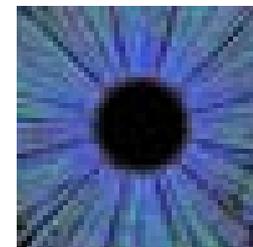


# Basics of sample preparation, detectors, signal chain

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Nov 3, 2016



## Sample Preparation:

- Little bit about synchrotron
- Importance of sample preparation
- Different states of samples
- Videos showing sample preparation

## Detectors:

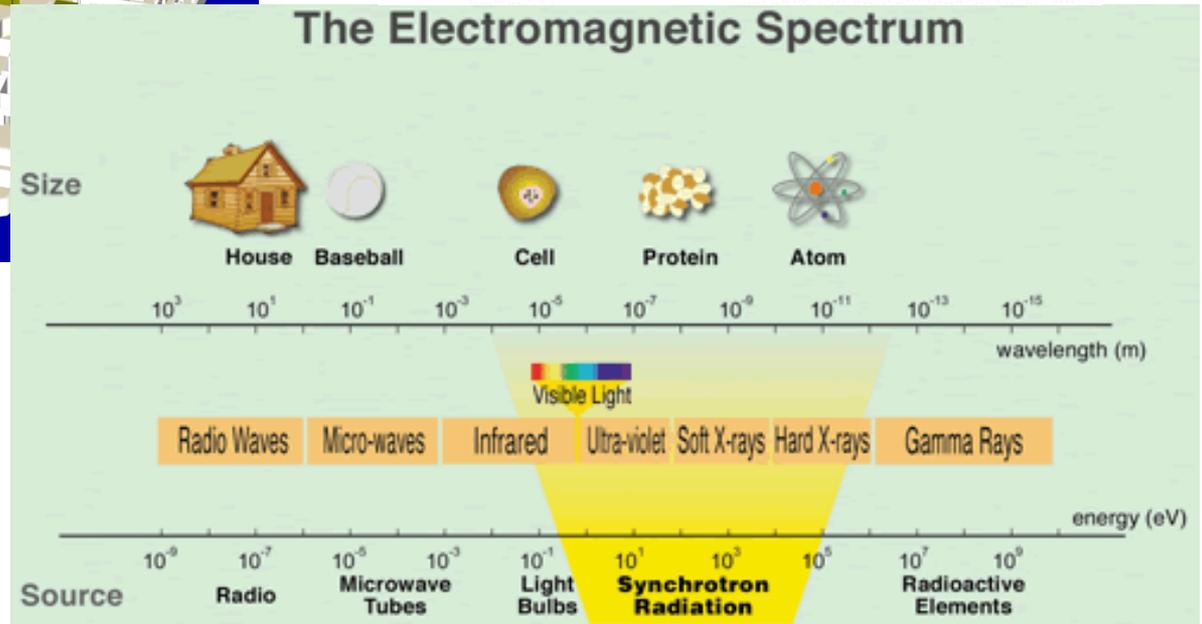
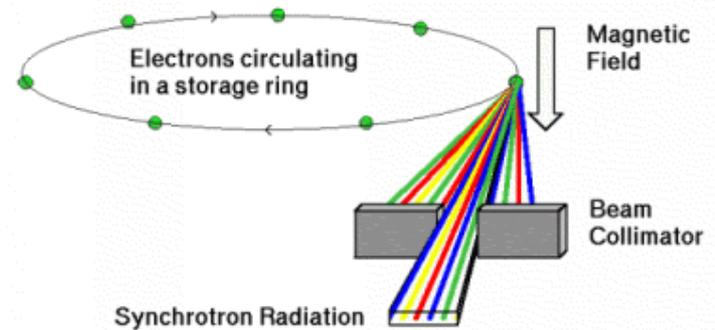
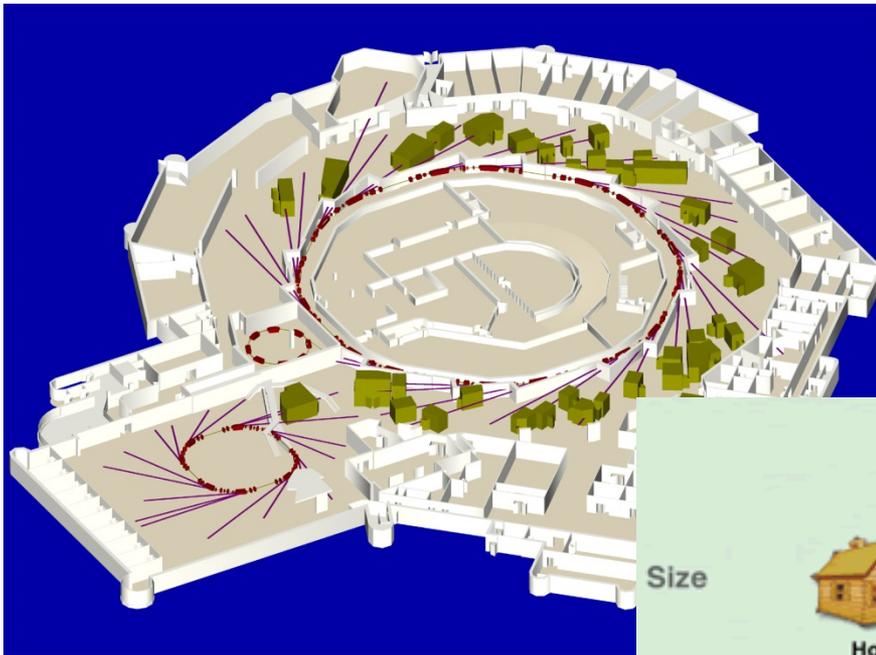
- Kinds of detectors
- What kind suitable for samples
- Care and caution

## Signal Chain:

- What happens during experiment
- Kind of signal and its treatment
- Data format

# SYNCHROTRON

In a synchrotron electrons are accelerated and stored at a certain energy: At NSLS-II the energy is 3 GeV and the current is 250 mA  
Top of the fill, will eventually be 500 mA.



# Brightness at a synchrotron. Comparing to a laboratory X-ray source (Rotating Anode X-ray generator).

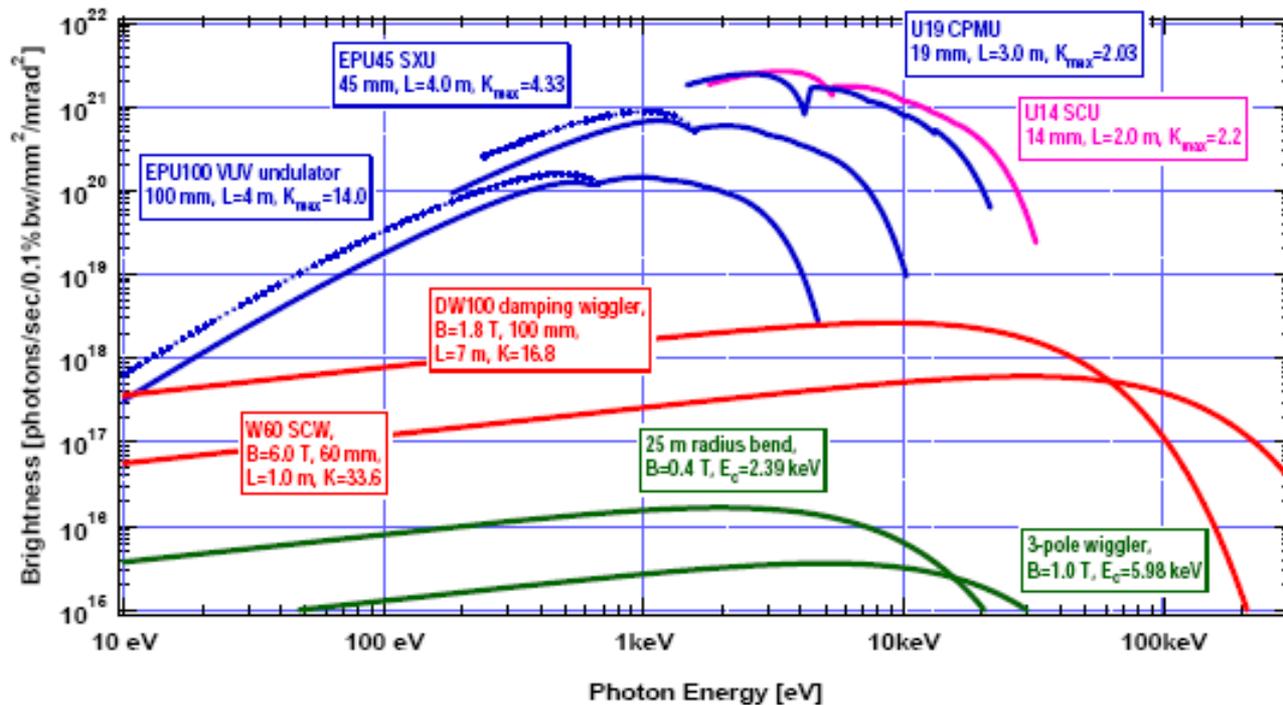


Figure 1. Brightness vs. photon energy for various devices at NSLS-II.

Bending Magnets, Wigglers, Undulators accelerate  
Electrons: Result: Radiation Emission

## Parameters of the ISS beamline at NSLS-II

Energy Range: 4.9 keV - 36 keV

Mono Crystal Grating: Si 111 double crystal high heat load and optional Si 220 high resolution monochromator

Resolution: medium resolution

Flux:  $10^{14}$  @ 10 keV

Spot Size: typically: 25  $\mu\text{m}$

Total Angular Acceptance: 1 mrad x 0.1 mrad

## Properties of TES beamline at NSLS-II

TES is a tender-energy beamline optimized for spatially resolved and in-situ XAFS and imaging in the 1-5 keV energy range, in a non-vacuum sample environment.

Energy Range: 1-8 keV

Mono Crystal Grating: Si(111), InSb, Beryl, Quartz

Resolution:  $10^{-4}$  for Si(111)

Flux: up to  $10^{12}$  ph/sec calculated for 500mA

Spot Size: tunable 1-100 microns

Total Angular Acceptance: 2.5 mrad H x 0.4 mrad V

Notes: Helium sample environment

## SAMPLE PREPARATION:

Once it is decided that XAS is one of the technique that can answer the questions you are looking for, and you also decided what kind of standards you will be using then the next question comes: What XAS method to be used:

Transmission

Fluorescence

Electron Yield

How much sample one needs ?

How to make the sample.

## TRANSMISSION:

The rule of thumb is that if the content of the element of interest is one weight % or more, you are better off doing XAS in transmission. ( Could be 5 % or more difference of opinion. TRY IT ).

The other criteria is the edge jump is  $>$  or  $= 0.1$

## Absorption Length: A useful term to know.

$\ln(I_0 / I_t) = \mu x = 1$ , then the thickness of the sample  $x =$  one absorption length

It is same as  $I_0 = e \cdot I_t$ , or  $I_0 = 2.718 \cdot I_t$

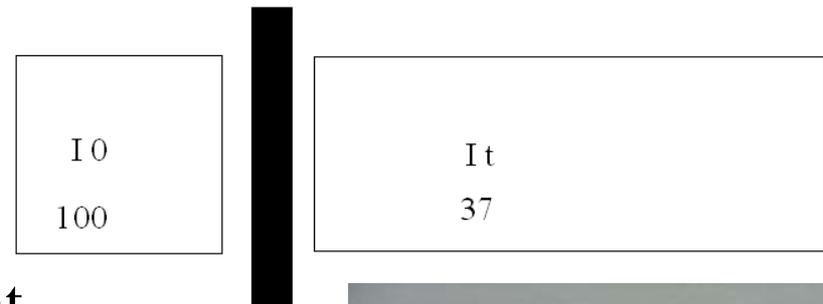
Rule of Thumb:

For K-edges of pure elements:

One Absorption length in micron is about half the the K-edge of that element in KeV.

e.g Cu K-edge = 8.979 KeV  
Absorption length  $\sim$  4 micron.

One Absorption Length



SAMPLE



# http://www.csrii.iit.edu/mucal.html

**Mucal on the web**

This is a program to calculate x-ray absorption coefficients. It uses the fortran subroutine mucal written by Pathikrit Bandyopadhyay. You can get the original subroutine (mucal.f and a version, mucal.c) [here](#).

If you want to know edge energies, fluorescence yield, etc. of an element fill in the symbol and submit query. For x-ray absorption coefficients, also fill in the energy of interest in the energy box.

Element Symbol:

Energy:  keV - Please note that values above 500 will be treated as eV rather than keV

To submit the query, press:  .

---

Calculations are based on data compiled By *W. H.McMaster et. al.*

Fluorescence yield data by *M. O. Krause, J. Phys. Chem. Ref. Data. 8, 307(1979).*

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Please report problems to [Carlo Segre \(segre@iit.edu\)](mailto:segre@iit.edu).

start Microsoft PowerPoint ... http://gbxafs.iit.edu/... Mucal on the web - W... 2:47 PM

## Answer from McMaster Table:

### X-ray properties

Data for Cu;  $Z = 29$  atomic weight = 63.5400009; density = 8.93999958

K-edge at: 8.97900009 keV

L-edges at: 1.10000002, 0.952000022, 0.931999981 keV

M-edge at: 0.119999997 keV

K-Alpha1,K-Beta1 at: 8.04699993 8.90400028 keV

L-Alpha1,L-Beta1 at: 0. 0. keV

K,L1,L2,L3 jumps: 7.95528412 1.15726078 1.40999997 2.87400007

Fluorescence yield for K,L1,L2,L3: 0.4400, 0.0016, 0.0100, 0.0110

Cross-sections at  $E = 9.$  keV Photoelectric 285.486938  $\text{cm}^2/\text{gm}$

Coherent 1.70745862  $\text{cm}^2/\text{gm}$

Incoherent 0.0718918592  $\text{cm}^2/\text{gm}$

**Total 287.266266  $\text{cm}^2/\text{gm}$**

The unit conversion factor (C) is 105.5  $\{(\text{Barns}/\text{Atom}) = C * (\text{cm}^2/\text{gm})\}$

Absorption coefficient 2568.1604 1/cm

1/ $\mu$  (element): 3.89383793 microns

Created by Pathikrit Bandyopadhyay, recent updates by Carlo Segre. Calculations are based on data compiled By *W. H.McMaster et. al.*

Fluorescence yield data by *M. O. Krause, J. Phys. Chem. Ref. Data. 8, 307(1979).*

Please report problems to [Carlo Segre \(segre@iit.edu\)](mailto:segre@iit.edu).

absorption coefficient ( $\mu$ ) = density ( $\rho$ ) (g/cm<sup>3</sup>) x total cross section ( $\sigma$ ) (cm<sup>2</sup>/g)  
For a pure element.

$$\mu = \rho \times \sigma$$

absorption length =  $1/\mu$

Example: Copper density = 8.94 g/cm<sup>3</sup>, total cross section at 9 KeV = 287.26 cm<sup>2</sup>/g (just above the copper K-edge)

Absorption coefficient =  $8.94 \times 287.26 = 2574/\text{cm}$  Or  $0.2574 / \text{micron}$

Absorption length =  $1/ \text{absorption coefficient} = 1/0.2574 = 3.9 \text{ micron}$

## Sample Calculation

$\text{Fe}_3\text{O}_4$  (magnetite) at 7.2 KeV;

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

density  $5.2 \frac{\text{g}}{\text{cm}^3}$

$$\text{MW} = 3 * 55.9 \frac{\text{g}}{\text{mol}} + 4 * 16.0 \frac{\text{g}}{\text{mol}} = 231.7 \frac{\text{g}}{\text{mol}}$$

$$\sigma_{\text{Fe}} = 393.5 \frac{\text{cm}^2}{\text{g}}; M_{\text{Fe}} = 55.9 \frac{\text{g}}{\text{mol}};$$

$$f_{\text{Fe}} = 55.9/231.7 = .724;$$

$$\sigma_{\text{O}} = 15.0 \frac{\text{cm}^2}{\text{g}}; M_{\text{O}} = 16.0 \frac{\text{g}}{\text{mol}};$$

$$f_{\text{O}} = 16.0/231.7 = .276;$$

$$\begin{aligned} \mu &= 5.2 \frac{\text{g}}{\text{cm}^3} (.724 * 393.5 \frac{\text{cm}^2}{\text{g}} + .276 * 15.0 \frac{\text{cm}^2}{\text{g}}) \\ &= 1503/\text{cm} = .15/\text{micron} \end{aligned}$$

$$\text{Absorption Length} = 1 \mu\text{m}/.15 = 6.7 \text{ microns}$$

Even if you don't know the density exactly you can estimate it from something similar. It's probably between  $2$  and  $8 \text{ g/cm}^3$

# SAMPLE THICKNESS:

Pure elements are useful as reference when doing EXAFS but not that much fun.

The Gurus of XAS suggest a good absorption length of 1-3 for the samples.  
Mostly Samples are not single elements: Real samples as well as standards.

Following formula should be used to find the amount of sample we need:

Following formula can be used to measure the amount of sample required for taking X-ray absorption data in transmission mode.

$$Wd = \ln(I_0/I_t) / \sum\{(\mu/\rho)_j \cdot w_j\}$$

Wd = mass of the sample in g / cm<sup>2</sup>

$\mu/\rho$  = total cross section (absorption coefficient / density) of element 'j' above the absorption edge of the EXAFS element under study in cm<sup>2</sup> / g

w = weight fraction of element j in the sample

The sum is over all the elements in the sample including the EXAFS element.

The value  $\ln(I_0/I_t)$  is 1-3 in most of the calculations.

(A 13 mm diameter die has the surface area of 1.33 square cm)

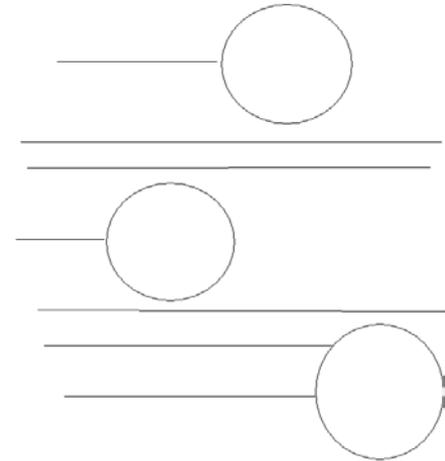
# Uniform Sample Thickness: Brick and Hole Effect:

**Best Sieve:** 600 mesh, meaning in one inch square there are 600 x 600 holes.

The size of particles we get from it =  
 $25400 \text{ micron} / 1200 \sim 21 \text{ micron}$ .

Too big a particle size for most of the EXAFS work.

**Suggestion:** Particle size much less than absorption length.



What type of XAS from  
this kind of sample?  
What if the particles were  
cubic or orthombic?

## When to choose Transmission

You need to get x-rays through the sample

Total thickness should be kept below  $<2-3$  absorption lengths including substrates to minimize thickness effects

Get rid of harmonics by monochromator detuning, harmonic rejection mirrors, etc.

Element of interest must be concentrated enough to get a decent edge jump ( $> 0.1$  )

Pinholes and large thickness variations should be minimized

If you can't make a good transmission sample, consider using fluorescence or electron yield

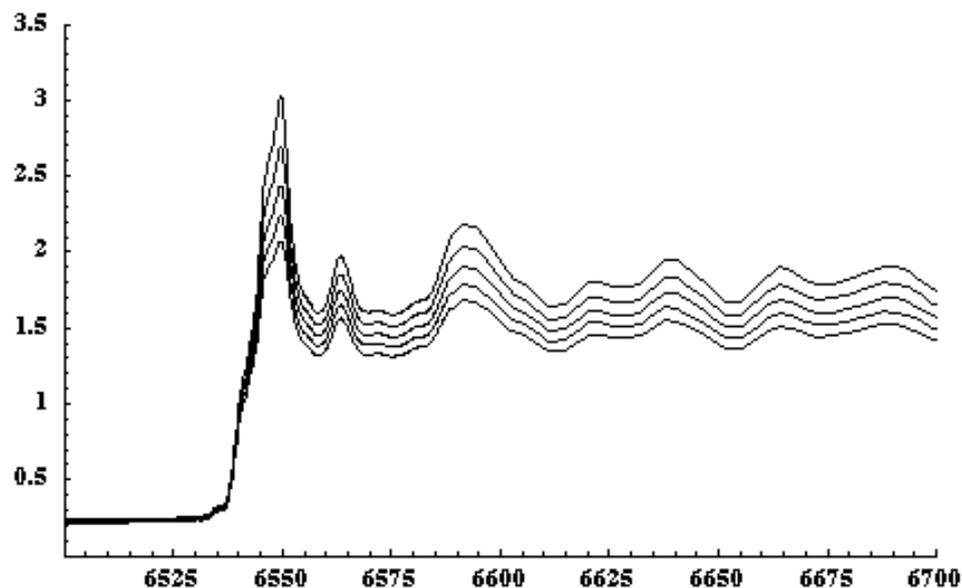
MnO 10 micron thick  $\sim 2$  absorption lengths

leakage varied from 0% to 10%

Edge jump is reduced, EXAFS amplitudes are reduced, white line height compressed

thickness effects distort both XANES and EXAFS - screw up fits and integrals of peak areas

If you are fitting XANES spectra, watch out for these distortions  
Effect of Leakage on spectra



## EXAFS in FLUORESCENCE:

EXAFS formula is valid for thin concentrated or thick dilute samples.

Watch for self absorption effects. They can be corrected during analysis.

The particle size should still be less than one absorption length, and sample should be on a uniform Surface and homogeneously distributed.

Measure a blank sample with no element of interest.

Aluminum holders, tapes, fillers etc. could have impurities.

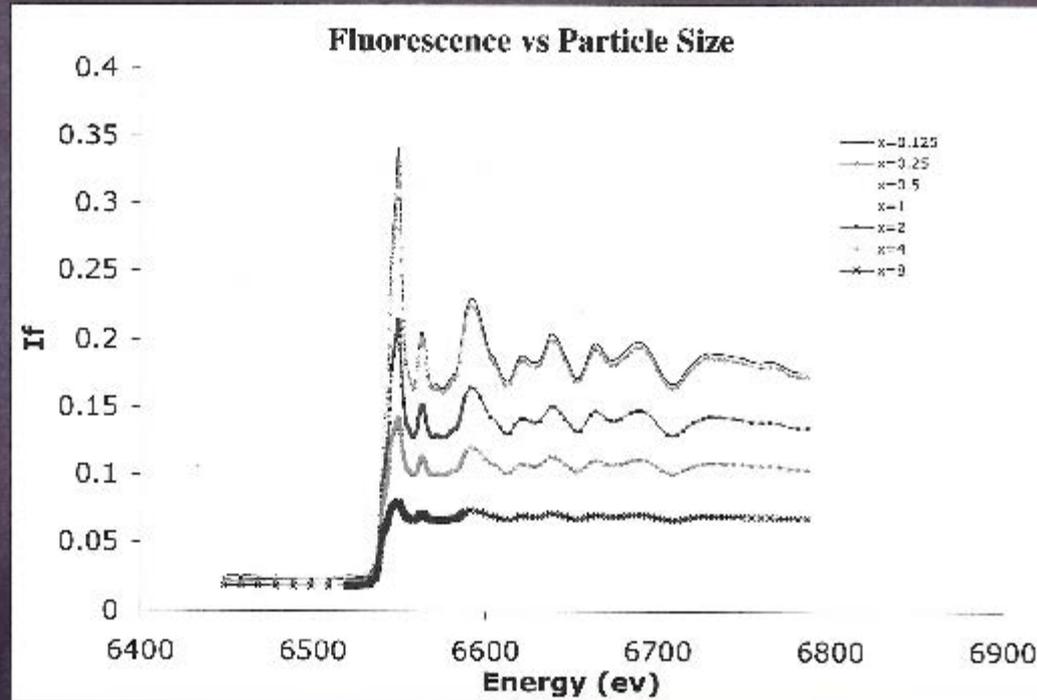
If particles are not small then their orientation and shape can affect the results: **WATCH OUT.**

Change the orientation of the sample in all cases, transmission or fluorescence

For details one should check Grant Bunker's notes and Koningsberger's Book.

## Speciation problems

Nonlinear distortions of the spectra depend on particle size and distribution. This affects speciation results



## SEDIMENTATION:

To make the particles even smaller:

After sieving and grinding the sample. It can be placed in a non-reactive liquid.

If the density of the sample the liquid and the height of the liquid column is known, then The time can be calculated to find a certain size of the particles to settle at the bottom.

For example:

To get MnO particles less than one micron:

After grinding, put MnO in a test tube with 5 cm column of acetone.

In 638 seconds 1 micron and greater particles will settle in the bottom.

Supernatant can be decanted with a pipette and can be dried.

(SEE GRANT BUNKER'S TUTORIAL ON THE WEB)

## THICKNESS EFFECT: HOLES : HARMONICS:

The edge jump is reduced. The EXAFS oscillation amplitudes are reduced.

The white Line and the Area is reduced.

# sedimentation

Selecting  
yet smaller  
particles

Drag force on a spherical particle of radius  $R$  moving at velocity  $v$  in fluid of viscosity  $\eta$ :  $F = 6\pi\eta Rv$ . Particles of density  $\rho$  will fall through the fluid of density  $\rho_0$  at a speed in which the particle's weight, less the buoyancy force, equals the drag force:

$$(\rho - \rho_0) \frac{4}{3} \pi R^3 g = 6\pi\eta Rv.$$

If the height of the fluid in the container is  $h$ , the time  $t$  that it would take all particles of radius  $R$  to fall to the bottom would then be:

$$t = \frac{9}{5} \frac{\eta h}{(\rho - \rho_0) g R^2}$$

# worked example

Example: MnO in acetone at 20C  
viscosity of acetone :

$$\eta = 0.0032 \text{ Poise}$$
$$= 0.0032 \text{ g}/(\text{cm} \cdot \text{s})$$

$$R = 1 \mu\text{m} = 3 \cdot 10^{-4} \text{cm}$$

$$\text{density of acetone: } \rho_0 = 0.79 \frac{\text{g}}{\text{cm}^3}$$

$$\text{density of MnO: } \rho = 5.4 \frac{\text{g}}{\text{cm}^3}$$

$$h = 5 \text{cm}$$

$$g = 980 \text{cm}/\text{s}^2$$

$$\rightarrow t = 638 \text{ seconds.}$$

## Use Sieve and Mortar and Pestle:

Grind the sample as good as you can. Sieve it before grinding.

Brush the finest particles on a 6 inch scotch or Kepton tape. Inside an exhaust system tap the back of the tape so that large particles will come out of it. This can also be brushed.

As a result you expect to have particles of the order of around 5 microns left on the tape. This tape can be folded to 4-6 folds to minimize the holes effect.



## MAKING PELLETS:

It turns out that for majority standard samples the amount of sample is not more than about 20-25 mg / square cm.

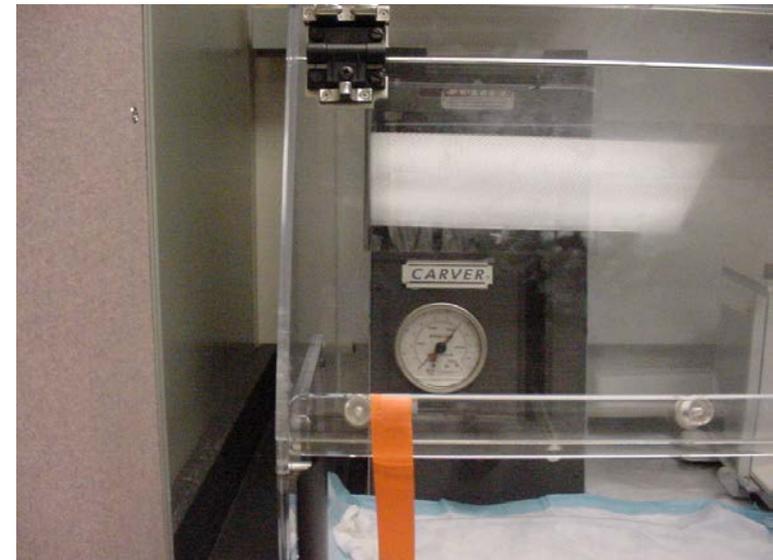
For a cm to half inch diameter pellets, this is very small amount.

Idea is use mixers of very light non-reactive elements to make pellets that will not crack. For this reason we add things like BC, BN, graphite, zeolites, sugar etc.

Recalculate the amount of filler and find the absorption length.

Makes life easier to make pellets.

**IMPORTANT:** Make sure the sample holder the fillers the tapes are free from any impurity, in particular they do not contain the element of interest.



## LIQUID SAMPLES:

Lot more uniform than solid powder samples.

Can be put in a thin mylar pouch sealed from all sides for fluorescent experiments.

For transmission sample can be injected in a sample holder.

Problems: Radiation Damage.

Precipitation could change the results

At low energies  $< 4 \text{ KeV}$ , in fluorescence:

Make sure to use thinnest mylar or Kepton

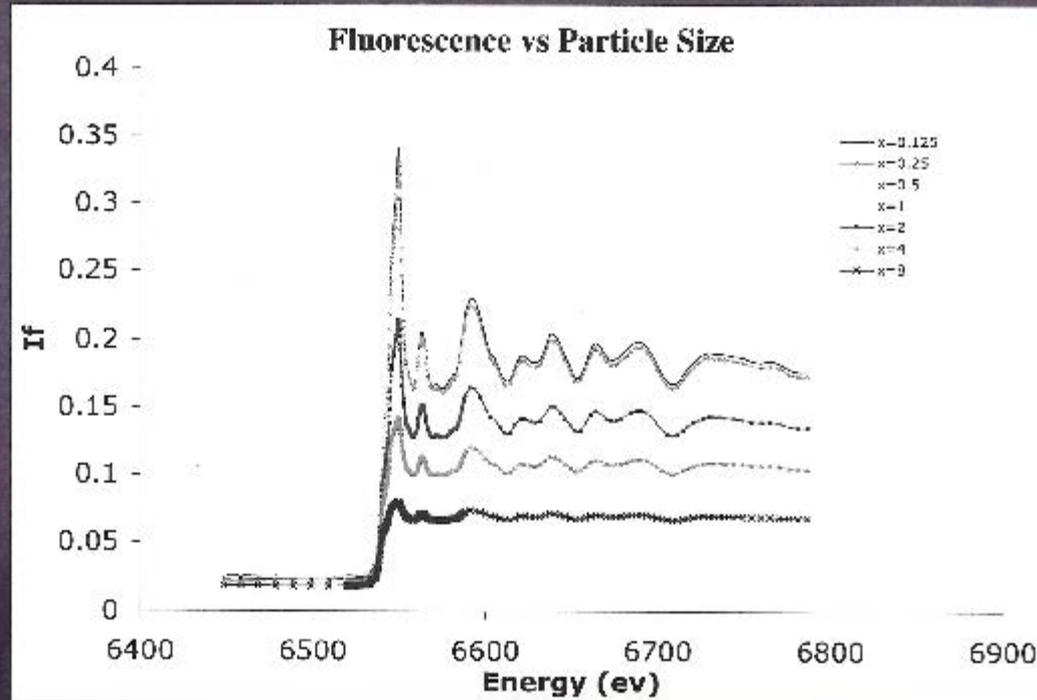
Free from element impurities.

Make sure He is flowing in the chamber.



## Speciation problems

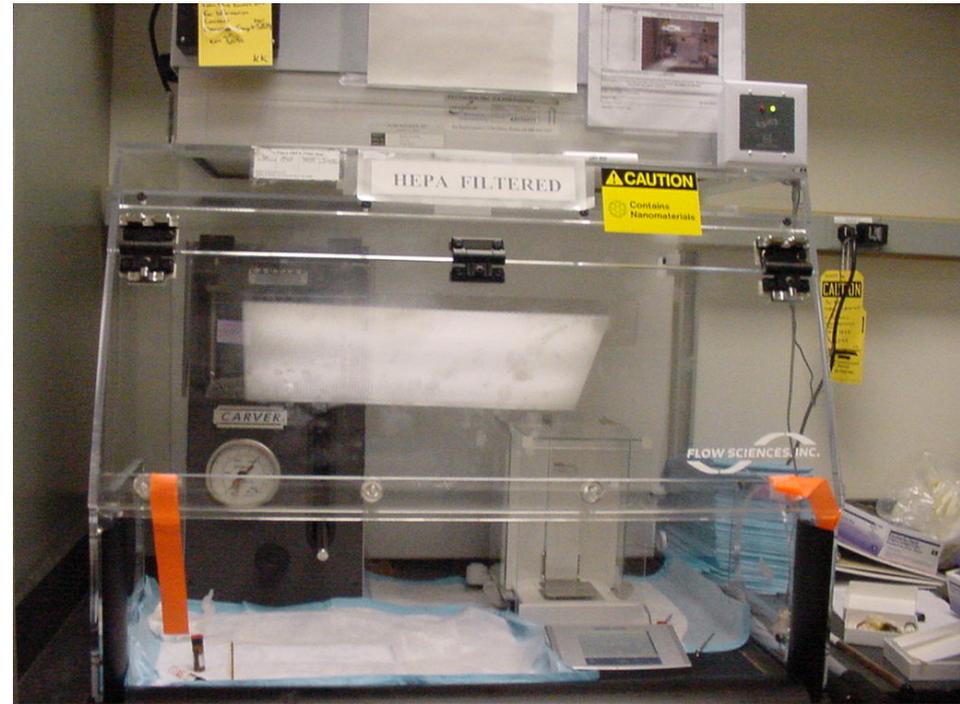
Nonlinear distortions of the spectra depend on particle size and distribution. This affects speciation results



# NANO PARTICLES- OXYGEN-MOISTURE SENSITIVE SAMPLES:

We have nano-hood hooked up to the exhaust system with HEPA filter:

Also Oxygen and H<sub>2</sub>O < 0.5 ppm Glove Box with HEPA filters.

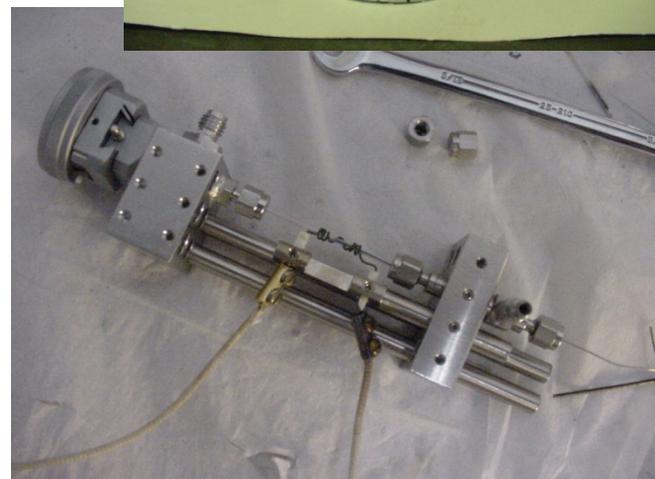


SAFETY FIRST

# In-situ Gas and Temp. Treatment of Samples:

Many catalysts can be treated with reacting gases at different temperatures.

The oxidation reduction and other reactions can be observed along with the quantitative analysis of reactants and product with the use of RGA.



This video shows the most common way of sample preparation



NSLS-1.wmv

For finer particles, decantation  
For liquid samples special cells



NSLS2-1.wmv

Making pellets using hydraulic press



NSLS3-1.wmv

# END STATION – INSIDE THE HUTCH

Ion Chambers: I0, It and Iref for Transmission

Lytle, PIPS, Or other energy resolution detectors.

Inert gas is ionized by X-rays, and produces current of the Order of nano-Amp to micro-Amp. Electrons are collected When high voltage in the ionization range plateau is applied. (25-30 eV is required to ionize inert gases like He, N2, Ar, Kr)

Sample is placed in the sample chamber: Rough alignment with Lasers, final alignment with burn paper. Also X-Z profiles are Used for even better alignment, using X-Z translation stage.



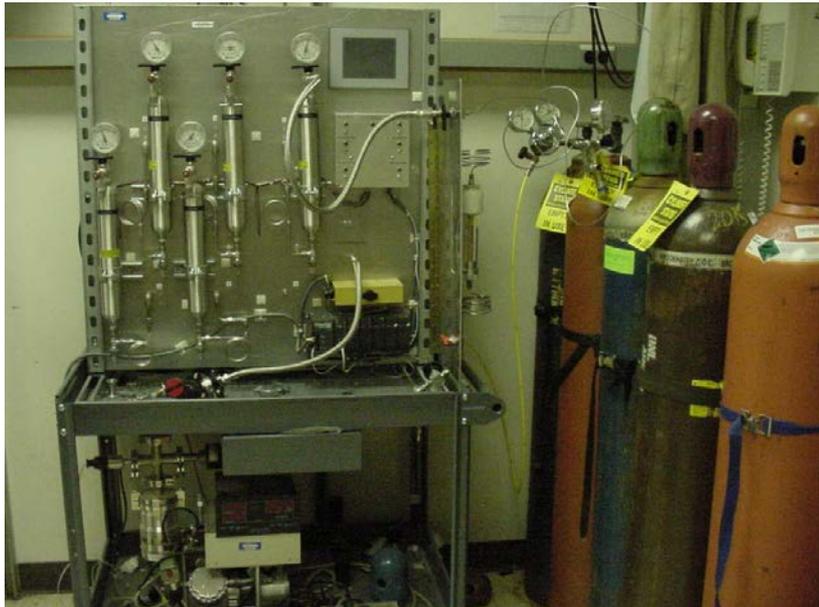
$$\ln(I_0 / I_t) = \mu x$$

For good statistics roughly 5-25 % is absorbed by I0, 50 – 90 % by It. In order to do that different proportion Of inert gases are filled in the sealed ion chambers.

The filling station is used to do that.

Standard is placed between It and Iref.

Ion chambers could be with flow gases or they can be sealed



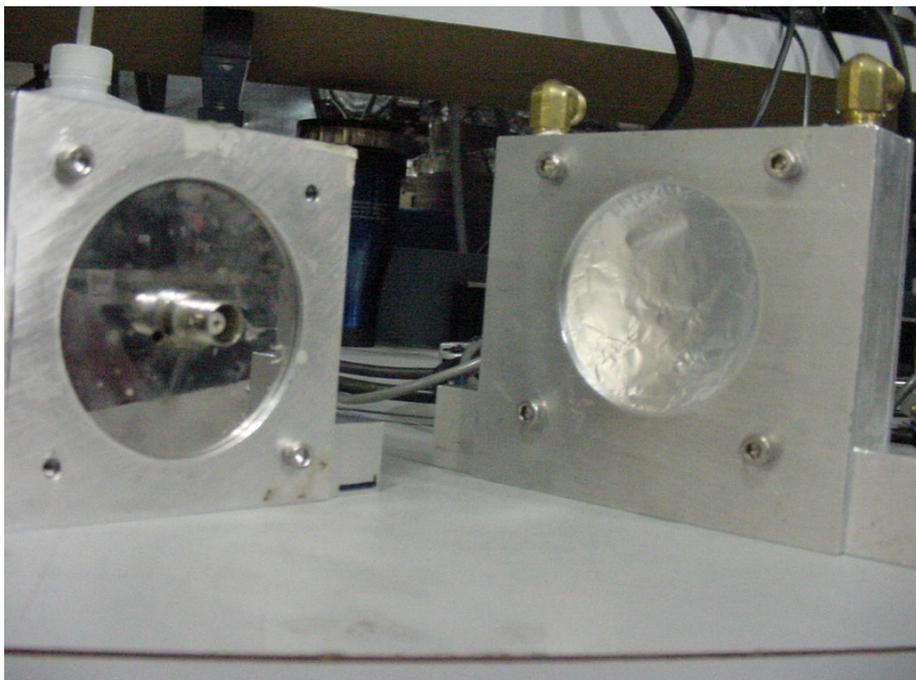
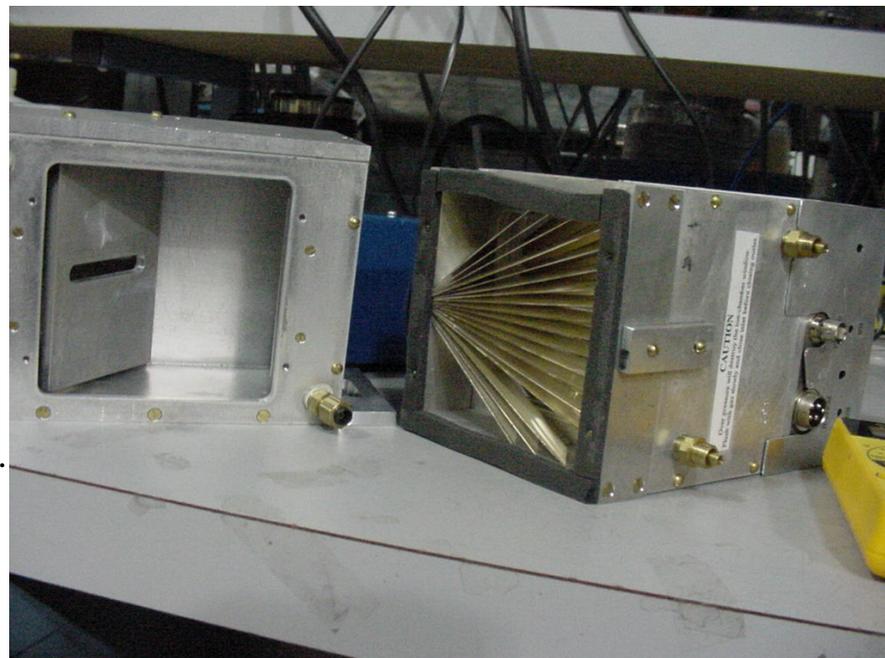
# Fluorescent Detectors Commonly Used:

## Lytle Detector:

Keep the sample at 45 deg. For best signal to noise ratio. Mount it at the back of the sample holder.

Single or double chamber, with widths of one or two inches. Flow appropriate gas.

Function of filters, and collimating fan type slit  
The end where the fans meet should be downstream of the beam.



## PIPS:

Passivated Implanted Planar Silicon (PIPS).  
An order of magnitude less energy to create electron hole pair.

**Plus:** No need of any gas flow. Output direct to amplifier.

**Minus:** Light sensitive. High heat sensitive.

# Electron Yield Detector:

The sample is conducting with cathode.

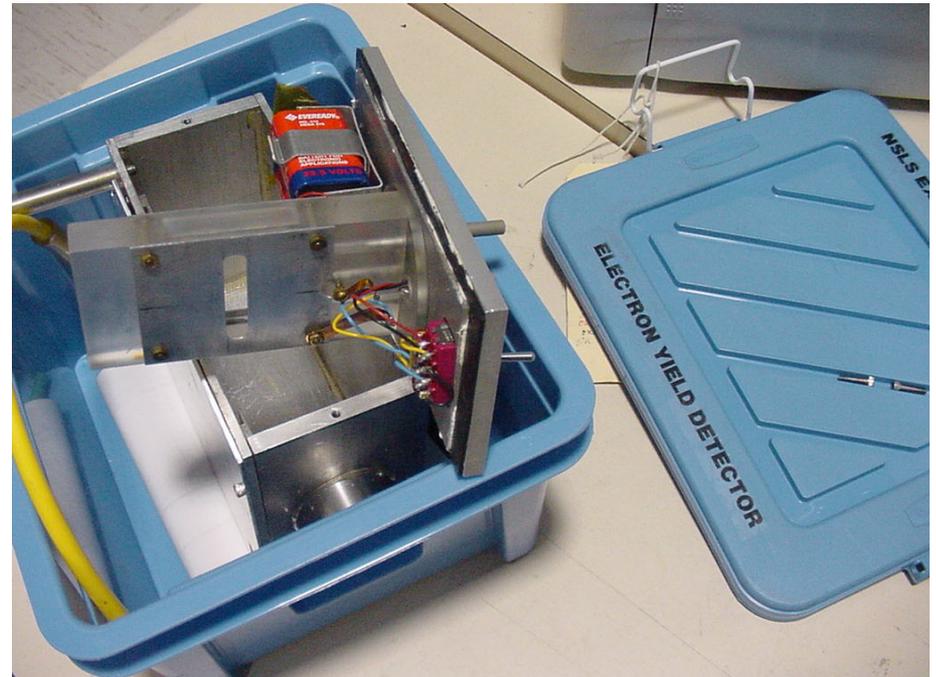
The sample chamber is filled with He.

Electrons are emitted, ionize He and the chamber acts like an ion chamber. The current produced is proportional to absorption coefficient.

Surface sensitive  
technique:

No self absorption effect:

Bulk materials cannot be  
done.



## 13-Element Germanium Detector:

This detector is used for very low concentration samples.

Directly measures photons from the sample, and is tuned to the fluorescence energy of the element of interest.

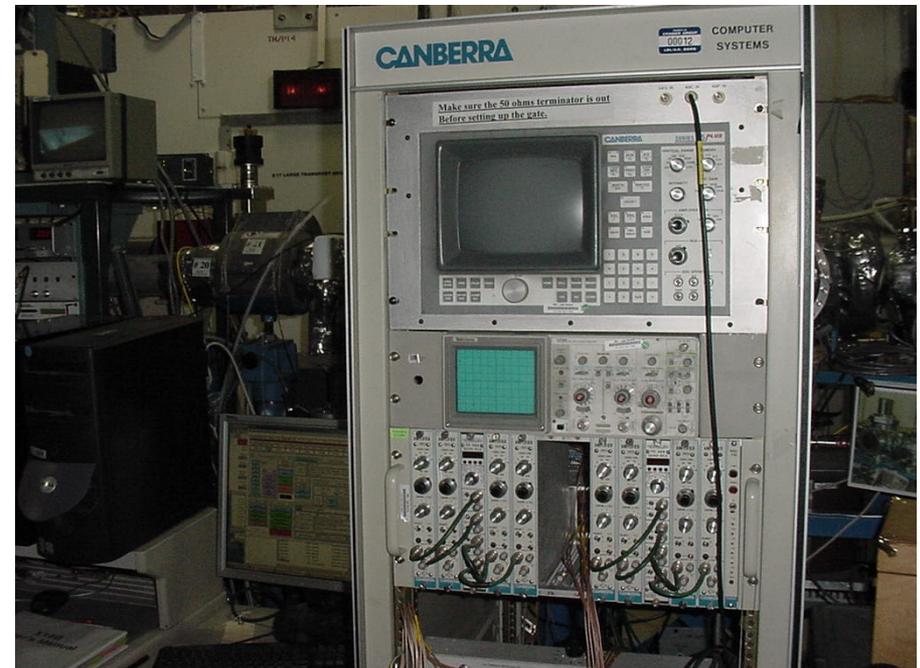
Stays cool at liquid nitrogen. Pre-Amplifiers, Amplifiers, Discriminators are used to select the required energy.

MCA to identify the right signal.

Disadvantage: It is count rate limited. 30 K / s is the limit of total internal counts for it to be linear.

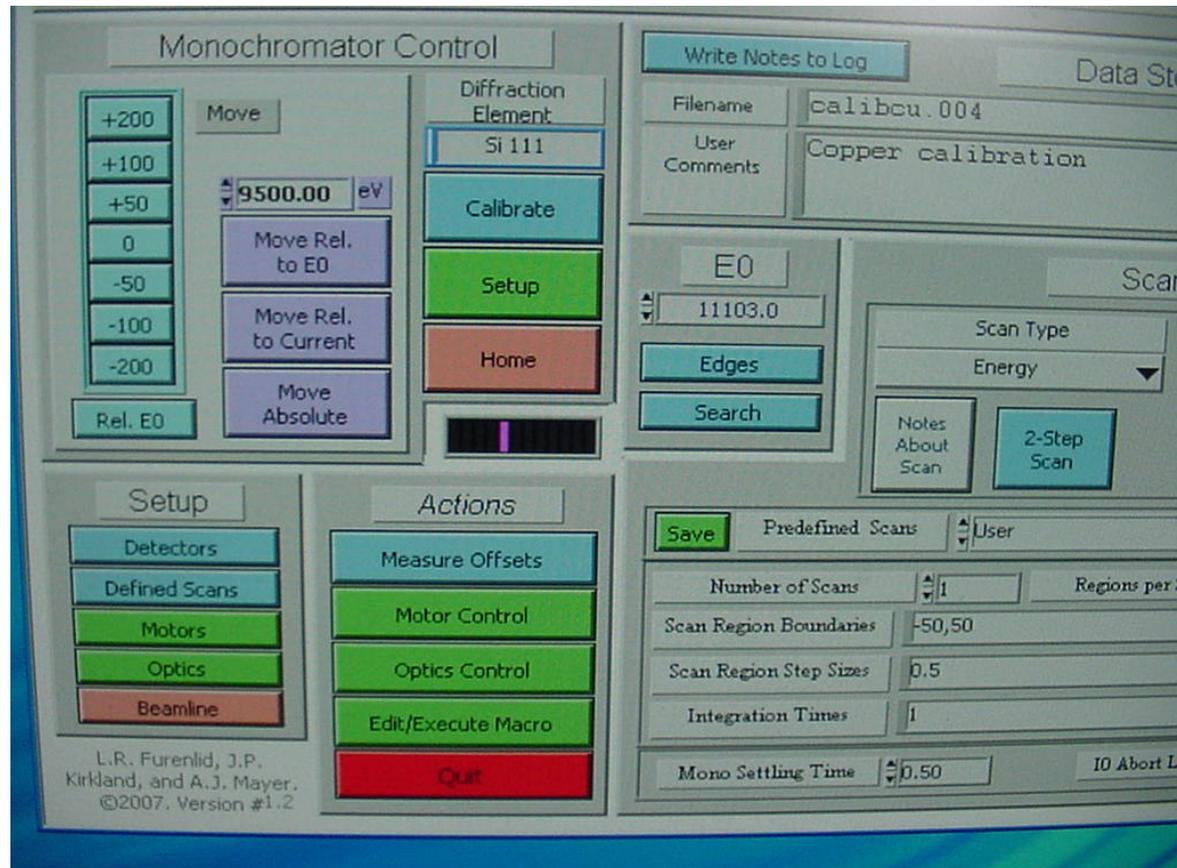
Corrections can be done for higher count rates.

High throughput detectors are also available. For example. Vortex detectors.



# Data Collection Program: XDAC

HARMONICS----ALIGNMENT  
LINEARITY OF DETECTORS----OFFSET



# Mirror and Its Important Role at the Beamline

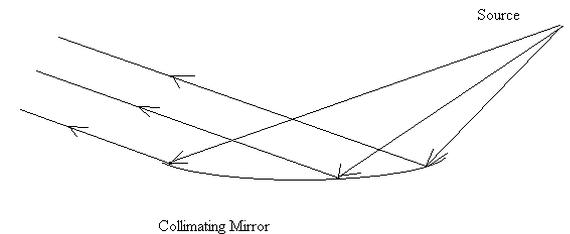
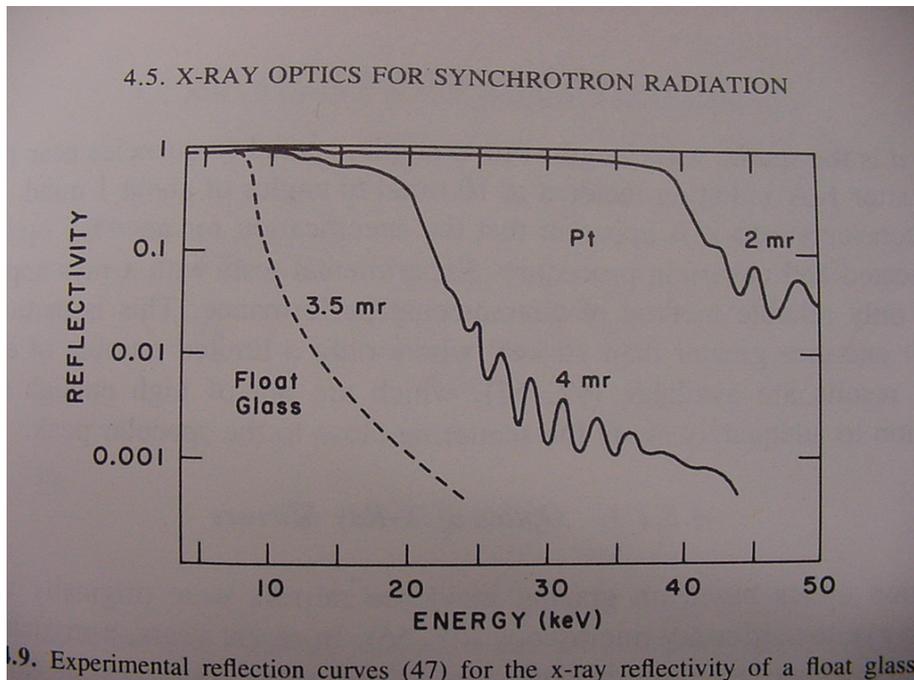
Two Types of Mirrors: Collimating and Focusing

Mirrors have Total External Reflection: Coatings of Rh, Pt, Au, Ni etc.

Function of Collimating Mirror:

Making the beam parallel and harmonic reduction.

Function of Focusing Mirror: Shape Toroidal, Bicycle Tire



1.9. Experimental reflection curves (47) for the x-ray reflectivity of a float glass

# ENERGY RESOLUTION:

Energy Resolution:  $\Delta E / E = \cot \Theta$

Relation Wavelength and Energy:  $E = 12.4 / \lambda$

E in KeV, Wave Length in Angstroms.

## EXAFS WITH SYNCHROTRON RADIATION

Table 4.4. Properties of Some Silicon and Germanium Reflections

	<i>h</i>	<i>k</i>	<i>l</i>	2 <i>d</i> (Å)	$\Delta E/E$
Si	1	1	1	6.2708	$1.3 \times 10^{-4}$
	2	2	0	3.8400	$5.6 \times 10^{-5}$
	4	0	0	2.7154	$2.3 \times 10^{-5}$
Ge	1	1	1	6.5328	$3.4 \times 10^{-4}$
	2	2	0	4.0004	$1.5 \times 10^{-4}$

# HARMONICS: How they are reduced.

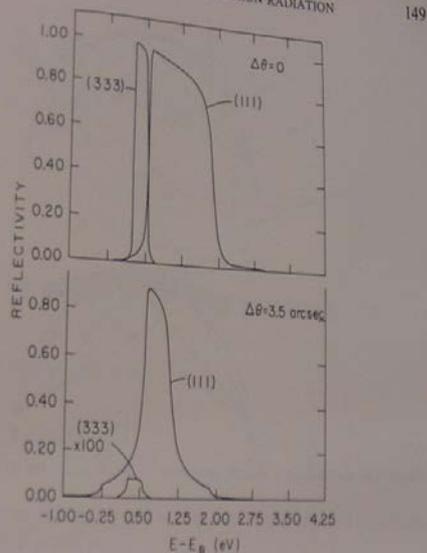
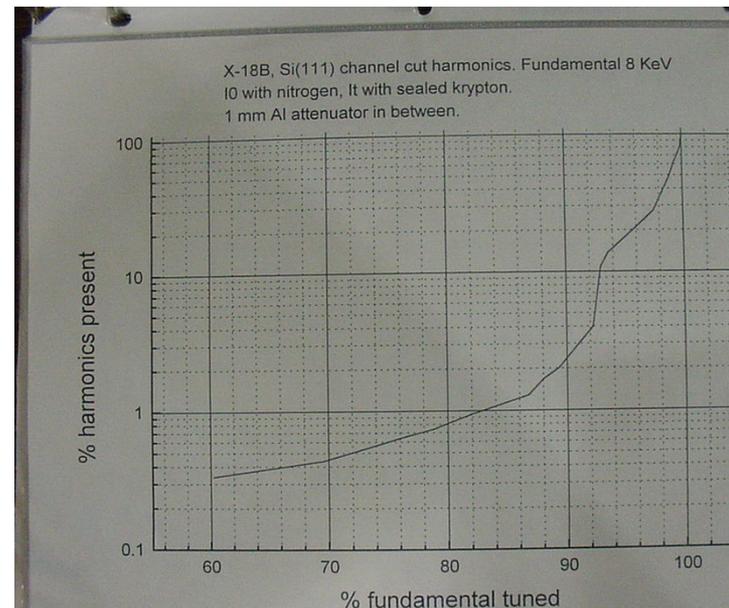


Figure 4.15. Reduction of the higher-order reflection by detuning for the Si(111) reflection. When  $\Delta\theta = 3.5$  arcsec the fundamental (111) reflection at  $E_p = 10$  keV has about one-half of its original intensity while the (333) reflection at 30 keV is reduced by about  $10^{-3}$ .



# Control of Signal Output:

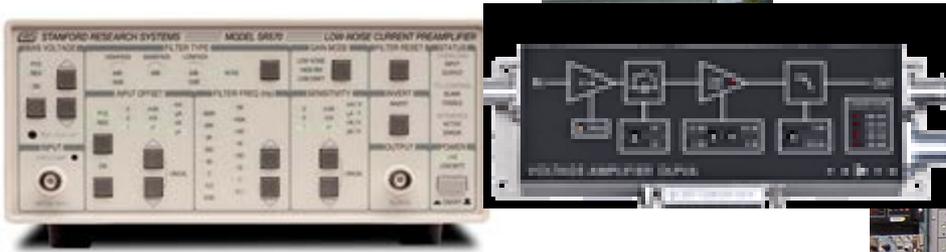
Current Amplifiers: Keithley 428

Offsets: Keeping positive value = 0.05 Volts.  
How to setup.

Gains: What values to keep, 0.5 to 7.0 Volts  
Signal converts from Voltage to Frequency. A NIM Module and then to hex scalers and recorded in your data column.

Zero Check = Off

Filter Time = Important for Quick EXAFS



Gas Flow combinations in ion chambers.

Single outlet to all three gases: Floating indicators in Gas flow meters have different values for different Gases.

Choice depends upon the percentage we need to absorb.



# COMMUNICATION:

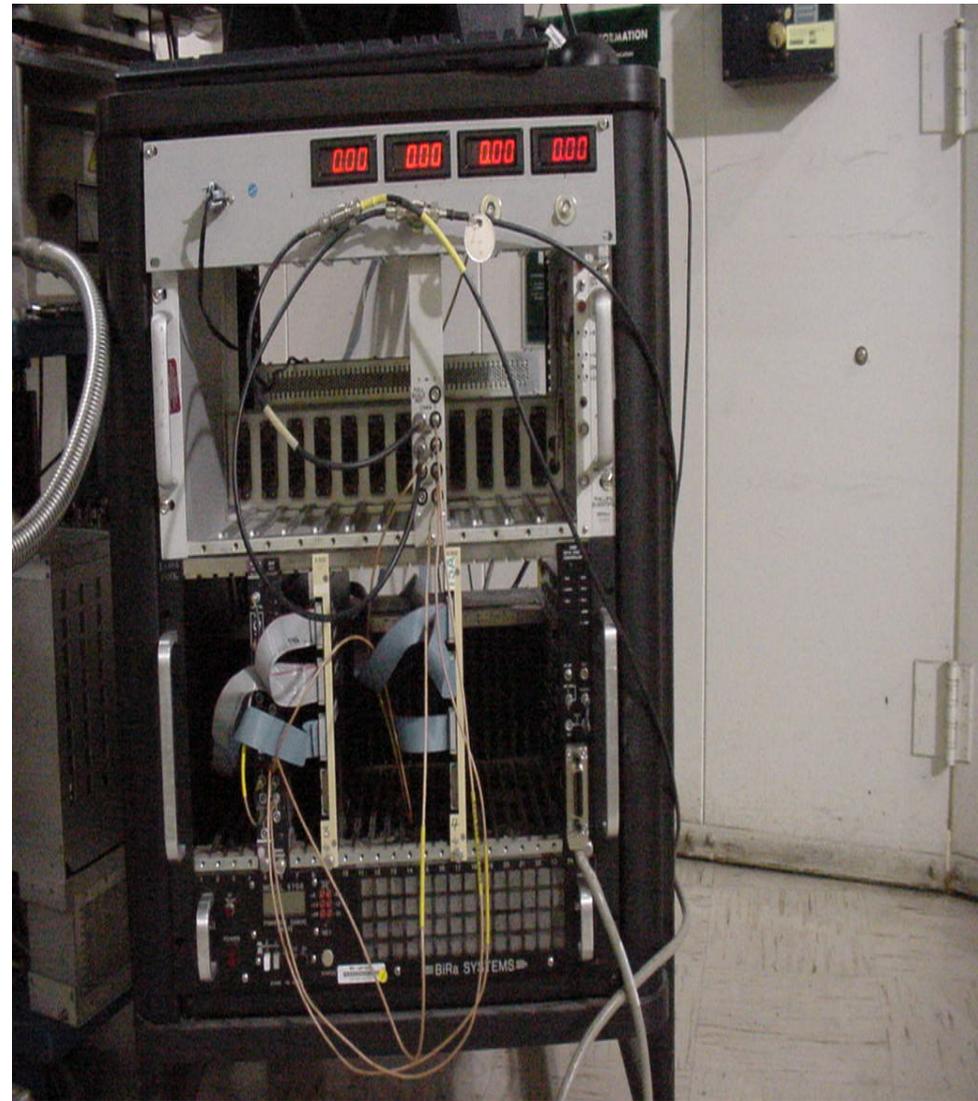
Between the computers and the hardware there is an important instrument which transfers the commands from the computer to the hardware. This instrument is called CAMAC, or PXI from National Instruments or VME.

Modules inside CAMAC: E500, Real Time Clock, Hex Scalars and many other according to need.

E500: sends pulses to move the motor and responds to hard limits.

Real Time Clock: Mainly controls the data collection time.

Hex Scalars: count the photons, or the ion chamber current signal, converted to voltage, converted to frequency.

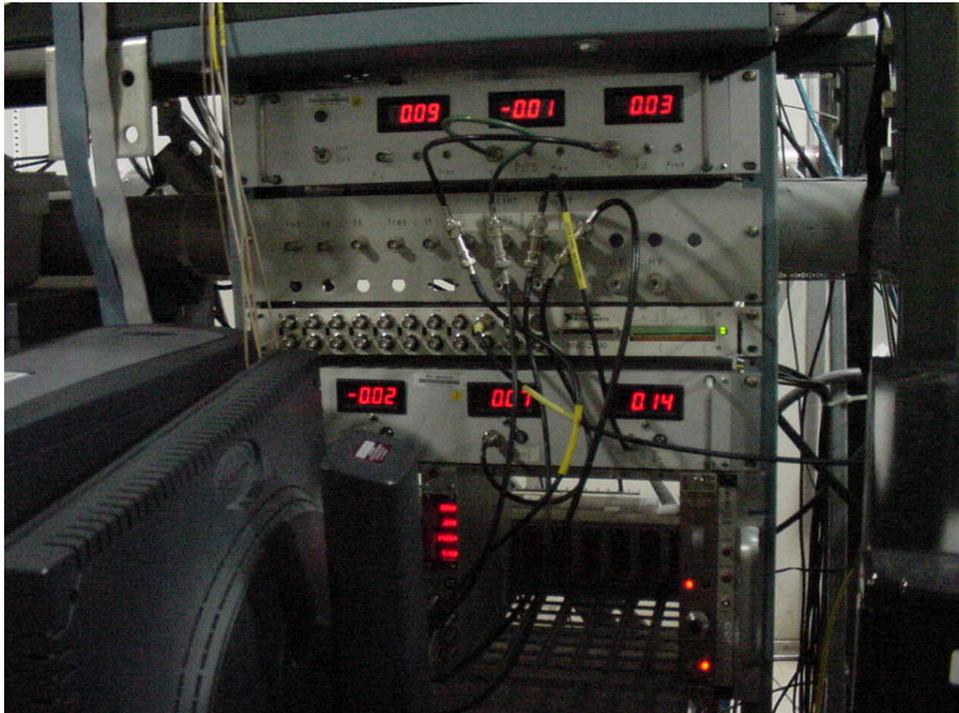


# CONTROLS:

In order to run all this hardware: The slits, the monochromator, mirror (angle and position), sample position etc. we need all kinds of motors, like 4-phase, 5-phase motors, DC and servo motors.

All these motors need drivers and power supply, the type depends upon the kind of motor we are using.

All data collection and moving the motors is done by computers with all kinds of operating systems.



# Monochromator: The heart of XAS Instrument

Bragg's Diffraction Law:

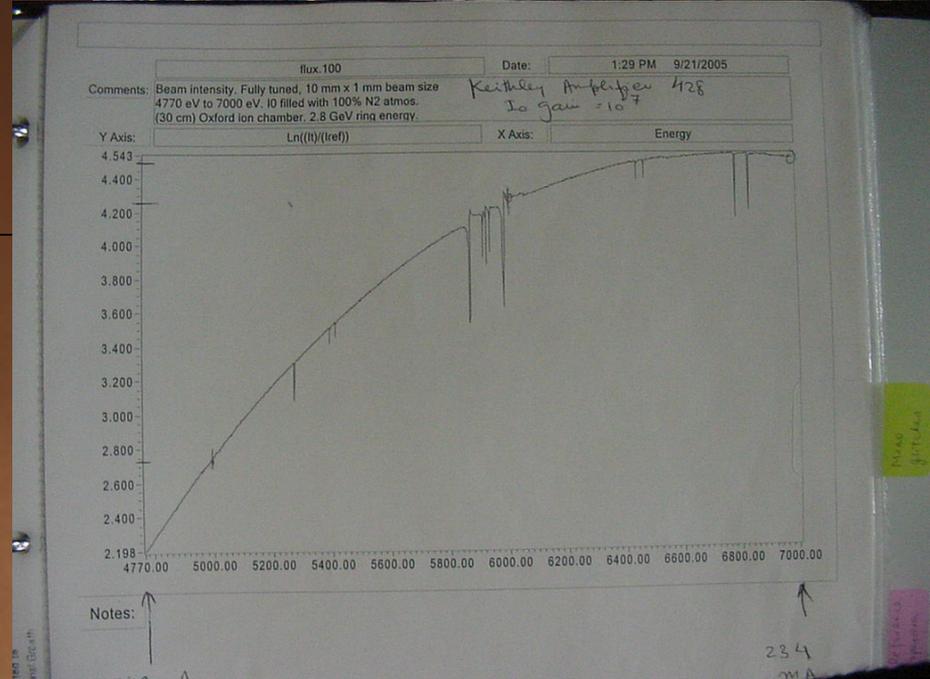
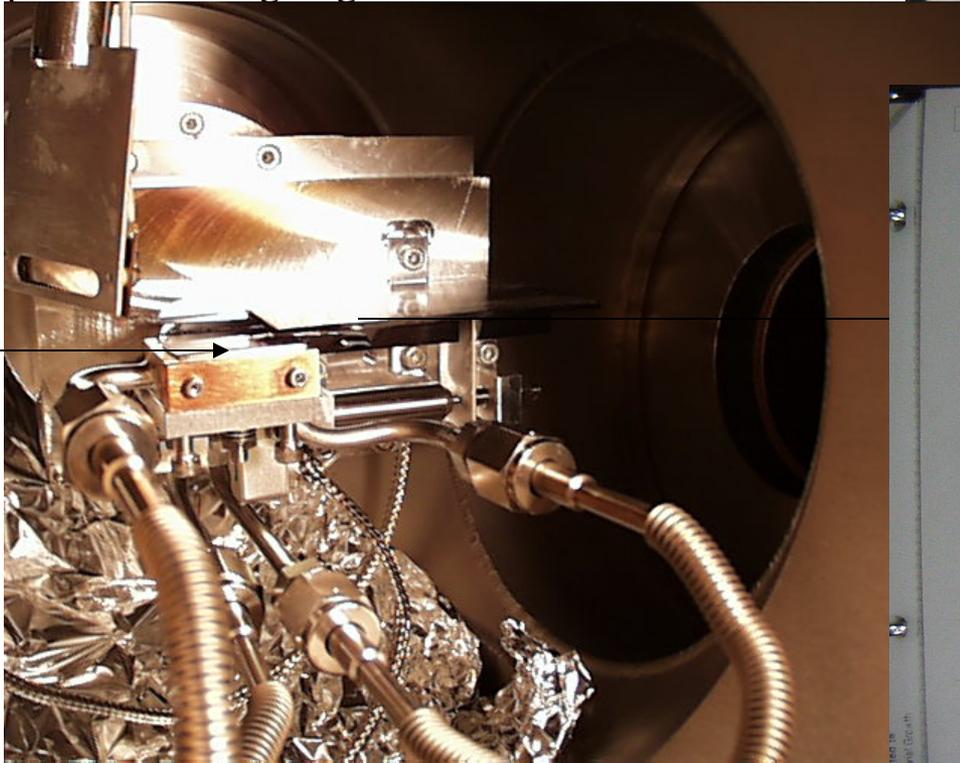
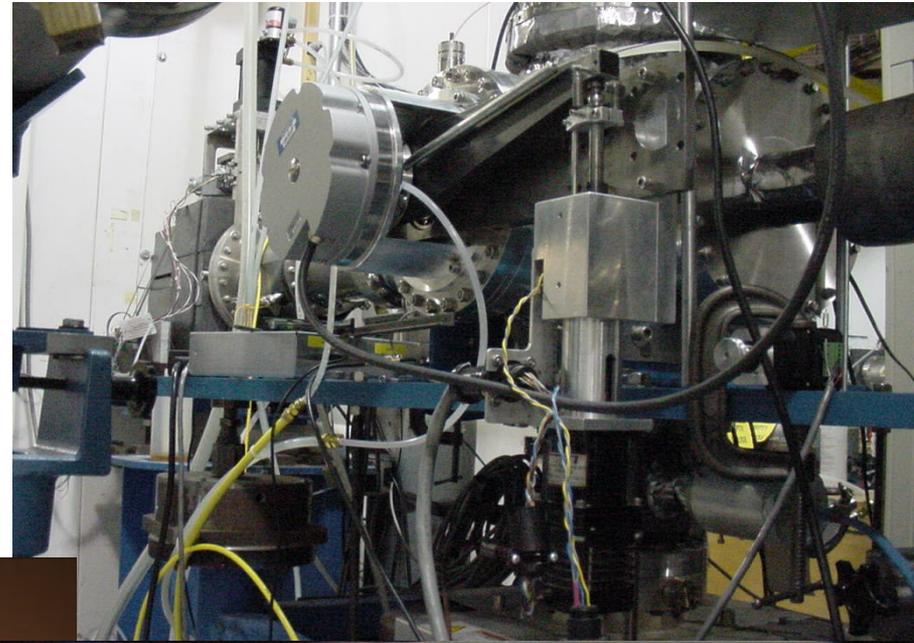
$$2d \sin\Theta = n\lambda$$

Rocking Curve of a crystal: GLITCHES:

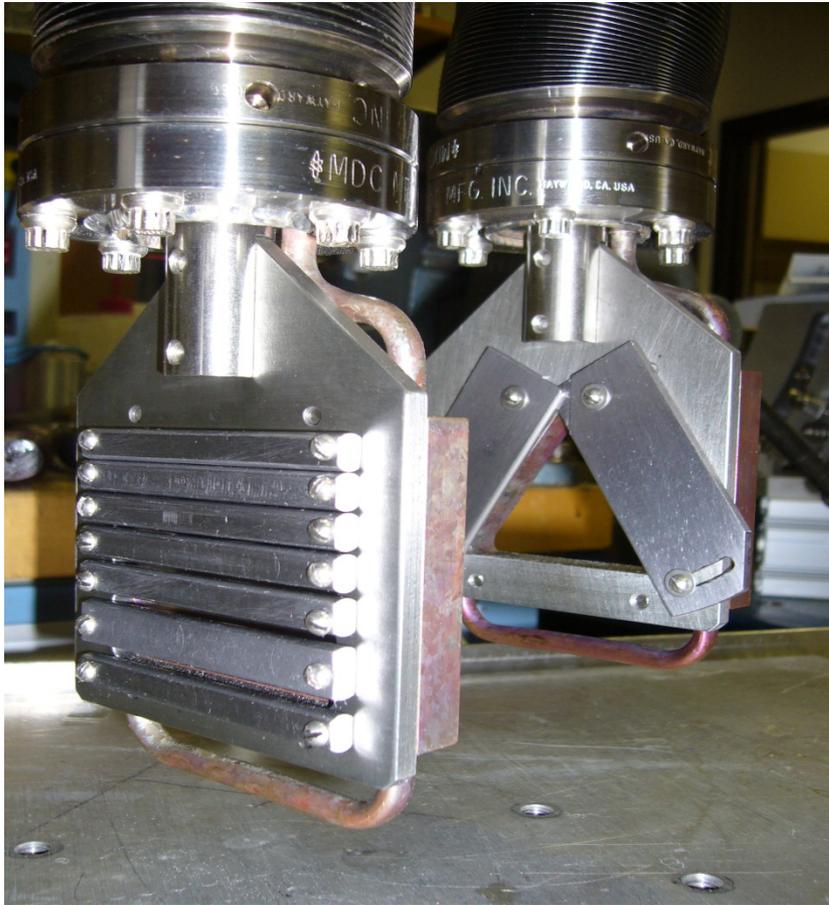


$S = 2h \cos \Theta$ ,  $h$  = separation of crystals

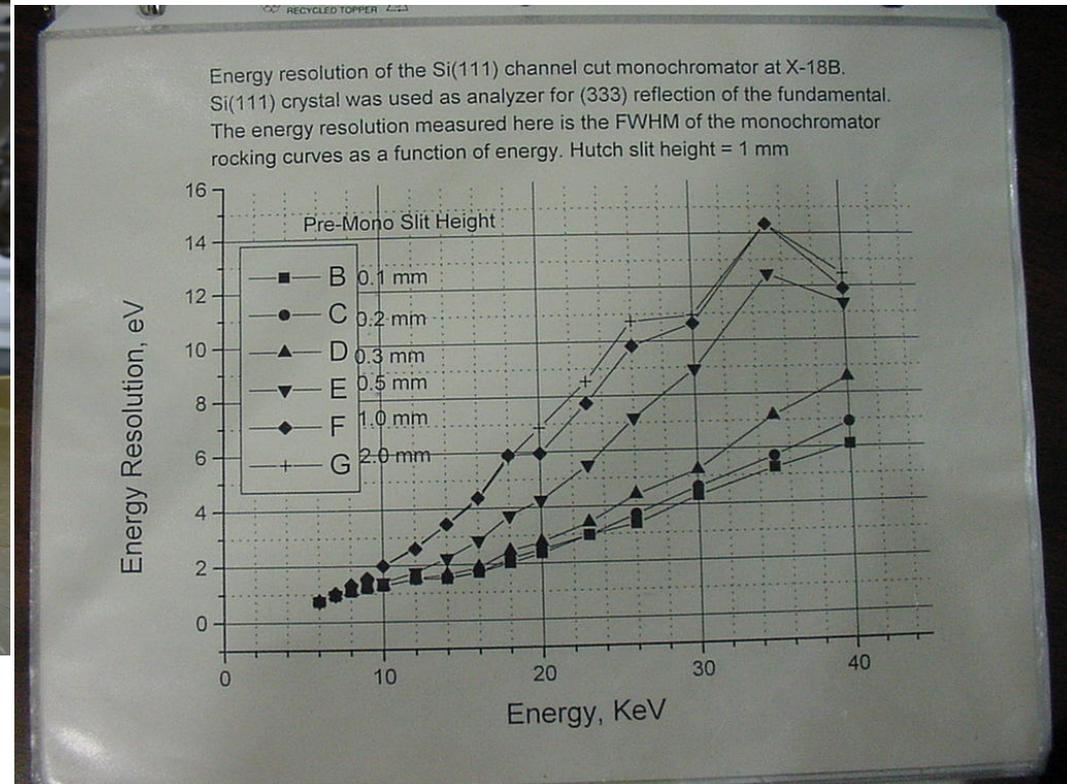
$S$  = Separation of outgoing beam from incidence beam.



# VERTICAL AND HORIZONTAL WHITE BEAM SLITS



Energy resolution is partly the function of vertical slit we choose. Smaller slit will give better resolution. Choice of slit depends upon the distance from the source. Choice of monochromator crystal and its planes also contribute to energy resolution.

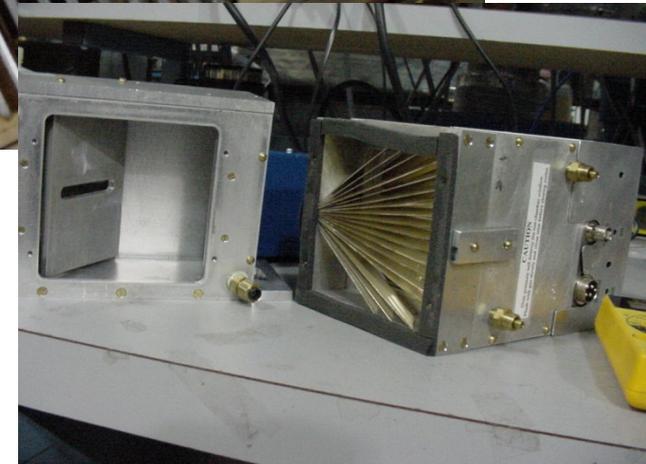


# USE OF FILTERS AND FOILS:

Filters enhance the signal of the element of interest.

Usually a Z-1 filter is used. It suppresses the elastic and Compton scattering. A must for low concentration samples.

Also when using solid state detectors, which are total count rate limited. How the slits help to reduce the fluorescence from the filter.



3.3. EXPERIMENTAL DETECTION OF EXAFS

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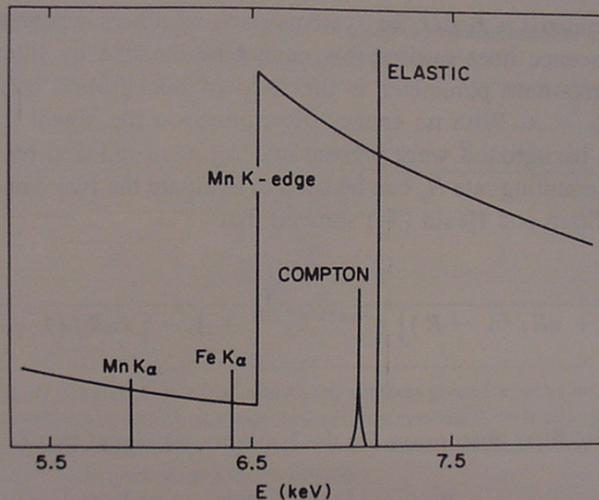


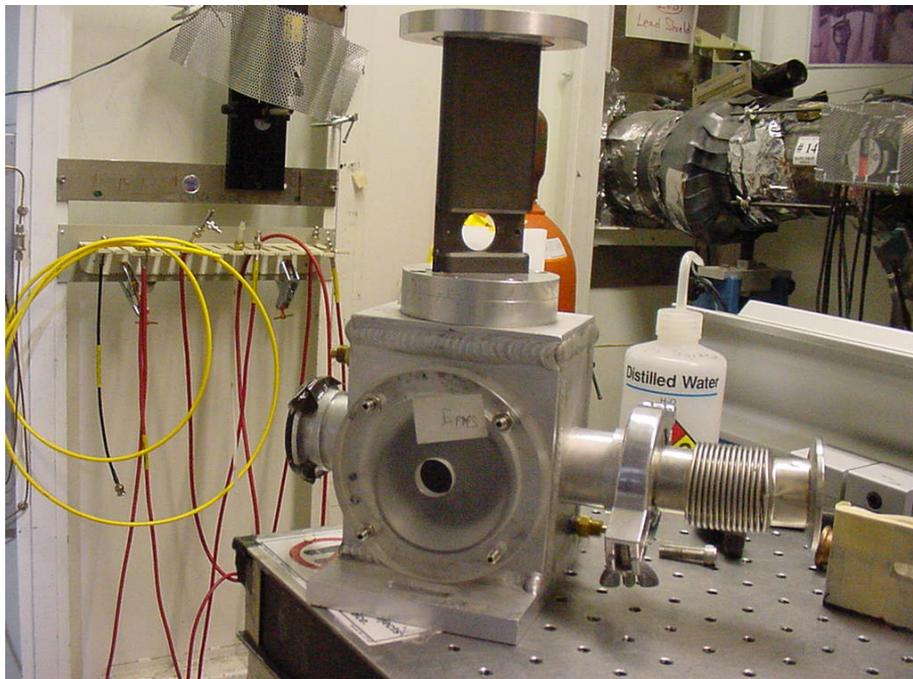
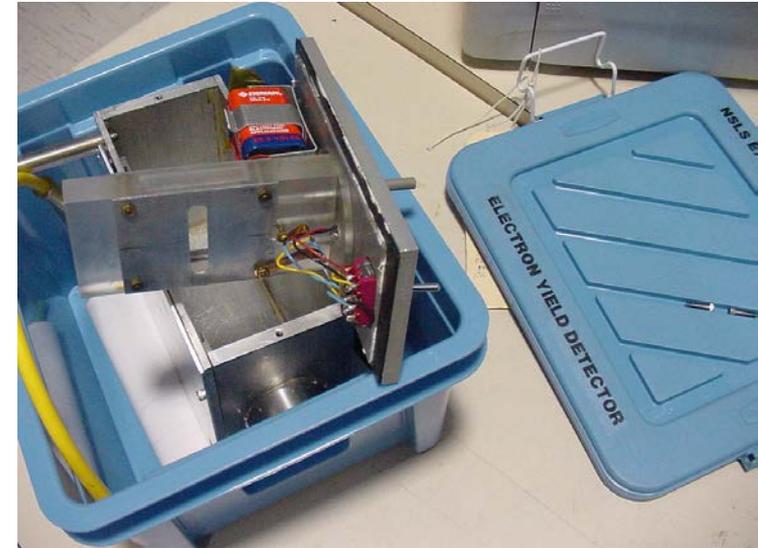
Figure 3.5. An iron fluorescence experiment using a manganese filter for background suppression. The absorption for the Compton and elastic peaks is much larger than for the iron K $\alpha$  signal.

## Other Fancy Detectors and Chambers:

Electron Yield Detector: Directly measures electrons emitting from the sample. Surface sensitive.

He-Displex: Close cycle He flow cools the sample.  $\sim 10\text{-}300\text{ K}$   
(Phase Transition Studies)

Sample Chamber and PIPS combination for low energy XANES and EXAFS- Mostly for P, S, Cl, Ar, K and Ca



## CONCLUSION

Grind your samples to few microns range 5-10 microns ideal

Choose the right method of data collection: transmission, fluorescence, or electron yield.

Use the right detectors: ion chambers, Lytle detector, energy dispersive or electron yield.

Right gases for the ion chambers, in all cases

Remove Harmonics, Align sample properly, Linearity of detectors and take Offsets (with the beam off)