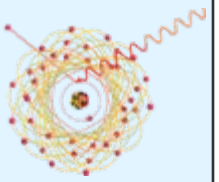
I. Set-up and optimization of beam lines

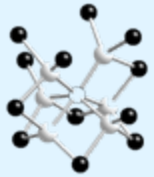


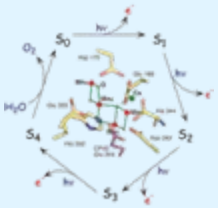
II. Sample optimization & choice of detector

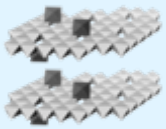
III. Data Acquisition







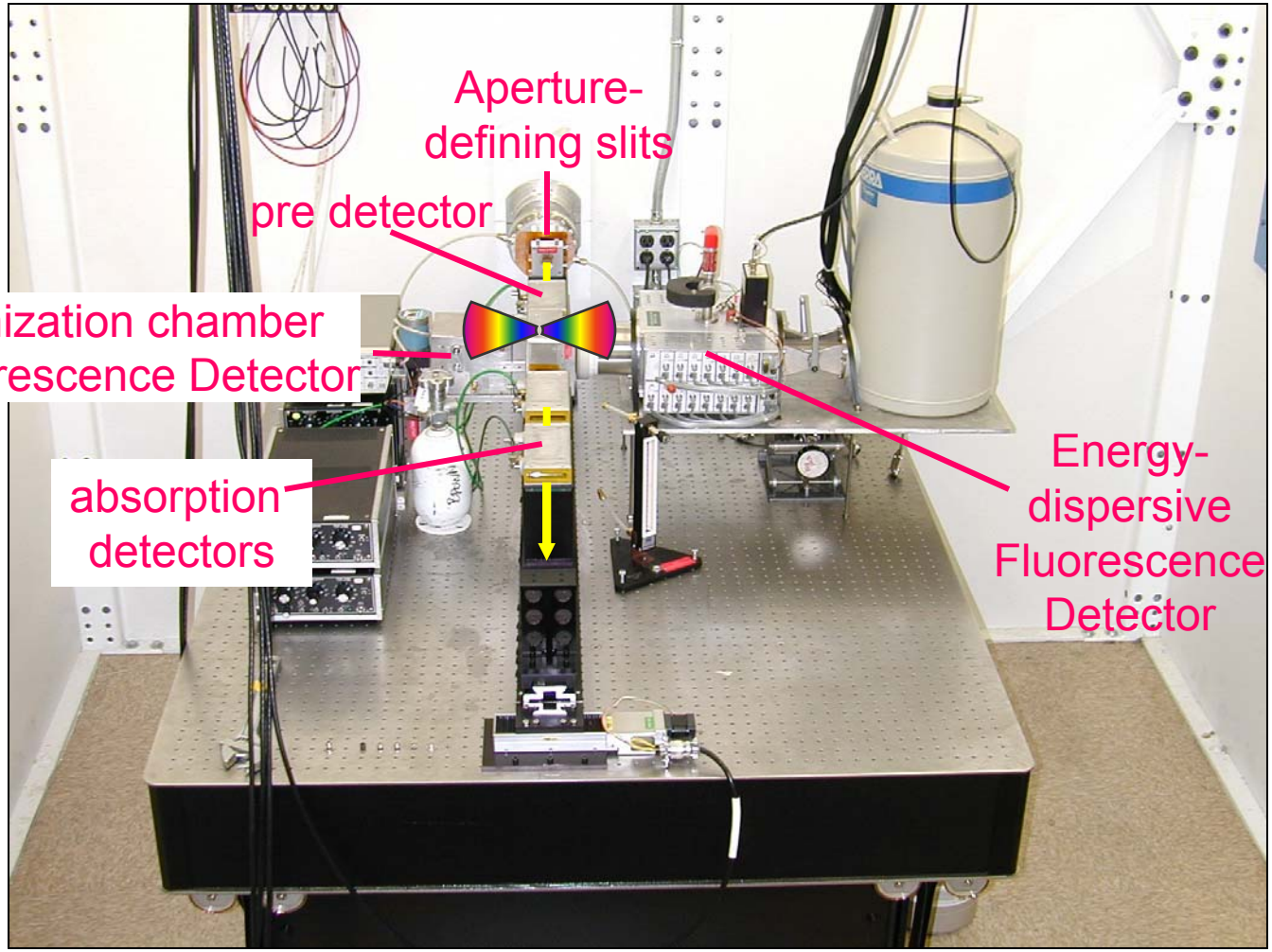




I. Beam line set-up and optimization

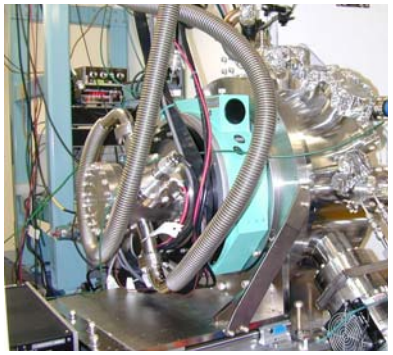
- Major elements of in-hutch equipment
- Major elements outside of hutch
- Ion chambers and their output signal chain
- Mono tuning - why, how, and how much?
- Slit size for samples, impact on resolution
- Energy calibration: why, how, how frequently?

I. Beam line set-up and optimization:
In-hutch instrumentation

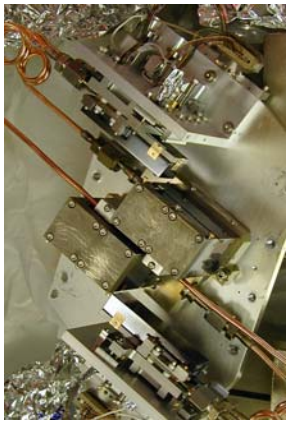


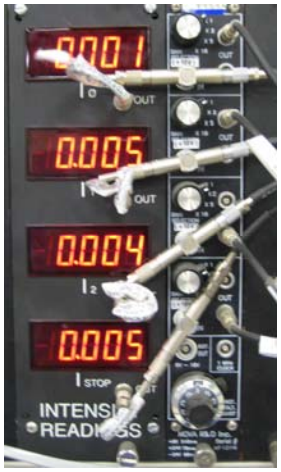
I. Beam line set-up and optimization:
Out-of-hutch instrumentation

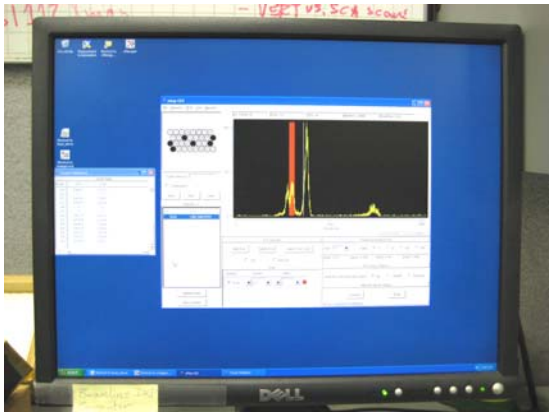
SSRL BL 11-2



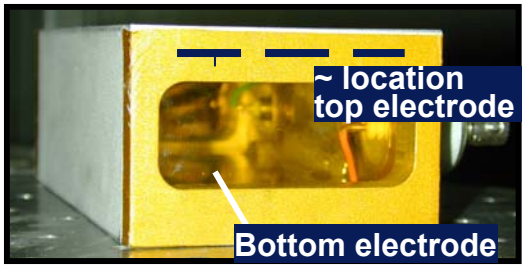
Monochromator

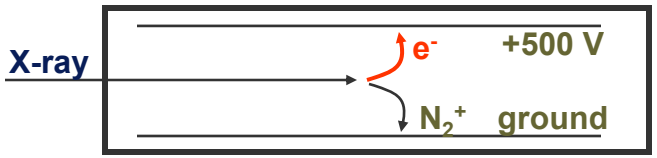






I. Beam line set-up and optimization: Ion Chambers





Gas selection:
< 5 KeV: He
5 – 15 KeV: N2
> 15 keV: Ar

Current (nA to μA)

Current amp: outputs voltage

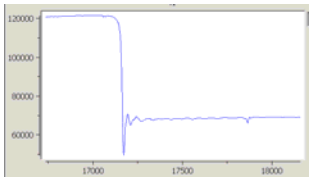
Linear range: up to 5 V (SR570) or 10 V (Keithley)

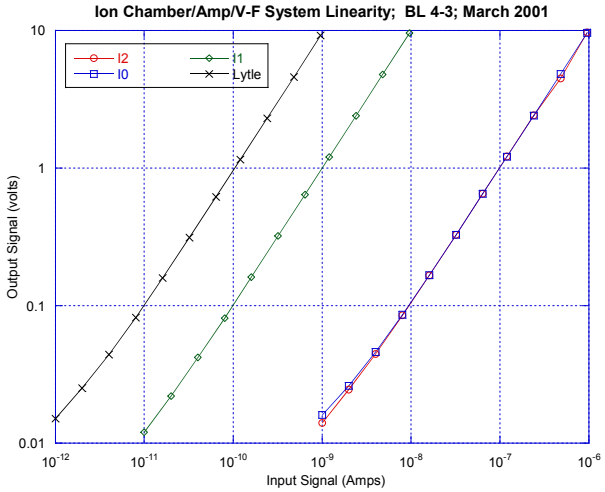
voltage

Linear range: 0.1 to 10 V

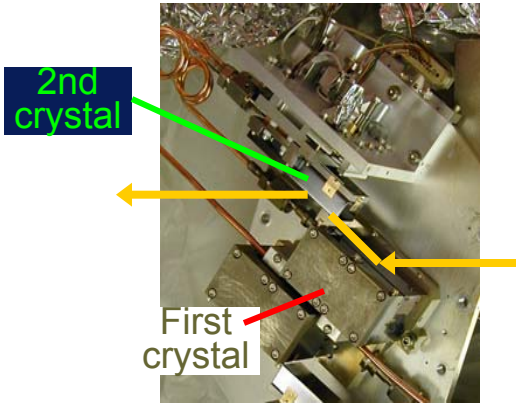
V-F converter: Pulses to computer

Maintain signal below ~ 5 V!!!



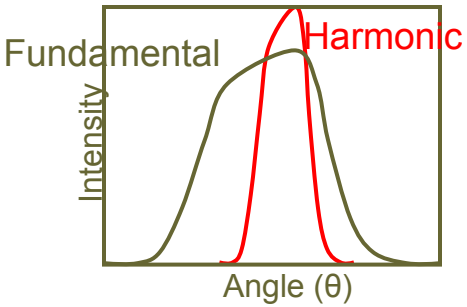


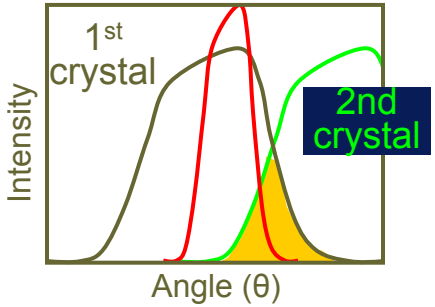
I. Beam line set-up and optimization: Monochromator tuning



Bragg's law:
$n \cdot \lambda = 2 \cdot d \cdot \sin(\theta)$

n=1 : "fundamental"
n>1 : "harmonic"





"Detuning": rotating 2nd crystal slightly away from diffraction condition.

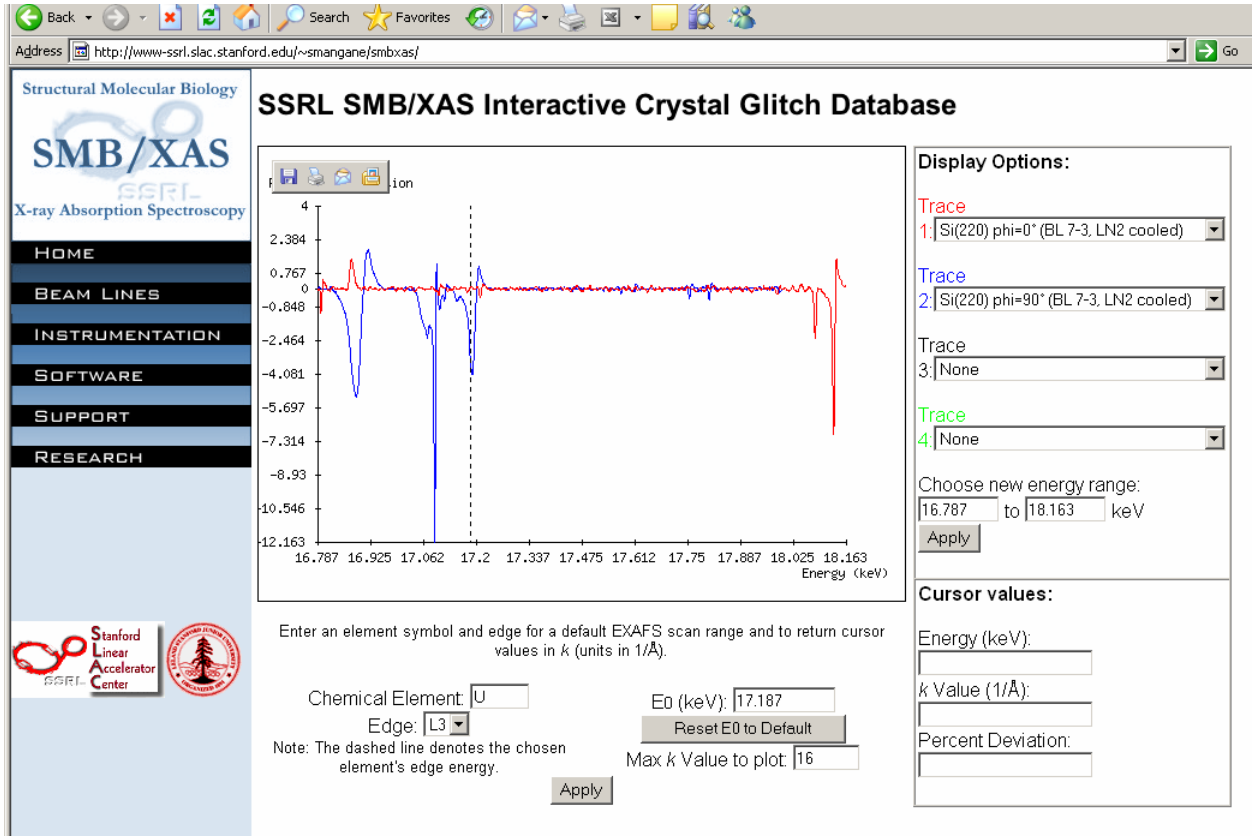
→ Reduces contribution from harmonics!

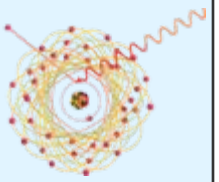
→ Typical values:
~40% @ 6 keV
~25% @ 13 keV
~15% @ 20 keV

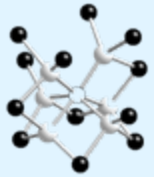
I. Beam line set-up and optimization:
Choice of monochromator crystal

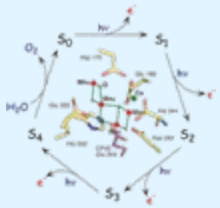
Si(220): Energy range: ~4 to 40 keV, higher E resolution

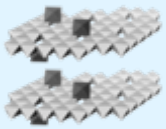
Si(111): Energy range: ~2 to 20 keV, lower E resolution



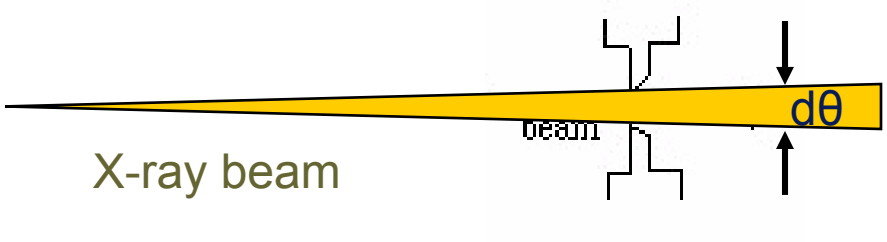








I. Beam line set-up and optimization:
Slits control energy resolution!

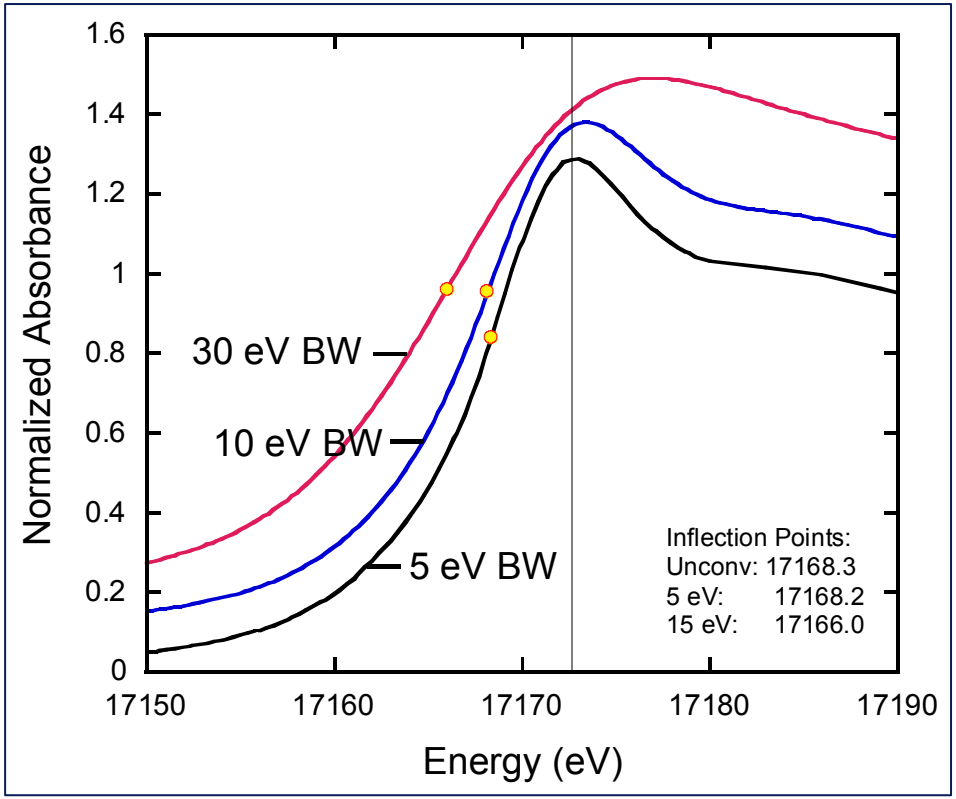


E resolution, dE/E
= dθ/Tan(θ_{bragg})

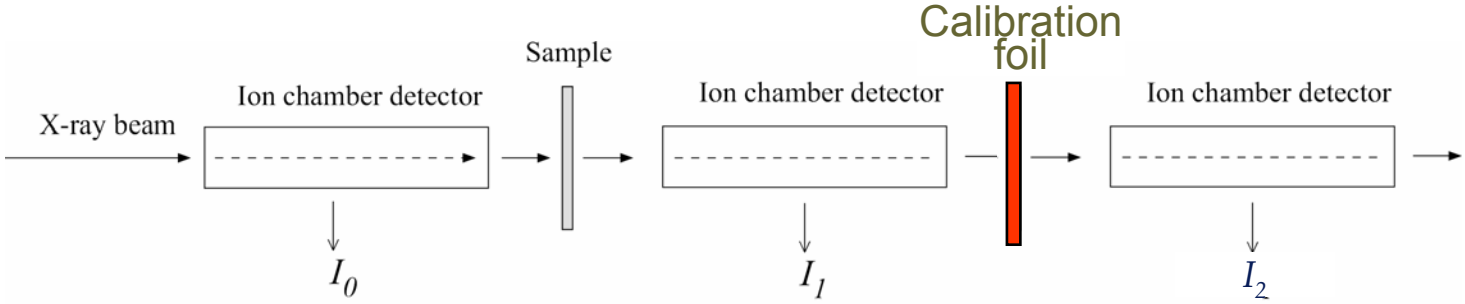
To change energy resolution: Change slit opening.

Big effect on edge shape AND apparent calibration!

ALSO – choice of crystal (e.g. (220) vs (111)) impact energy resolution

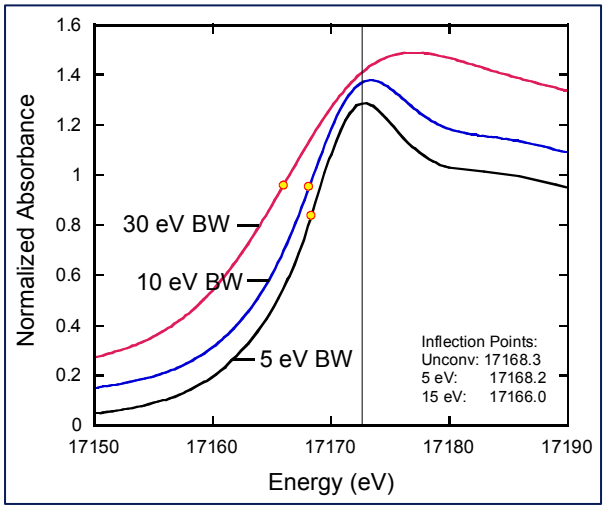


I. Beam line set-up and optimization:
Mono energy calibration



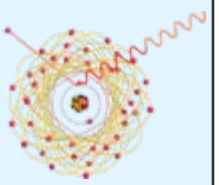
Calibration foil located between I_1 & I_2.

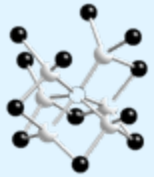
Remove foil after taking calibration (check calibration between every other sample).
- OR – use calibration foil ***different*** from sample element (continuous calibration).

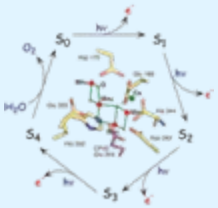


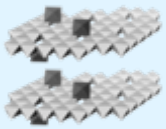
Calibrate on first inflection point of rising edge (preferred) or on top of white line.

Use consistent energy resolution!: mono crystal, same slit opening. Good strategy: close slits so spectrometer resolution is < core hole life time.



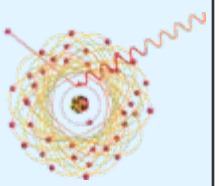






II. Sample alignment and detectors

- Transmission *vs* fluorescence geometry
- Transmission geometry
- Lytle detectors for fluorescence yield detection
- Ge detector: highly dilute, chemically complex samples



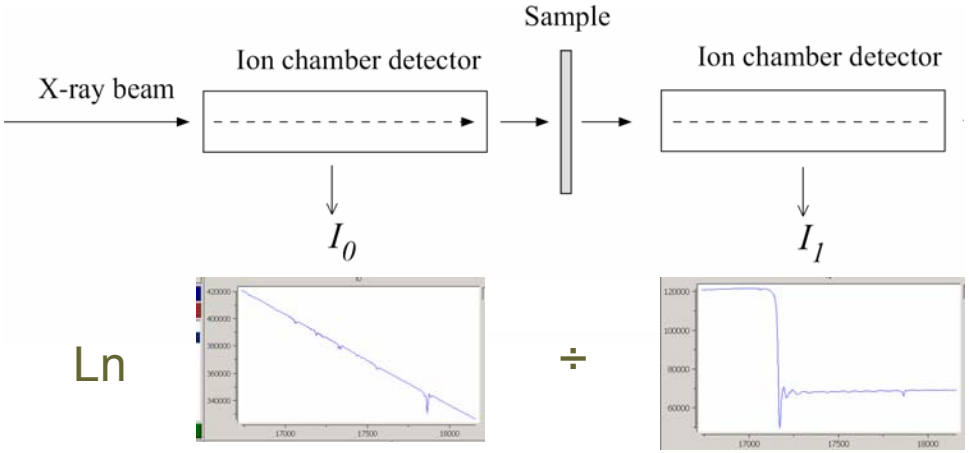
II. Sample alignment and detectors: Transmission *vs.* fluorescence geometry

	Advantages	Requirements	Comments
Transmission mode with ion chambers	Simple Collect 100% of signal No count-rate limitation	Constant sample density, thickness!!!!! Concentrated, rel. pure samples.	Eliminate harmonics!
Fluorescence mode with ion chambers	Simple Collect ~10% of sphere No count-rate limitation	> 500 ppm No strong interfering elements	Beware: over-absorption!
Fluorescence mode with energy-dispersive detectors	Excellent for dilute samples or samples samples with interfering fluorescence lines	< 300 KHz count rate total count rate	Beware: over-absorption and dead-time!

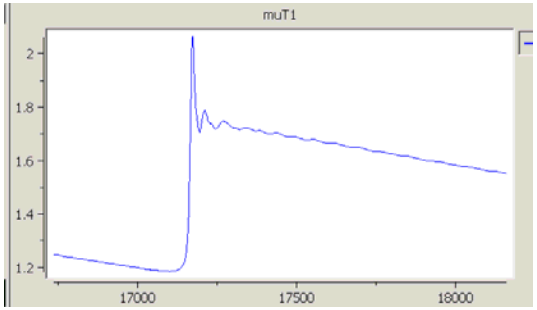
Examples:

Concentrated solids: grind to fine powder, thoroughly mix with BN or $LiCO_3$, use trans mode.
Thick solid suspensions: run in trans if mechanically stable and can make thin enough.
Aqueous solutions: typically fluor mode with E-disp. detector. Maximize concentration.
Soils: fluo mode typically with E-disp. detector

II. Sample alignment and detectors: **Transmission geometry**



Beer's law:
Absorbance ~ $(\mathrm{Ln} I_0/I_1)$

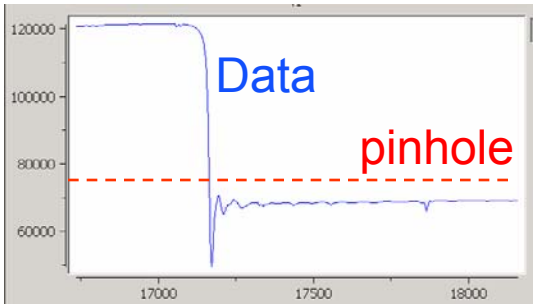


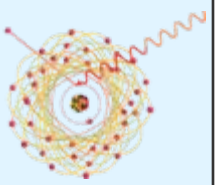
Beware, I0 and I1 can contain "junk" intensity not proportional to EXAFS: *e.g.,*

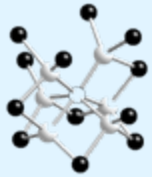
I_1 = data + pinhole intensity + harmonics + dark current

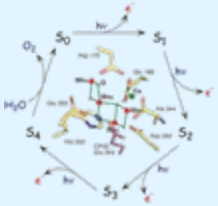
When junk intensity ~ data then spectra will be screwed up!

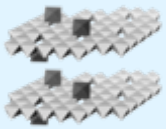
I_1





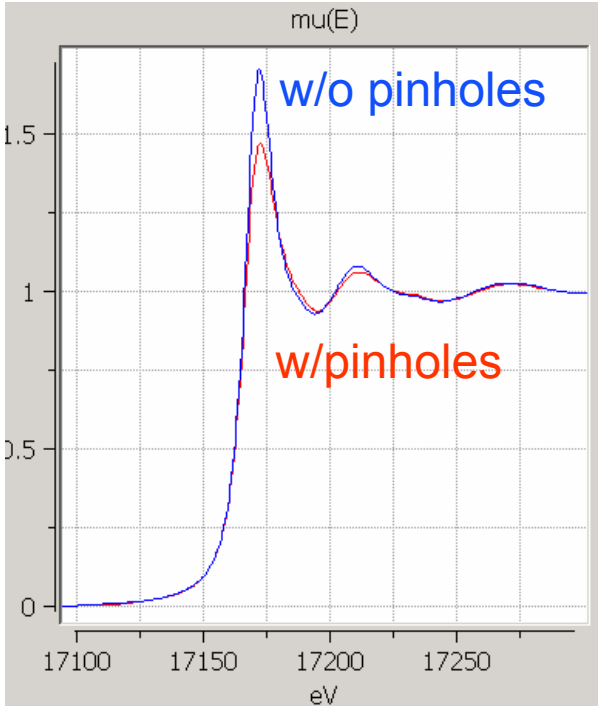






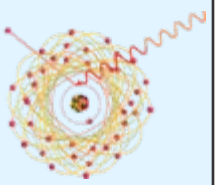
II. Sample alignment and detectors: **Transmission geometry**

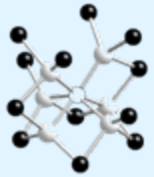
And, your data will look like:

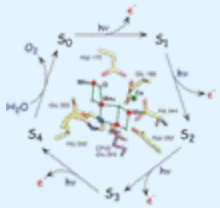


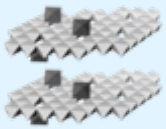
Rules for transmission samples:

- Must be homogeneous on *1 μm* scale
- Use small slits –typically NOT count-rate limited!
- Must be of rigorously constant thickness
- Must rigorously eliminate harmonics
- Must measure/subtract dark current
- Ideal sample: I_1 drops by 70 to 90% over edge







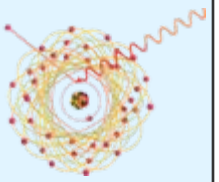


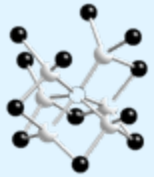
II. Sample alignment and detectors:
How to prepare transmission samples

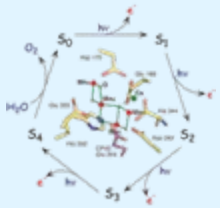
Ideally, wish to prepare powder samples that have the same homogeneity of a *~2 μm-thick metal foil!*

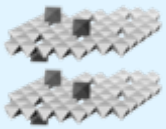
How do we do this in a sample that is typically ~1 mm thick?

- *Proper density* – achieved by mixing small quantity of sample into a weakly-absorbing matrix.
  - Typical matrices: BN, sucrose, Al_2O_3. *Al_2O_3 is often best because it is not redox active and it is very hard, so it can be used to further mill the sample.*
- How much compound to add? – Can be calculated using web tools at http://www.cxro.lbl.gov/ to obtain ~80% absorption by the metal of interest above the edge. Typical ratio is 20 mg of sample in 70 mg of BN or Al_2O_3.
- *Homogeneity* – is achieved by first milling your sample and matrix separately and thoroughly using mortar/pestle to obtain particle size < 1 μm. Then, weigh sample into matrix and continue to mix
- Must be of rigorously constant thickness: load into stiff sample holders.
- Pressing pellets is helpful, but beware of preferred particle orientation!









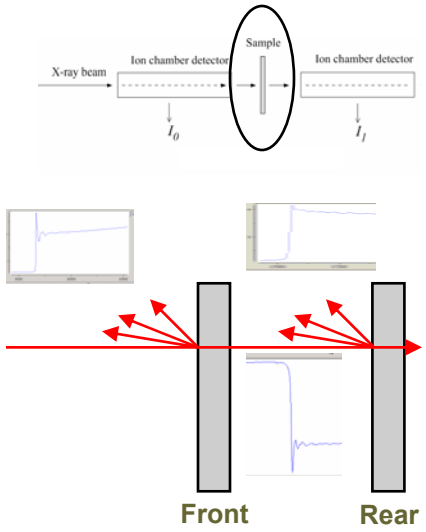
II. Sample alignment and detectors: **Fluorescence geometry**

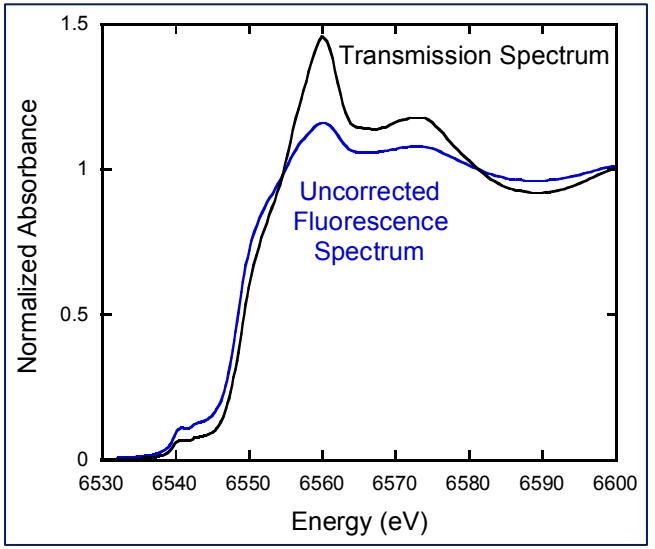
Dilute sample paradigm – assumes absorption of beam is so weak that it does not corrupt amplitudes from rear of sample.

Concentrated samples will suffer amplitude reduction, so called, "***over-absorbance"*** effect.

Can strongly modify XANES region.

Mitigation: run concentrated samples in transmission, with electron yield. In some cases, it is possible to analytically correct for self absorbance (Corwin Booth's talk this AM.





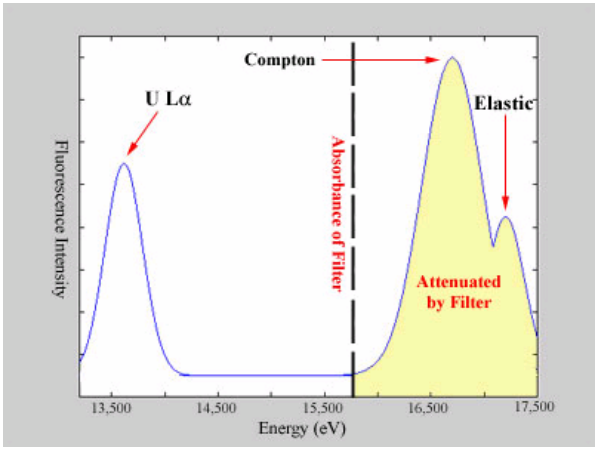
II. Sample alignment and detectors: **Lytle detector**

Good for relatively pure and moderately dilute samples (~1,000 to 20,000 ppm range).

Ionization chamber detector: *no* practical count rate limit

Gases: Ar (< 10 KeV), Xe (10 – 15 keV), Kr (>15 keV) – energies of *emission* lines!

Use **x-ray filters** in conjunction with Soller slits to reduce elastic scattering from signal.



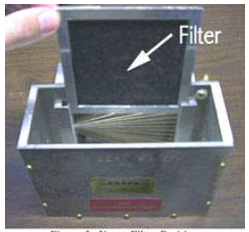


Figure 3. X-ray Filter Position

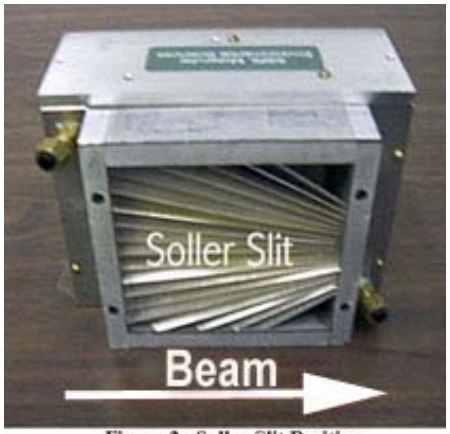
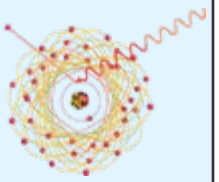
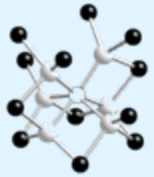
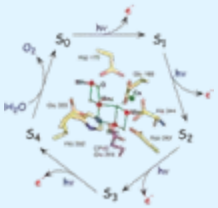
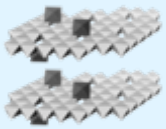


Figure 2. Soller Slit Position



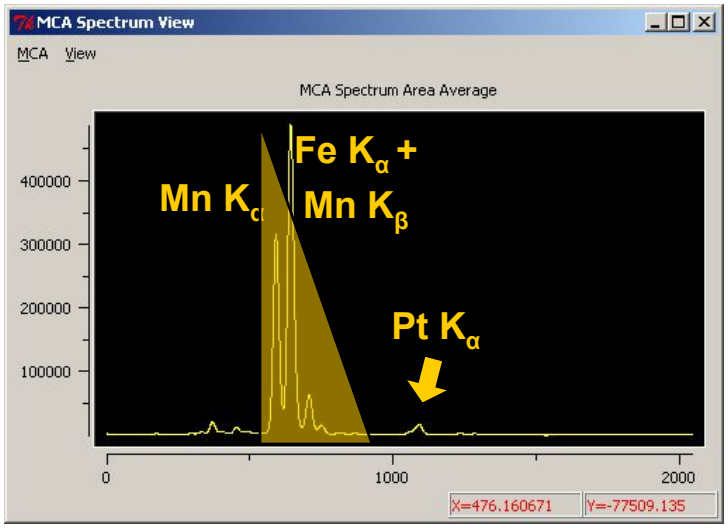






II. Sample alignment and detectors: **Dilute & chemically heterogeneous samples**

Pt in marine ferro-manganese crusts

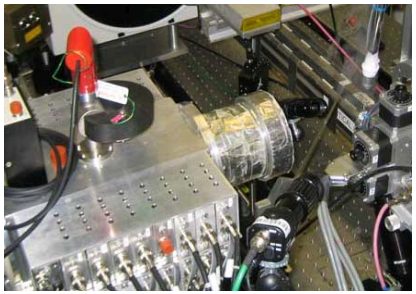


Solid-state detectors (single Ge and Si crystals) provide energy resolution of *ca* 250 eV FWHM and can resolve individual emission peaks.

Disadvantage: count-rate limitation to ~280,000 counts/sec

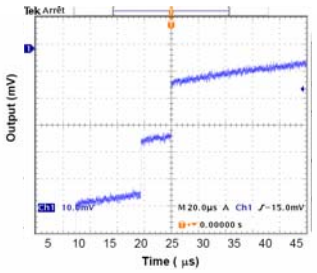
Use high-pass **x-ray filters** (in this case, V or Al) to cut “background” counts and thus allow for more Pt counts.

II. Sample alignment and detectors:
Solid state detectors: basics



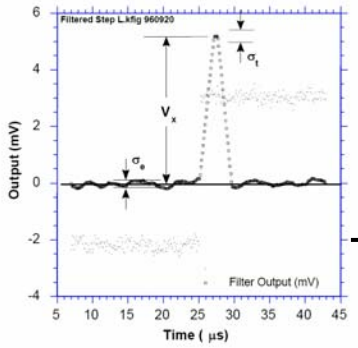
Preamp

Voltage ramp



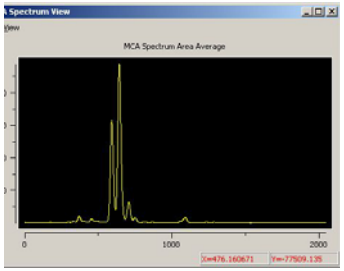
Amplifier

Voltage pulse train

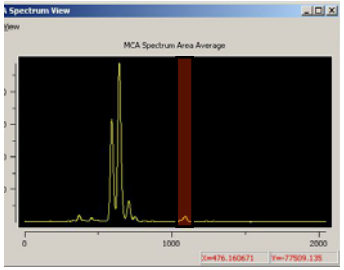


Incoming Count Rate, "ICR" ~1,000,000 cps

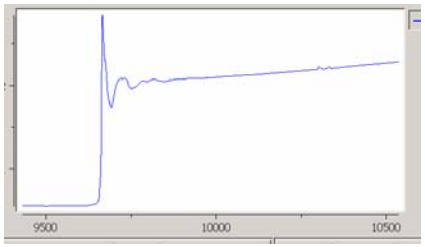
Multichannel analyzer



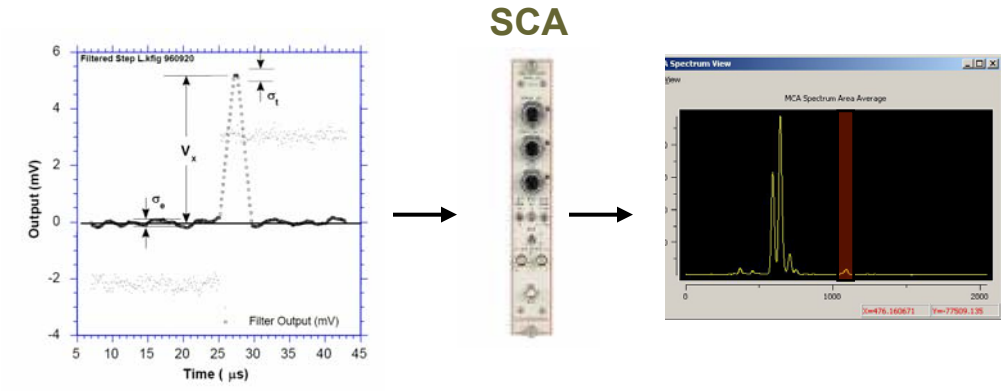
SCA



Windowed or "SCA" counts, < 600,000 cps



II. Sample alignment and detectors:
Solid state detectors: basics



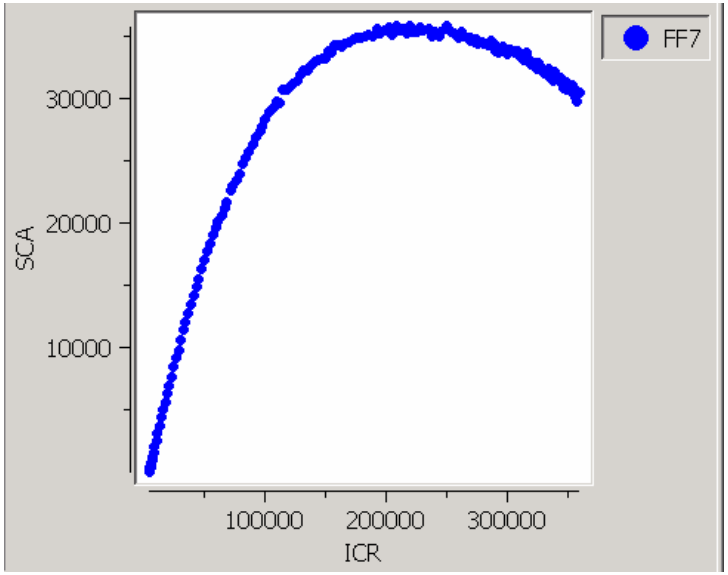
~ 1 µsec

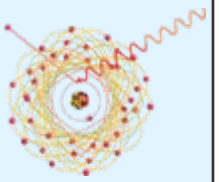
When count rate approaches ~100,000 counts/sec, detector becomes paralyzed during some events = “deadtime”, according to:

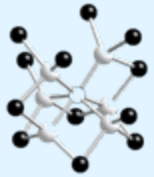
$SCA = K \cdot ICR_t \cdot \exp(-ICR \cdot \tau_d)$

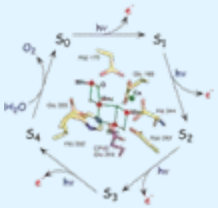
κ = constant, τ_d = dead time.

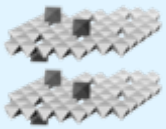
Data can be quantitatively corrected (hands on sessions)











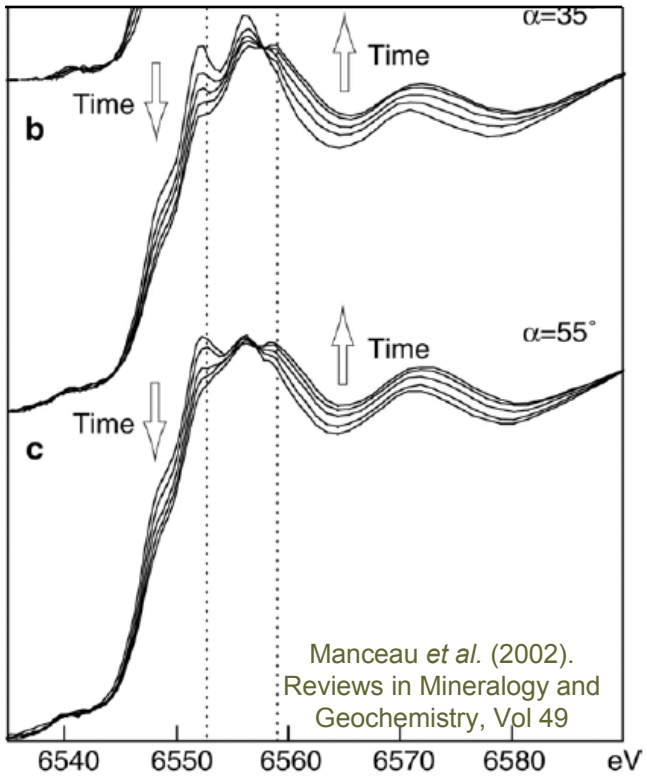
III. Data acquisition

To be discussed during hands-on sessions:

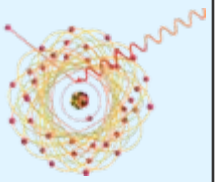
- Setting up regions files - optimizing counting time, data range
- How to check data quality
- What will be the good data range?
- How many scans are enough?

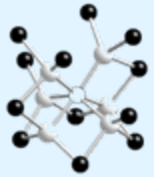
Beam damage…

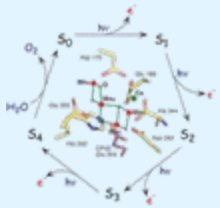
some samples are particularly subject to photo-induced redox changes. Mitigation: typically cryogenic temperature for data acquistion.

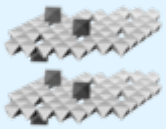


Manceau *et al.* (2002). Reviews in Mineralogy and Geochemistry, Vol 49









III. Data acquisition
which beam line should I use?

Model compounds (concentrated, compositionally simple):
BL: 4-1, 4-3, 10-2

Moderately dilute samples:
BL: 4-1, 4-3, 10-2

Highly dilute and/or chemically heterogeneous samples:
BL: 7-3, 9-3, 11-2

Low-energy XAS (~2.1 - ~6 keV):
BL: 6-2, 4-3

High-energy XAS (~17 - 38 keV):
BL: 4-1, 7-3, 10-2, 11-2

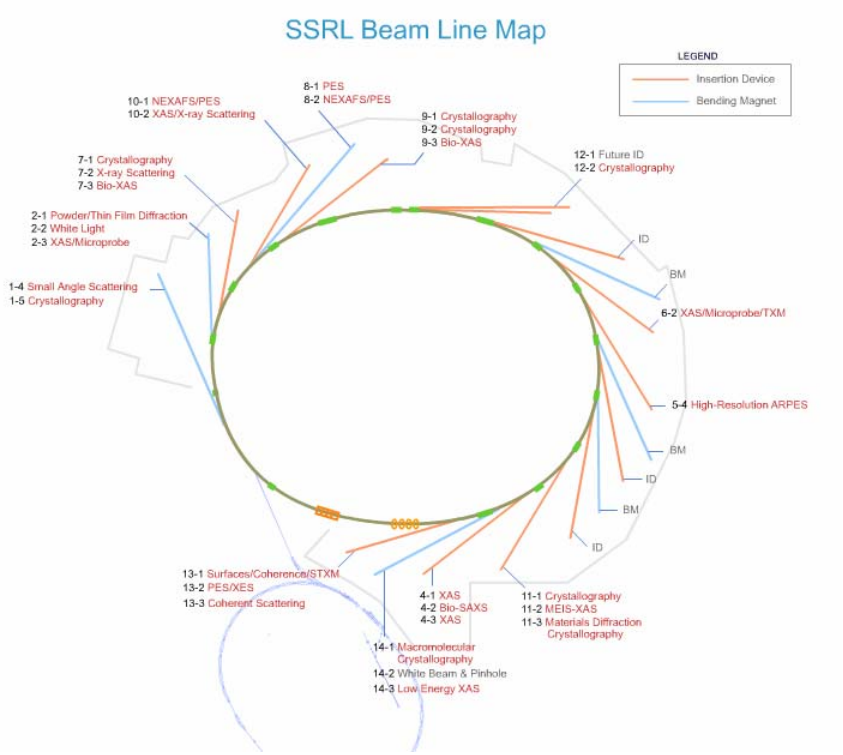
Mat Sci: BL: 4-1, 4-3, 10-2

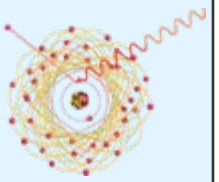
Environmental: BL: 4-1, 4-3, 10-2, 11-2

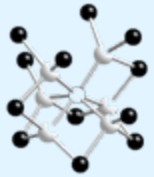
Biological: BL: 7-3, 9-3

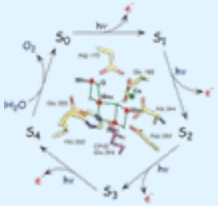
Micro-XAS: BL 2-3

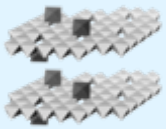
Grazing-incidence XAS: BL 11-2











Quiz!

Connect the pictures to the data…

Bragg's law:
$n \cdot \lambda = 2 \cdot d \cdot \sin(\theta)$