Instrumentation for XAS

X-ray sources, optics and detectors for absorption spectroscopy beamlines

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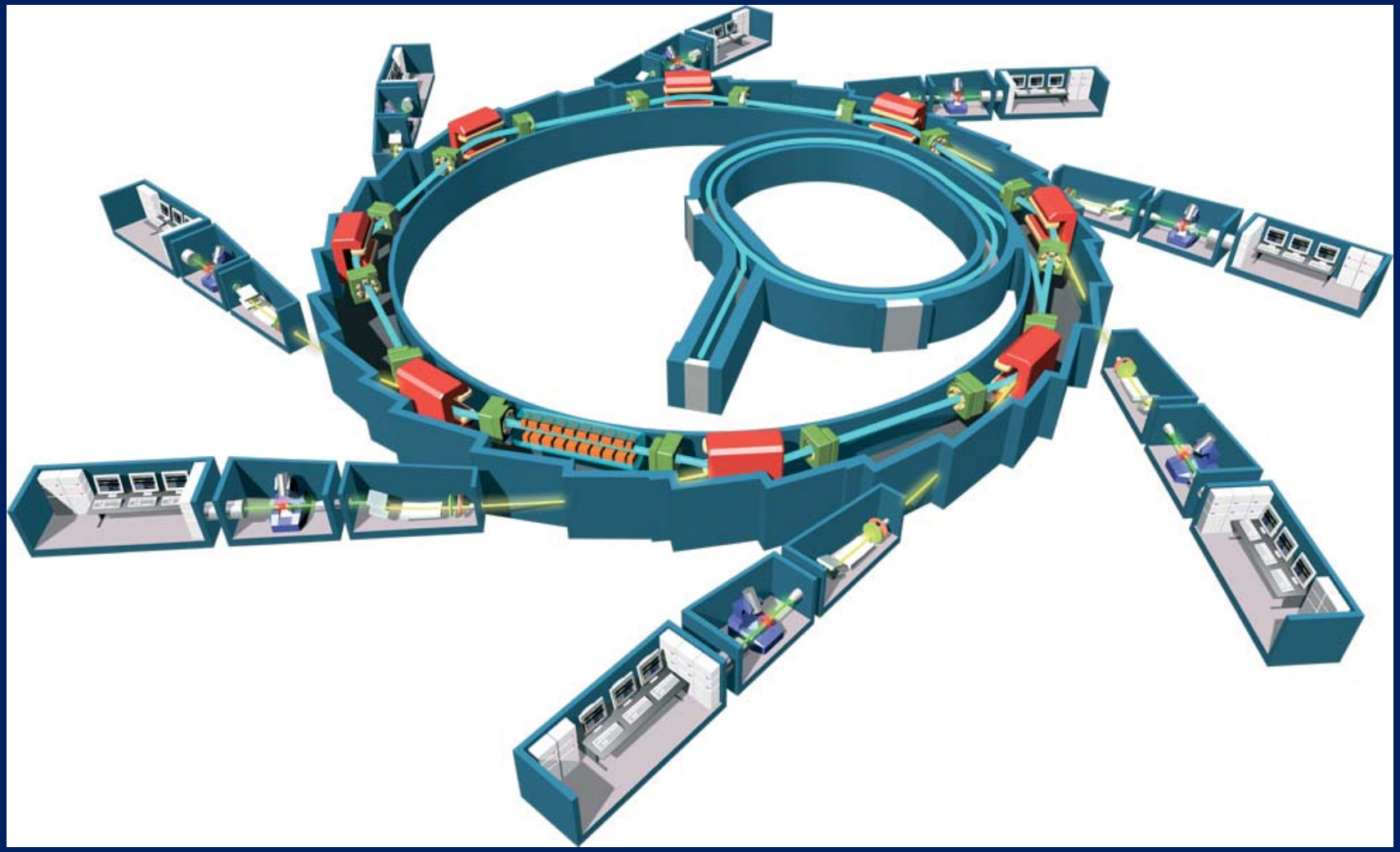
The floor of the synchrotron



All synchrotron facilities have the same basic layout consisting of a storage ring with radiation emitted radially into beamlines. Beamlines consist of optics to condition the beam for experiments.

Drawing courtesy of Synchrotron Soleil.

Overview of this talk

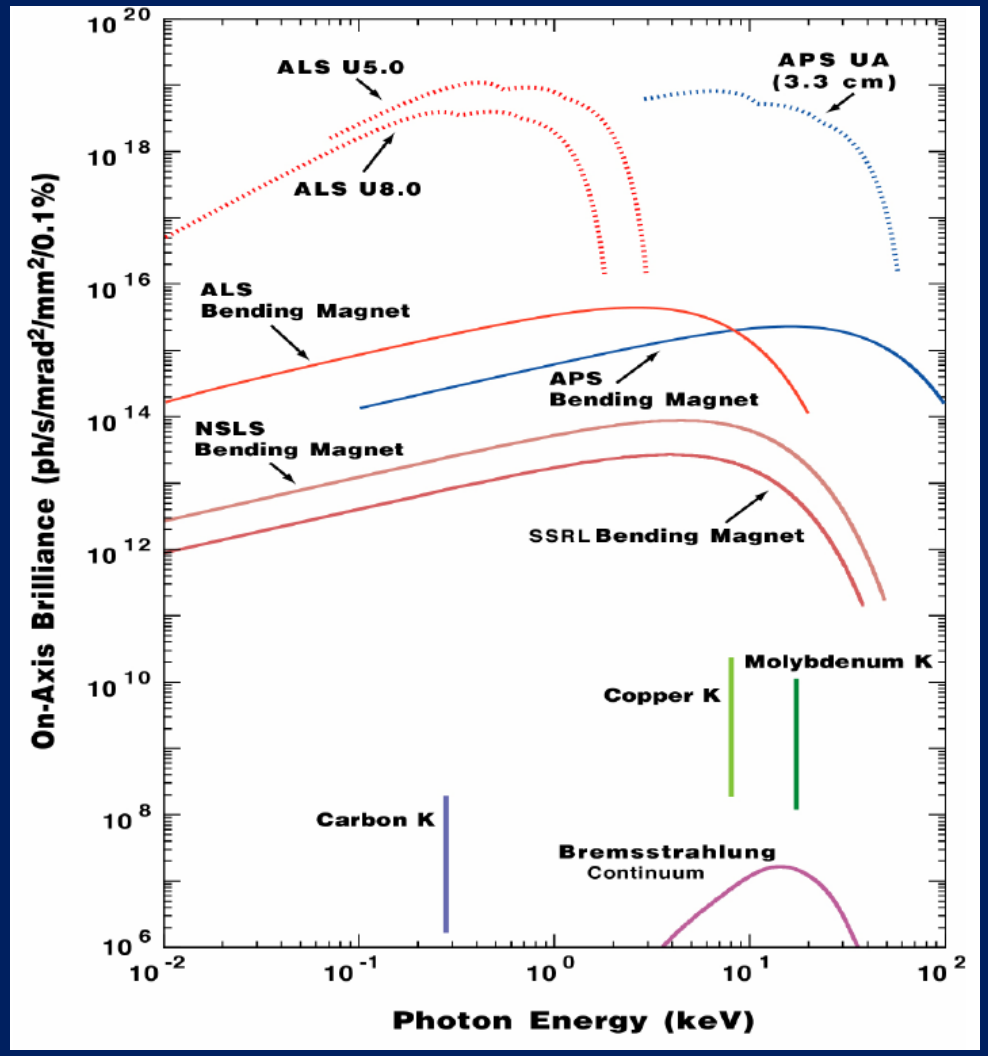
X-ray sources How bending magnets, wigglers, and undulators produce x-rays and how XAS experiments use these sources.

Optics How monochromators, mirrors, and other components condition the beam for an XAS experiment.

Detectors How X-rays are detected and what different detector technologies offer for the XAS experiment.

Hutch instrumentation Other things one commonly finds on an XAS beamline.

Why build synchrotrons?



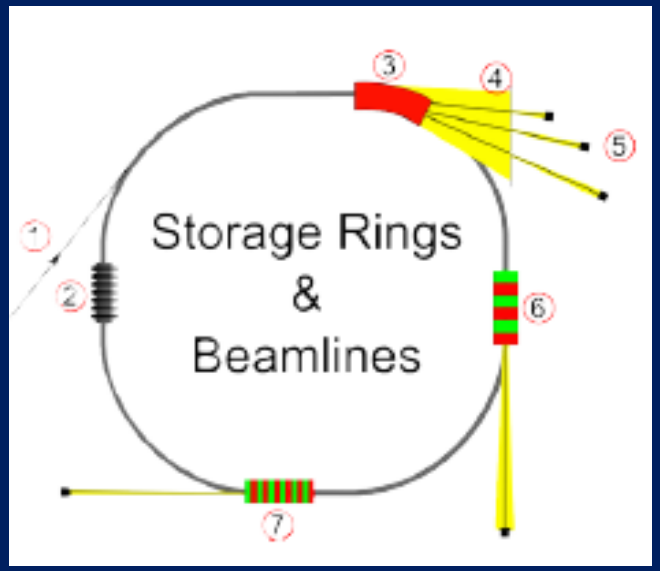
Photon properties produced by a synchrotron:

- High flux
- Small source size
- Broad range of energies (wavelengths)
- Extremely collimated
- Time structure
- Polarized

Brilliance

A metric that positively quantifies more flux, less divergence, and smaller source size.

The storage ring



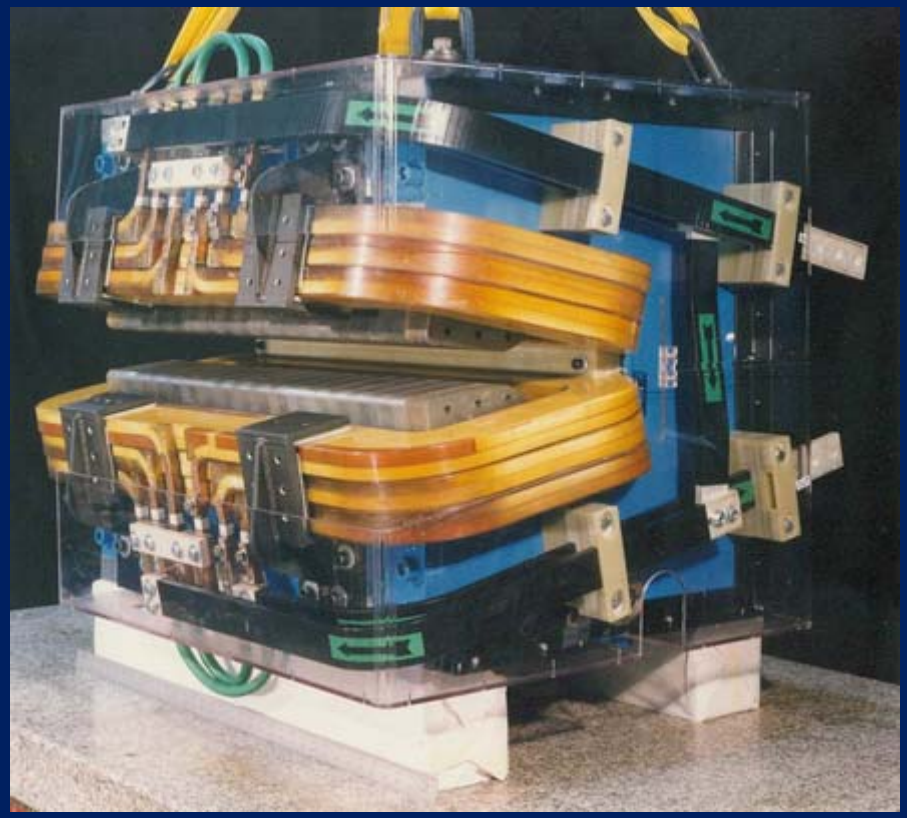
The storage ring is a large, evacuated, polygonal tube for containing relativistic electrons. Along with various kinds of magnets used to condition and shape the stored current, the ring has special magnets which generate useful X-rays as the electrons pass through.

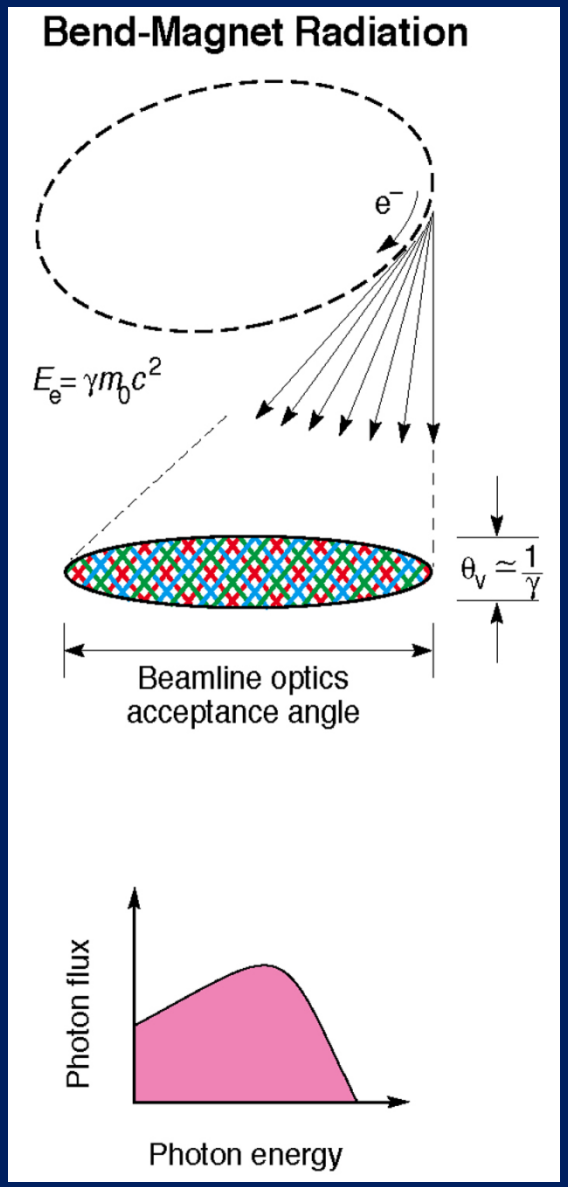
Bending magnets

Insertions devices: wigglers and undulators

Photo courtesy of the Swiss Light Source and drawing courtesy of DESY.

Bending magnets

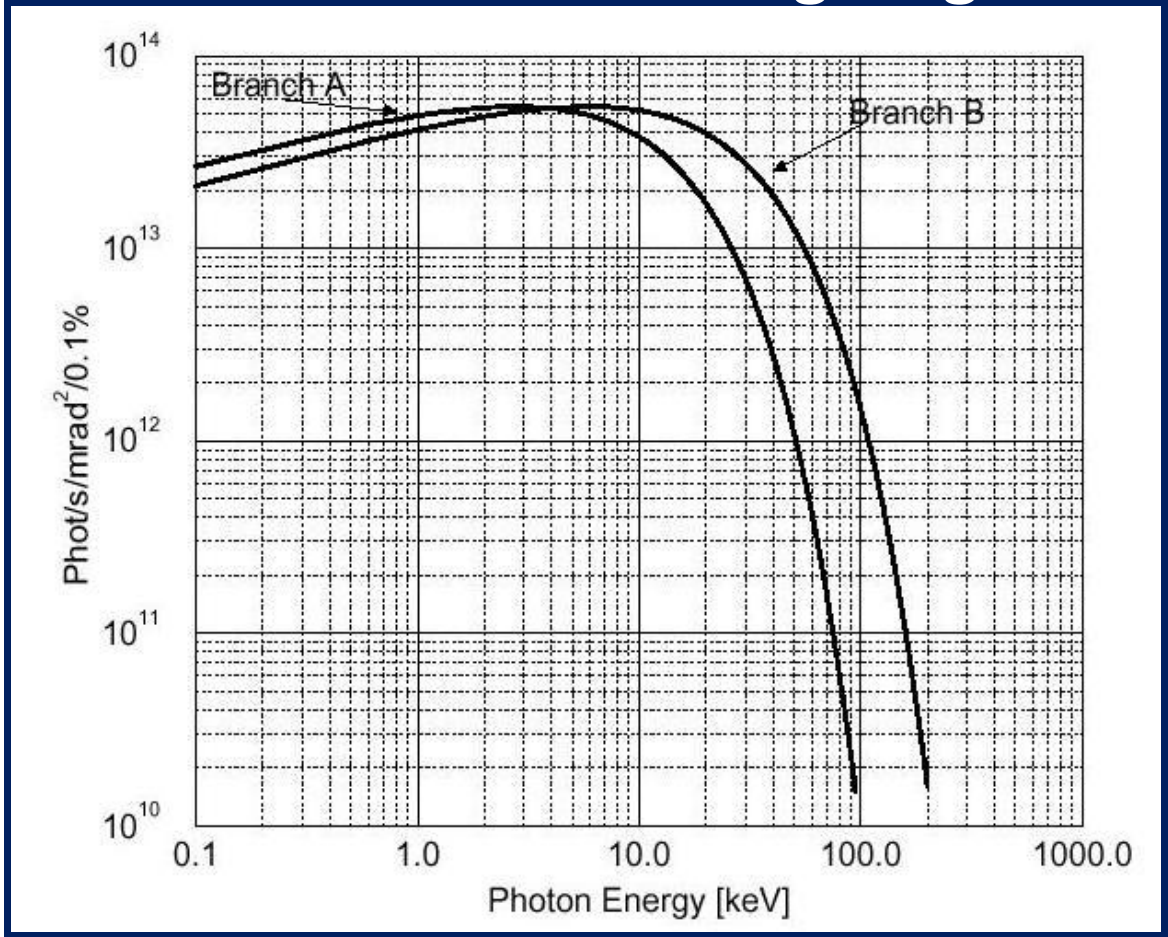




Bending magnets serve two purposes:
Steer the electrons between straight sections
Generate photons for use in a beamline
With relativistic electrons, the light emitted by the bending magnet is in a narrow cone.

Photo and drawing courtesy of the Advanced Light Source.

Bending magnet radiation



BM radiation has a characteristic energy ε_c , the *critical energy, above* which half of the total power is radiated:

$\varepsilon_c = 0.665 B_0 E^2$

B_0 is the bending magnet field strength

E is the energy of the storage ring

All bending magnets excel at delivering photons from the IR through the VUV and into the X-ray

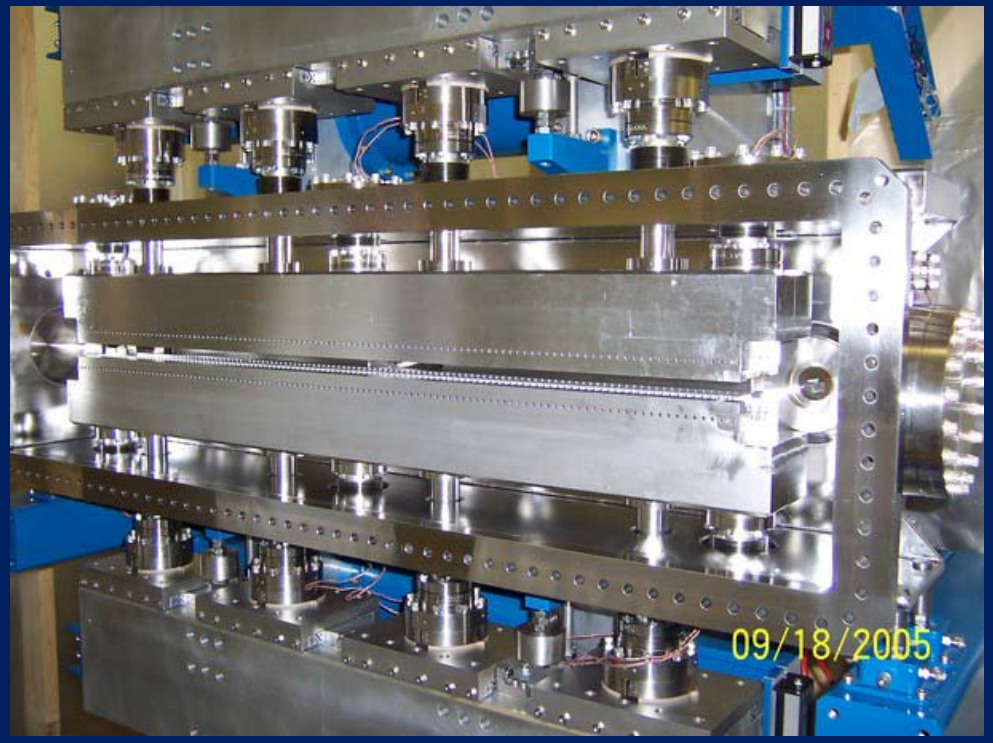
Bending magnets at high energy facilities (APS, ESRF, SPring-8) deliver useful flux beyond 100 keV.

High energy performance can be tuned by increasing field strength, e.g. ALS or SLS superbend devices.

Drawing courtesy of the ESRF

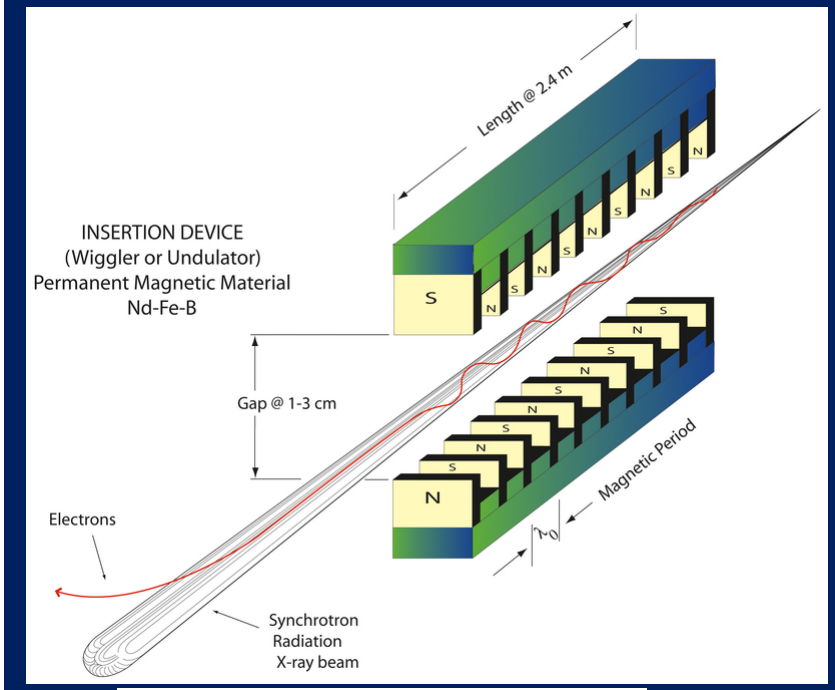
Insertion devices

Insertion devices periodic magnetic structures designed to improve upon the performance of bending magnets.
They are inserted into the straight sections of the storage ring.
Insertion devices in use around the world range from the enormous (APS undulator A, > 2 m, on the left) to the compact (the NSLS X25 minigap undulator, < 1 m, on the right).



Photos courtesy of the APS and NSLS.

Wigglers and Undulators

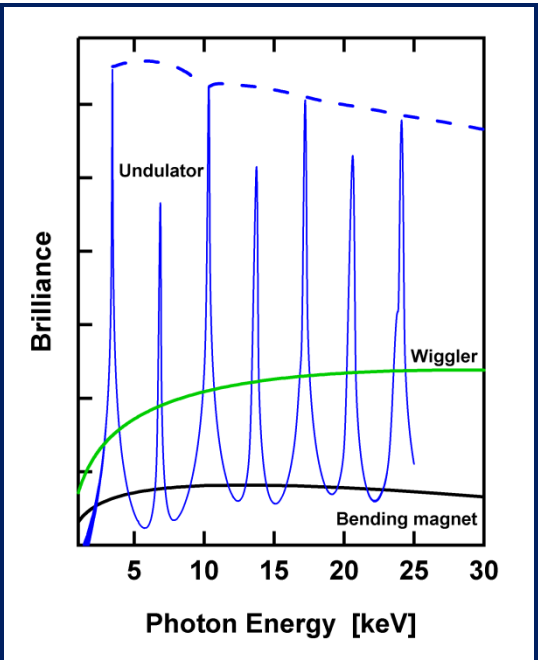


Wiggler

A wiggler is, in a sense, a sequence of high field dipole magnets. It is an improvement over a bending magnet through a multiplicative effect.

The broadband wiggler spectrum is very similar to the BM spectrum, although with much higher flux.

The price a wiggler beamline pays is managing higher heat loads.



Undulator

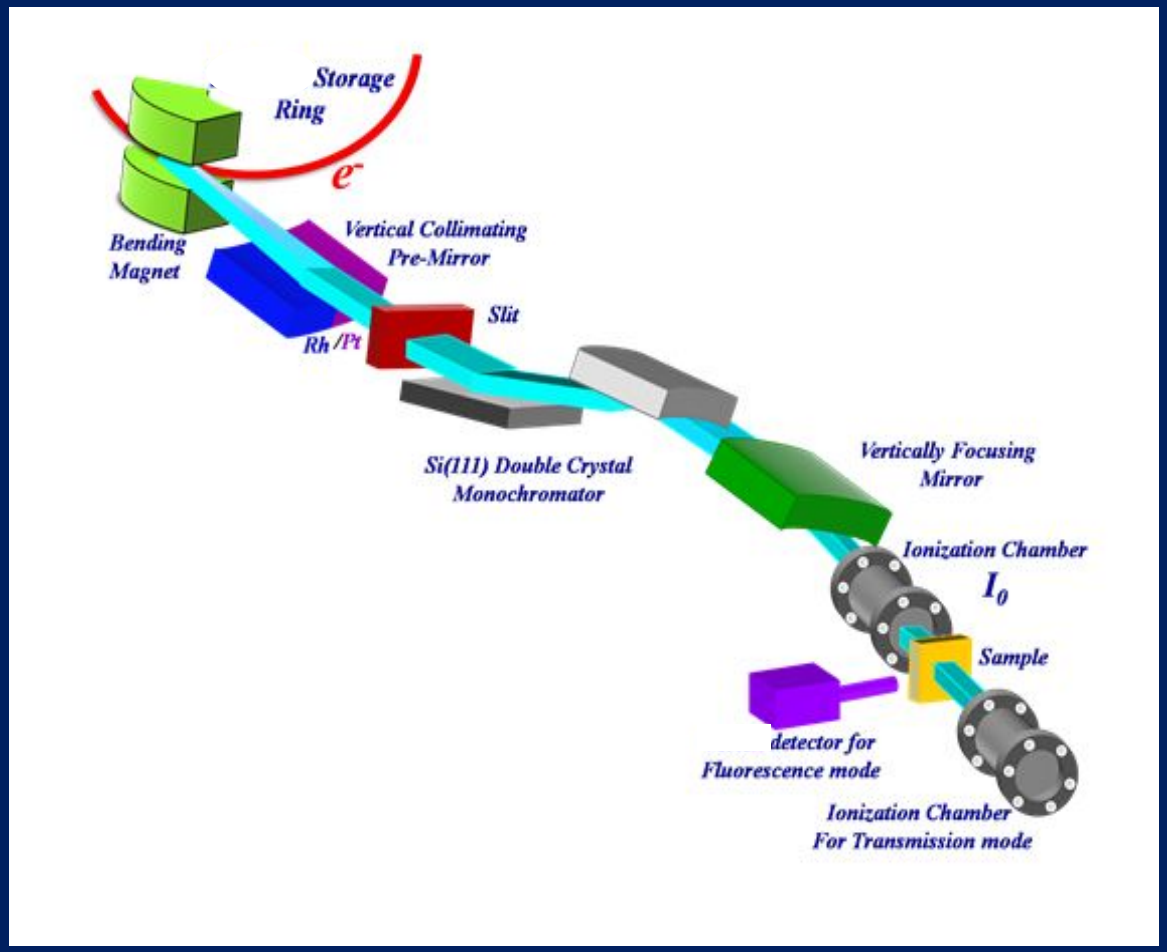
Undulators are similar to wigglers, but the magnet period is shorter and the gap is often smaller. The light from each dipole is coherent, resulting in constructive interference and greatly enhanced flux at special wavelengths.

Undulator XAS beamlines

XAS requires that the gap and the monochromator be scanned in a coordinated manner.

Drawing courtesy of the APS

A typical XAS beamline



Drawing courtesy of INDUS-II.

Source Behind the shield wall, part of the ring

Collimating mirror Removes the vertical divergence of the source, making the instrumental energy resolution independent of beam size

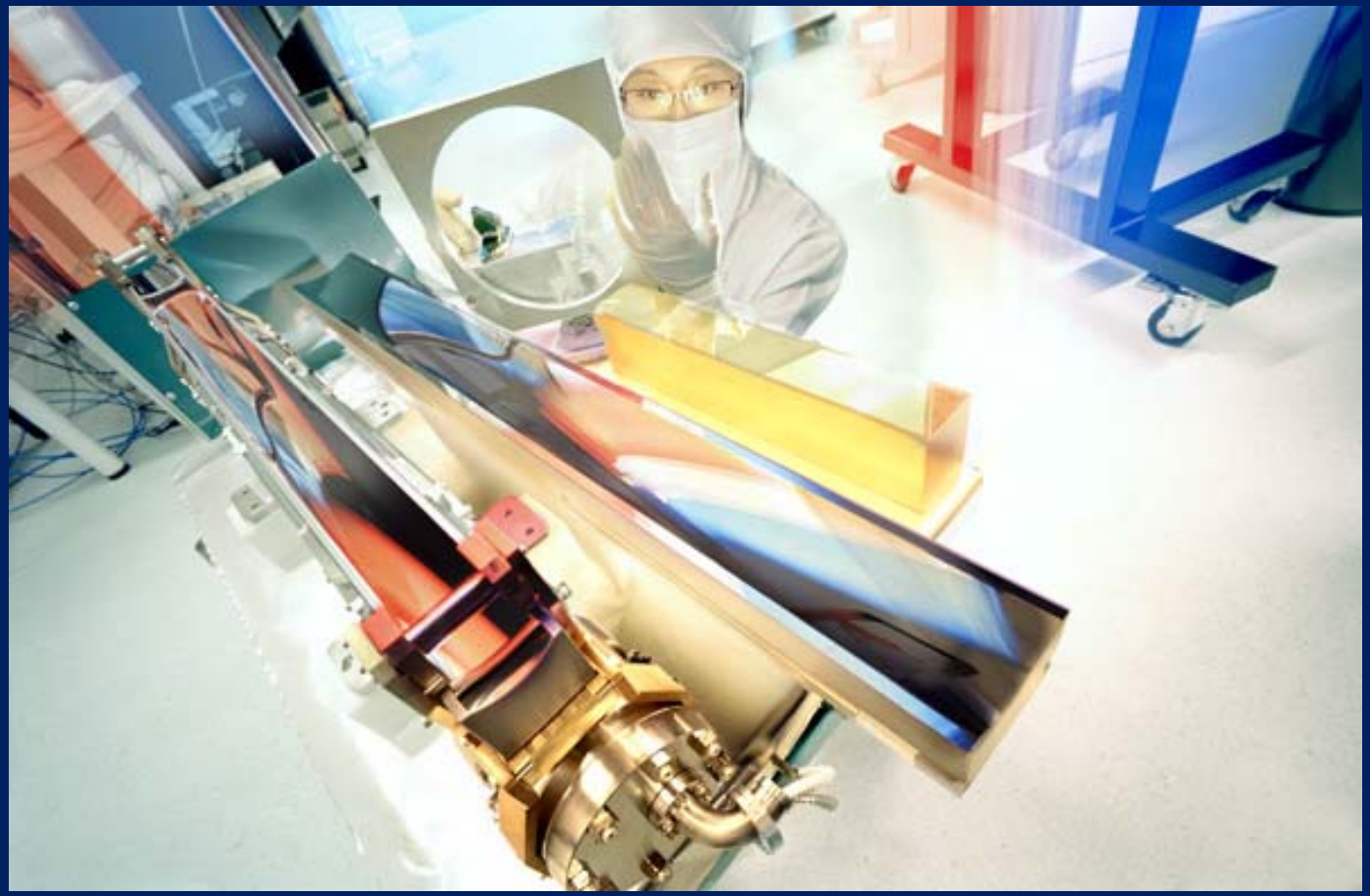
Monochromator Select a single wavelength from the white light

Focusing mirror Focus the beam into a small spot

Endstation Enclosed space for the sample positioning motors, detectors, etc.

Mirrors

•An X-ray mirror is a long, flat piece of silicon (or similar material), often coated with metal such as Pt or Rh.
•When striking the mirror at a sufficiently glancing angle, the X-rays undergo total external reflection.
•This property is exploited in several ways....



Photos courtesy of ESRF.

Collimating and Focusing Mirrors

A mirror is smooth (Angstrom roughness) Si, SiO2 or other material, often coated with a metal (Ni, Pt, Rh).

Focusing

Parabolic curvature ∥ beam	$R_m = \frac{2pq}{(p+q)\sin\theta}$	typically km
Cylindrical curvature ⊥ to beam	$R_s = \frac{2pq\sin\theta}{p+q}$	typically cm
(De)Magnification	$M = \frac{q}{p}$	

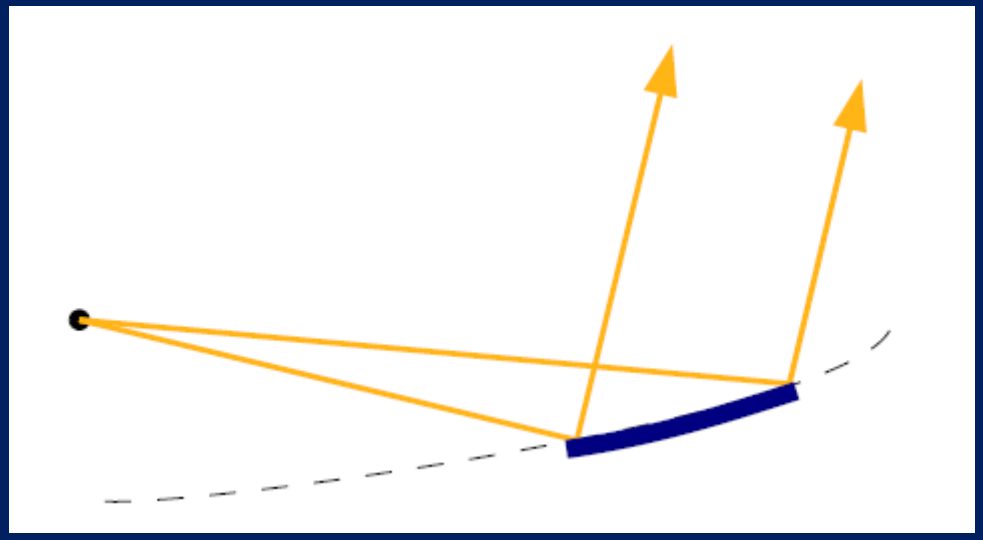
Collimation

$q \to \infty$	$R_m = \frac{2p}{\sin\theta}$
Collimation limited by source size	$\delta\theta = S_v/p$

Mirrors

Vertical collimating mirror

A mirror is bent along a figure that will correct the divergence of the source. All points on the mirror are below the critical angle and reflect the beam in the same direction.



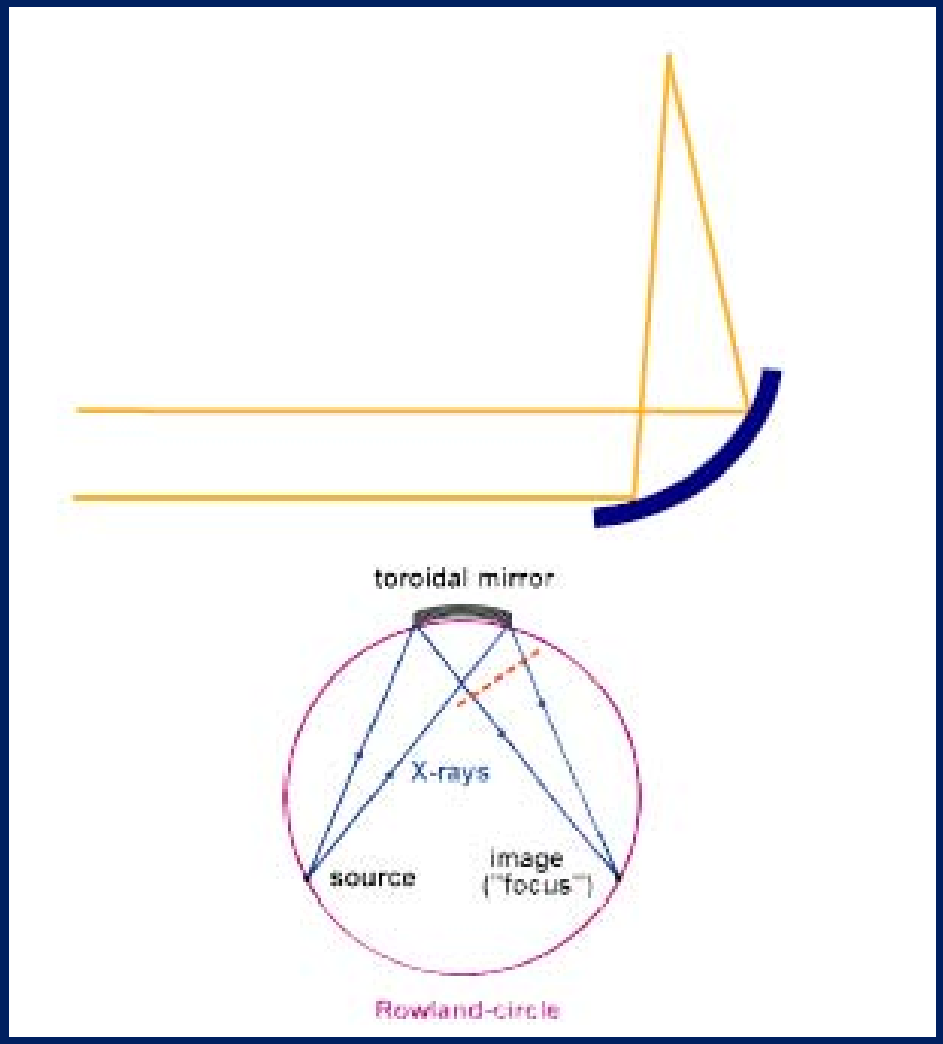
The VCM corrects the divergence of the beam, thus the instrumental resolution is defined by the mono crystal.

Mirrors

Toroidal focusing mirror

A toroidal mirror is bent lengthwise to focus vertically and is shaped in a circle to focus horizontally.

Photo courtesy of the ESRF.

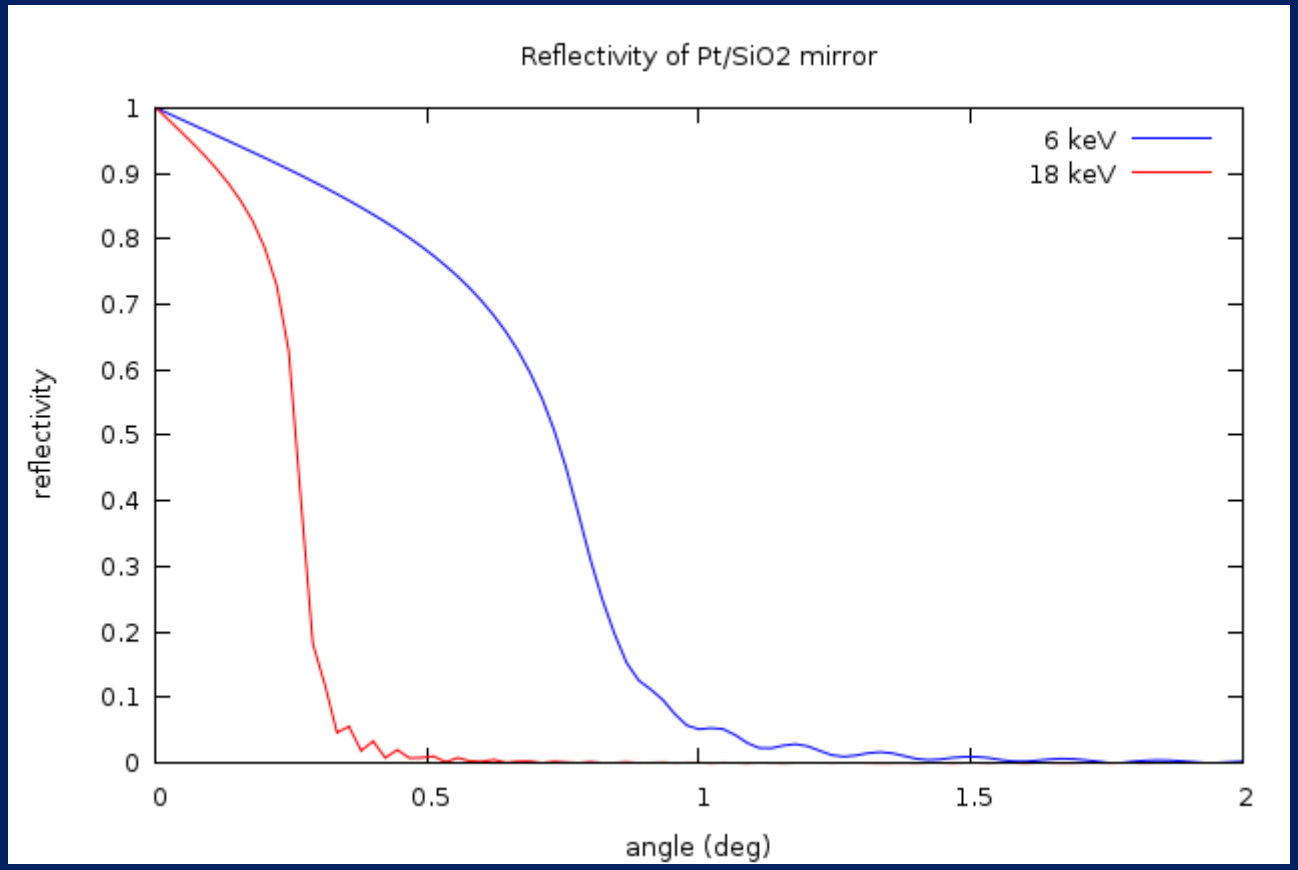


This can easily focus bending magnet radiation to a 500 µm spot.

Mirrors

Harmonic rejection mirror

The angle at which total external reflection happens is energy dependent.



Setting a at mirror to an appropriate angle (here, 0.5 deg) will pass most photons at 6 keV and absorb most photons at 18 keV.

Calculations made at the Center for X-ray Optics website.

Kirkpatrick-Baez focusing mirror

Kirkpatrick-Baez mirrors are a pair of flat mirrors. One mirror focuses vertically, the other horizontally.

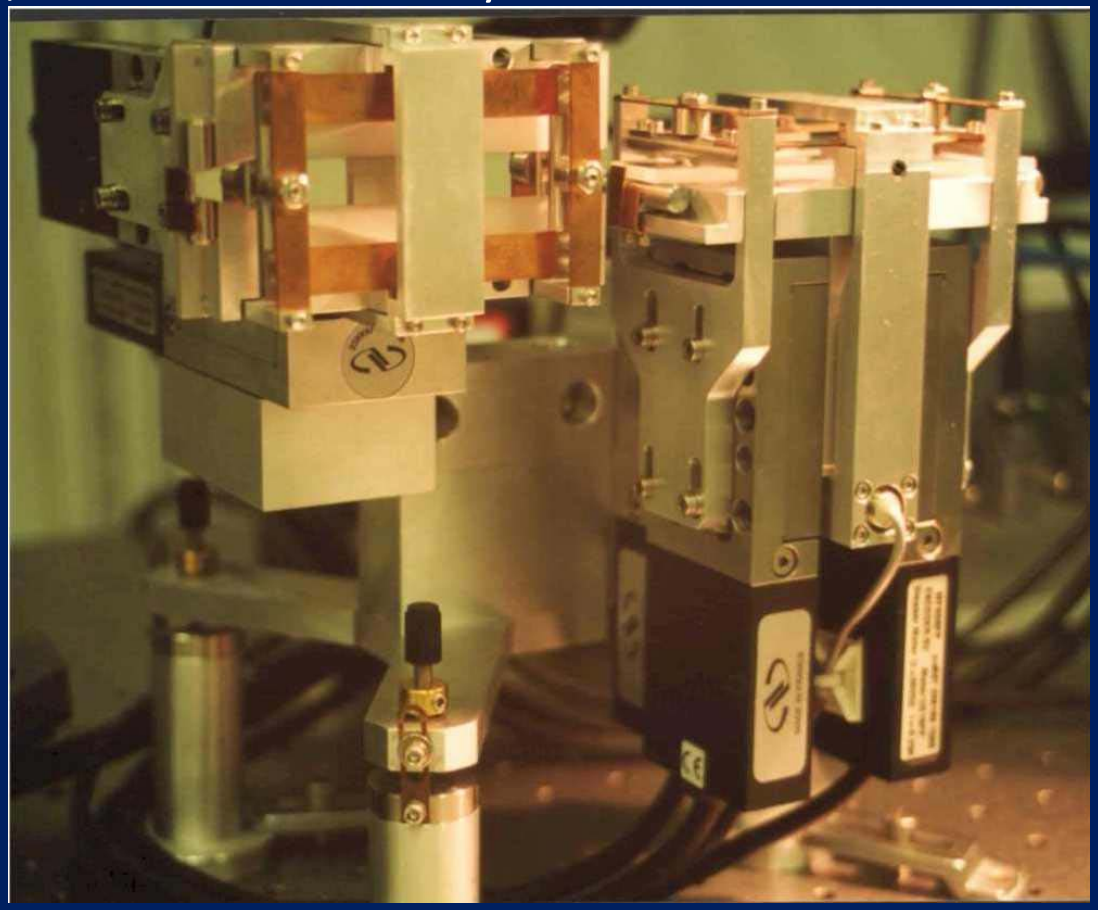


Photo courtesy of Matt Newville.

Depending on the details of the source, KB mirrors can focus from 25 µm to below 100 nm.

KB mirrors are required for micro-fluorescence, micro-XAS, and micro-XRD.

Slits

Blades made of W or Ta are used to define the size of the beam incident on various parts of the beamline.

White beam slits define the size of the beam and absorb some of the heat of the beam.

Slits are often places in front of each optical element.

Hutch slits define the size of the monochromatic beam relative to the sample.

Without a collimating mirror, the vertical aperture helps define the energy resolution by limiting the divergence of the beam from the source and mono.

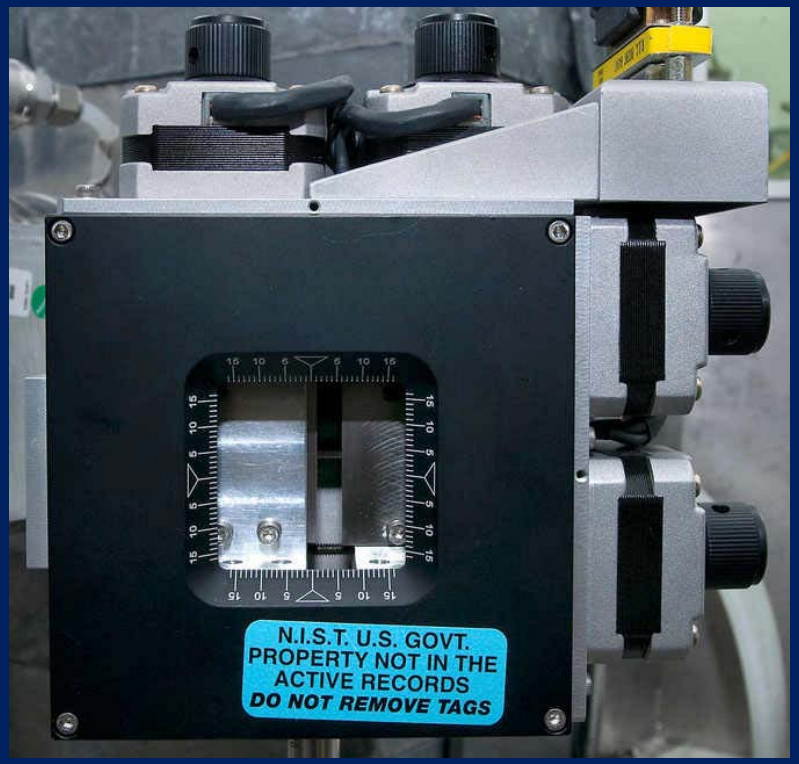
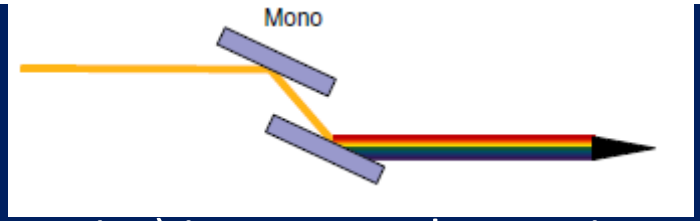
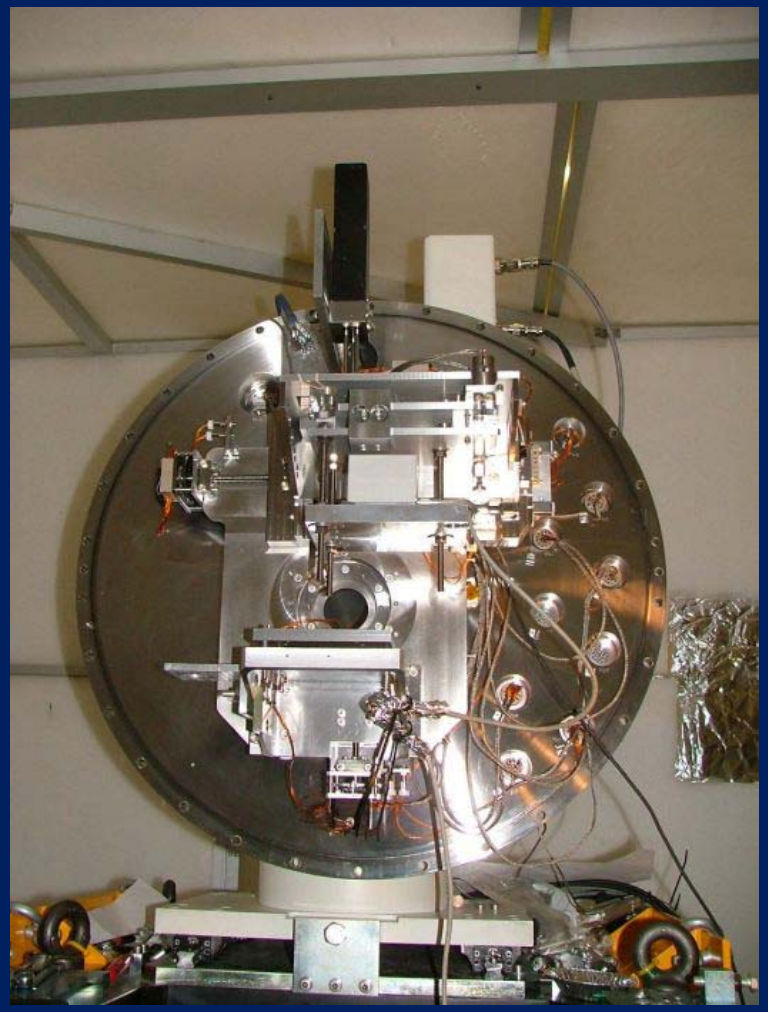


Photo courtesy of Matt Newville.

Monochromator



The mono is the device that turns white light (all energies) into monochromatic light (single energy).

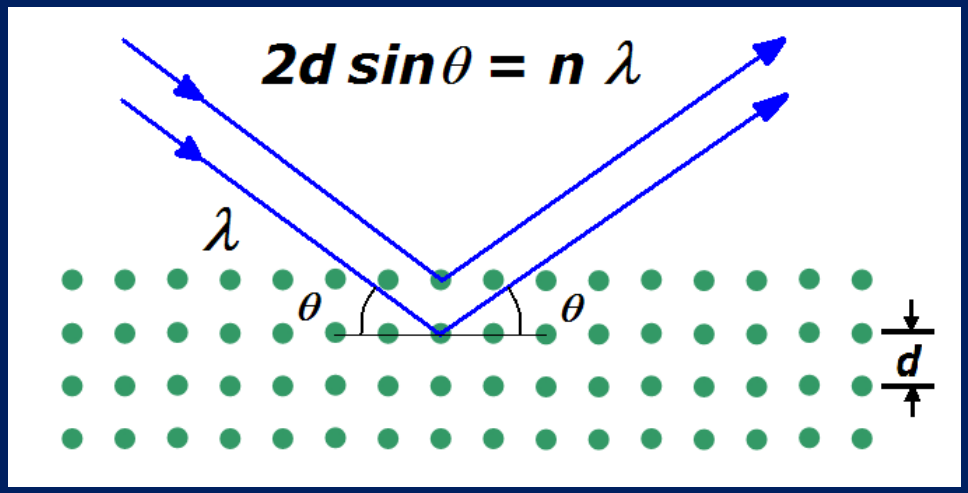


Photos courtesy of the APS and NSLS.

Monochromator : Bragg diffraction

The mono uses a very pure crystal to select specific energies (wavelengths) by Bragg diffraction.

The crystal diffracts according to Bragg's law:



$$\lambda = \frac{2\pi\hbar c}{E}$$

At a specific angle , photons of a specific energy (equivalently, a specific wavelength) meet the Bragg condition.

The first crystal directs the beam towards the ceiling!

The second crystal steers the beam in the same direction as the incident beam, but displaced vertically.

Common crystals: Si(111), Si(220), Si(311), InSb, beryl, diamond, YB_{66}

Caution: Harmonic energies

Other, higher energies also satisfy the Bragg condition! Something must be done to remove harmonics from the beam.

Monochromator

Common crystal types

Si(111) Most common XAS mono crystal, 2.1 to 25 keV

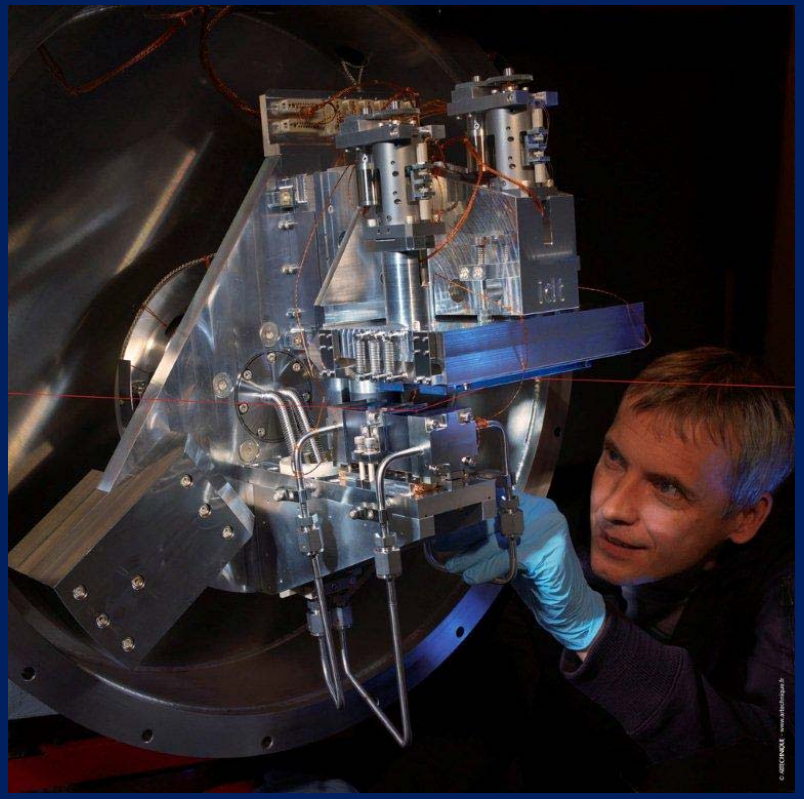
Si(220) Higher resolution, second harmonic, about 3.5-35 keV

Si(311) High resolution, about 4-50 keV

Diamond(111) High heat conductivity, difficult to make large crystals

Ge(111) Low resolution, high flux (rare for XAS applications) InSb, YB_{66}, Beryl Various crystal materials used below 2.5 keV.

Each has drawbacks, but each is particularly useful in narrow energy bands between the regions served by grating monochromators and Si crystals



Detuning of second crystal

One way of rejecting harmonic content uses a harmonic rejection mirror.
Another way is by detuning the second mono crystal.

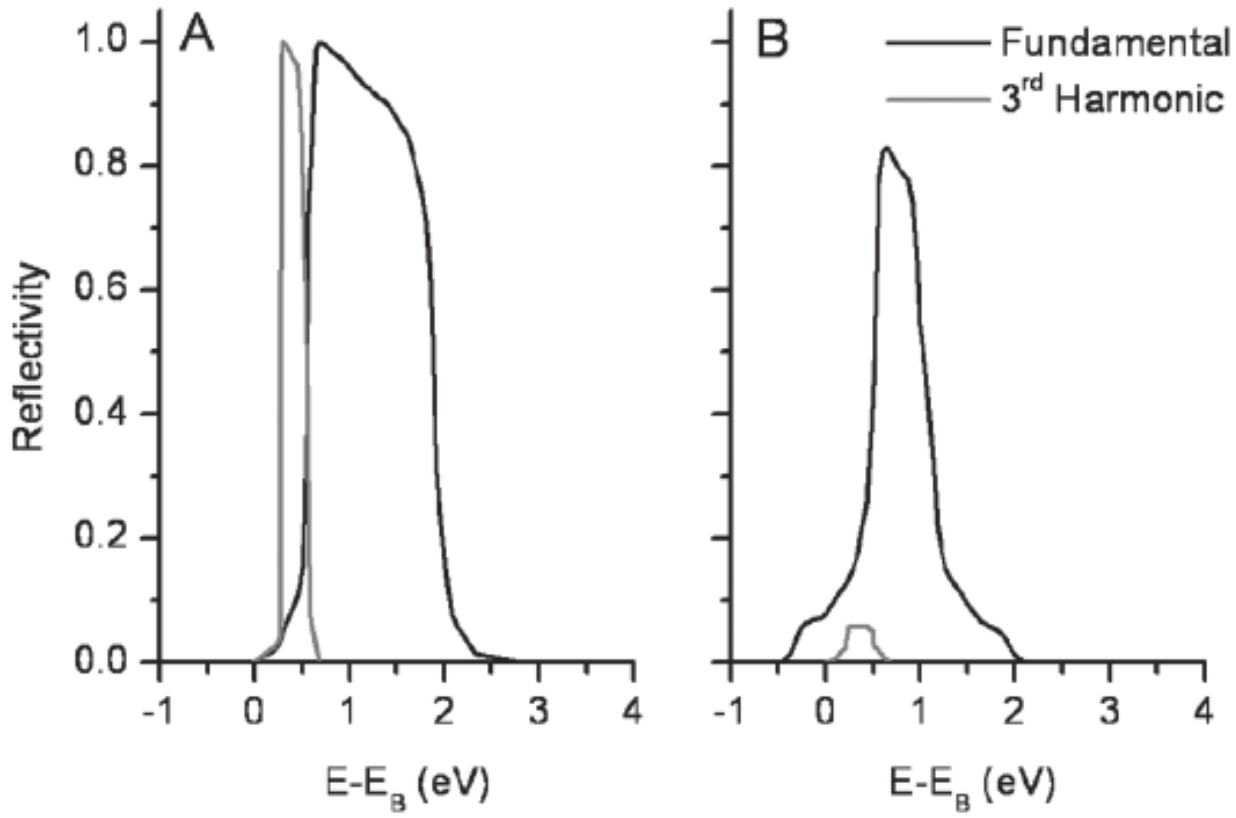


Fig. 14–13. Reflectivity of fundamental energy of 10 KeV and the third harmonic of 30 KeV from a Si(111) monochromator crystal as a change in relative energy from the Bragg energy (E_B) (A) without detuning and (B) with a detuning angle of 3.5 arcsec. The intensity of the third harmonic in B has been multiplied by 100.

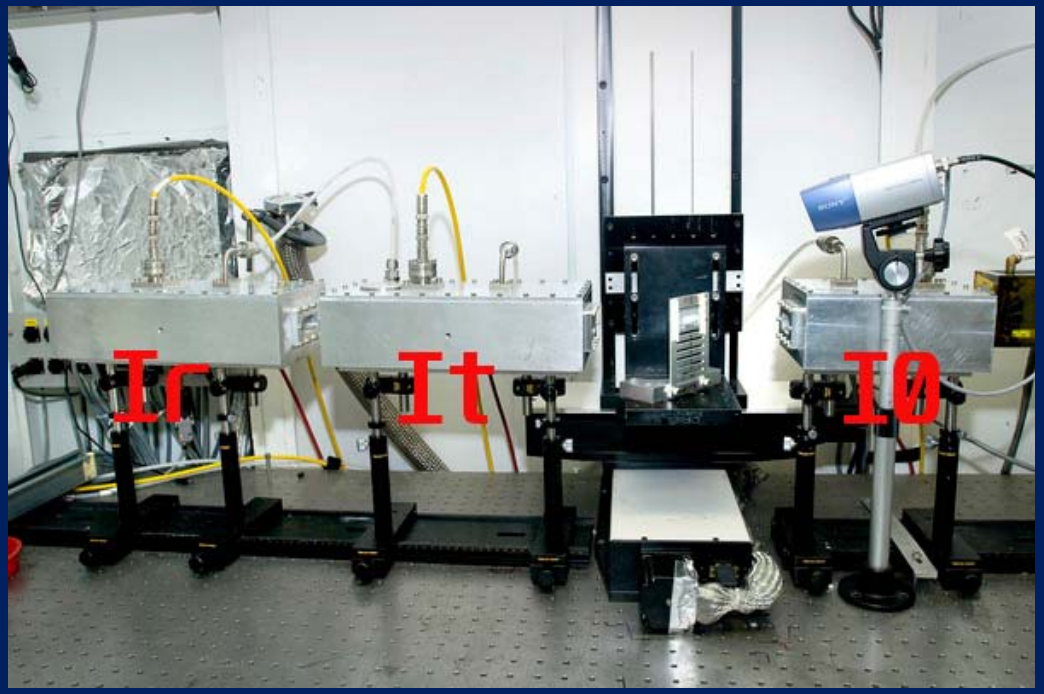
Figure from SD Kelly, D Hesterberg, B Ravel (2008), Analysis of Soils and Minerals Using X-ray Absorption Spectroscopy, in Methods of Soil Analysis, Part 5 { Mineralogical Methods, ed. AL Ulery & LR Drees (Madison, WI: Soil Sci. Soc. of America)

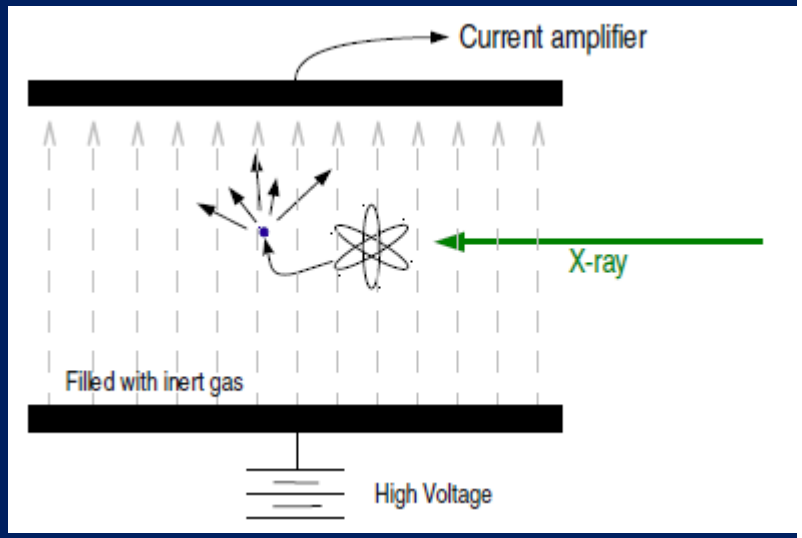
By tilting the second crystal by a few arcseconds relative to the first, the fundamental is attenuated slightly while the harmonic is reduced by more than 2 orders of magnitude.
This is typically done my tilting the second crystal with a piezoelectric actuator.

Ionization chambers

Ion chambers are usually used to measure the incident flux and the transmitted flux. They are sometimes used to measure the fluorescent signal.

I0 Incident detector
IT Transmission detector direct measure of absorption cross-section
IR Reference detector precise relative energy calibration



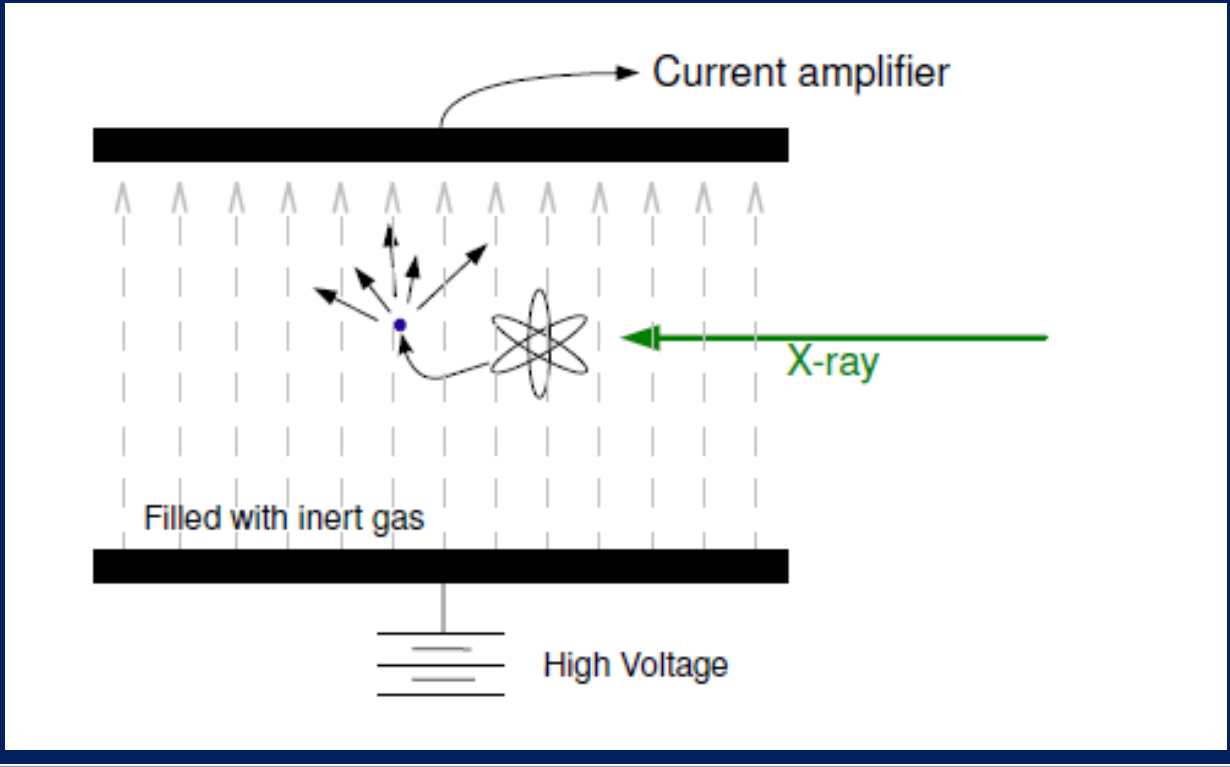


An ion chamber is a gas-filled capacitor. When an X-ray hits a gas molecule, an ion/electron cascade is formed. The electrons strike the grounded plate, generating a current.

Photo courtesy of Matt Newville.

Ion chambers

Count rate



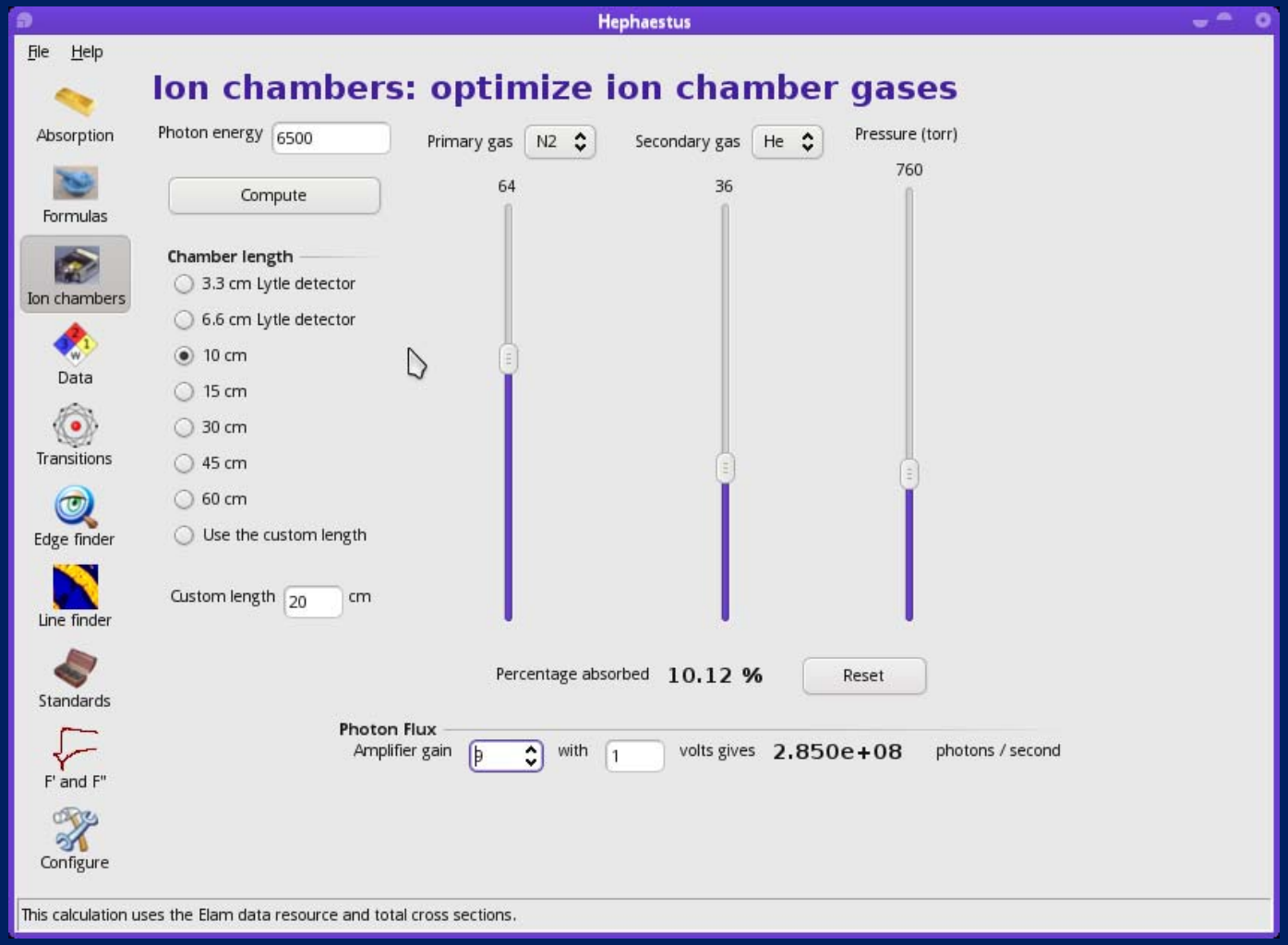
Flux on an ion chamber is easily computed

$$V = \frac{eE_\gamma NG}{E_{eff}} \quad \longrightarrow \quad N \approx \frac{4 \cdot 10^{20} V}{GE_\gamma}$$

G is the amplifier gain, E_γ is the incident photon energy, e is the electron charge, E_{eff} is the effective ionization energy (about 30 eV), and V is the voltage on the detector.

Ion chamber fill gas

The fill gas must be chosen appropriately for the energy measured.

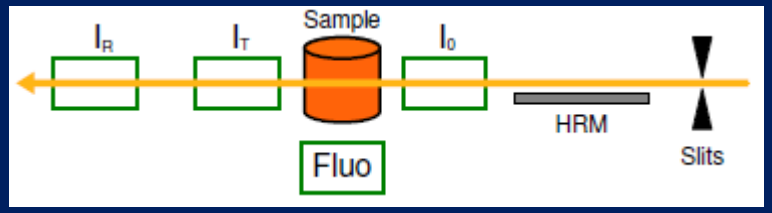


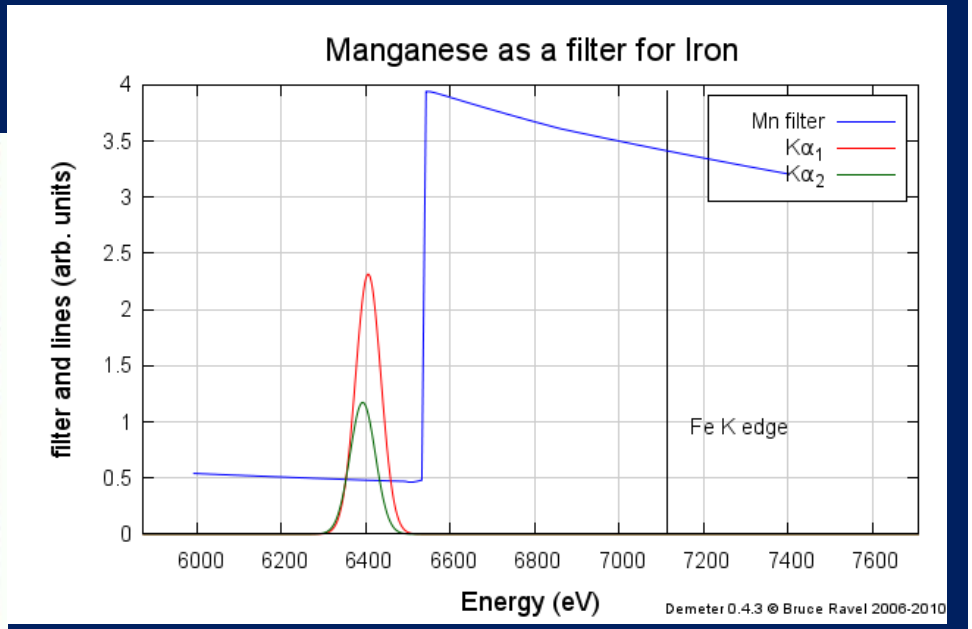
In this example, a 10 cm I0 chamber requires 64% N2 and 36% He to absorb 10% of the incident flux.

High energy edges might require the use of Ar or even Kr.

Ion chambers for fluorescence

An ion chamber can also be used to measure the fluorescence signal. To increase efficiency (by increasing the signal-to-noise ratio), this detector is often used with a slit assembly and fluorescence filters.





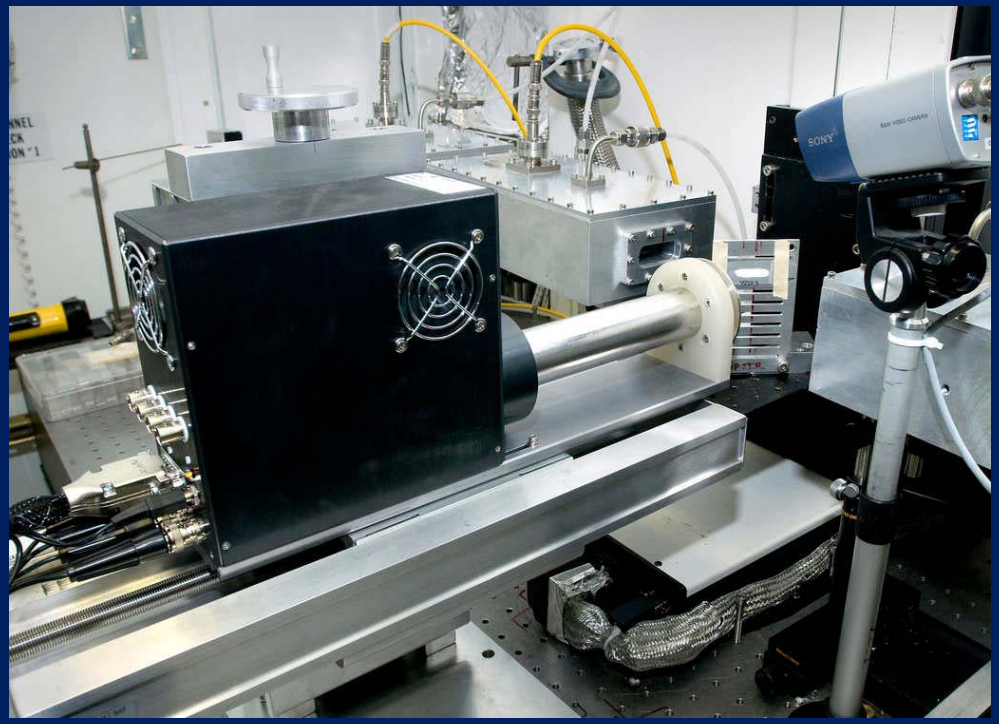
This sort of ion chamber is called a Stearn-Heald detector (EA Stern & SM Heald, Rev. Sci. Instrum. 50, 1579 (1979)), also known as a Lytle detector.

The Z-1 filter works by preferentially absorbing the elastic and Compton scattering and passing the K fluorescence.
This works well for when the signal to background is not too small.

Energy discriminating detection

For very dilute or very heterogeneous samples, an energy discriminating detectors offers many advantages over an ion chamber.

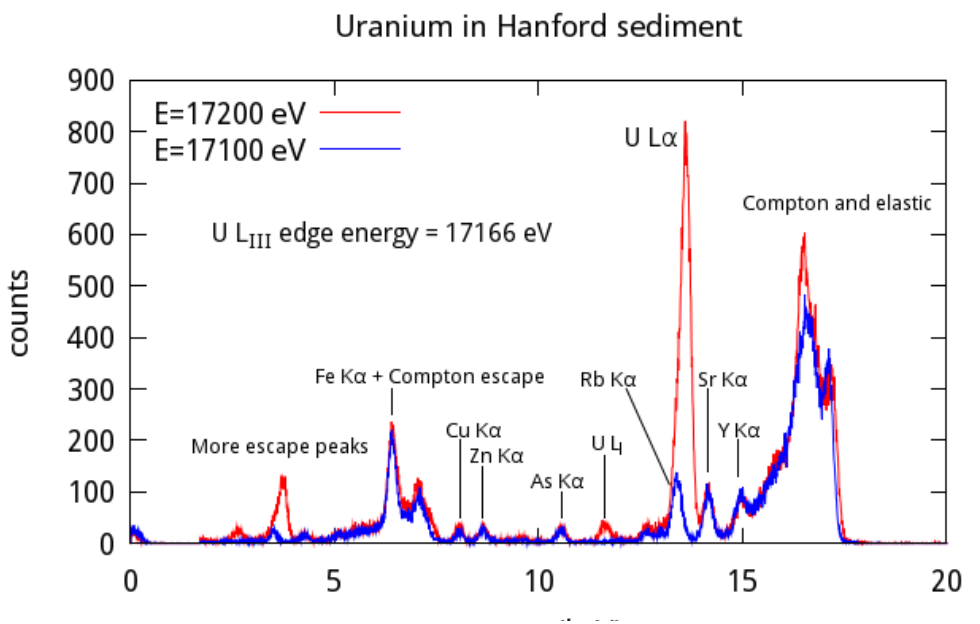
Canberra germanium detector
13 (or more) elements LN2-cooled

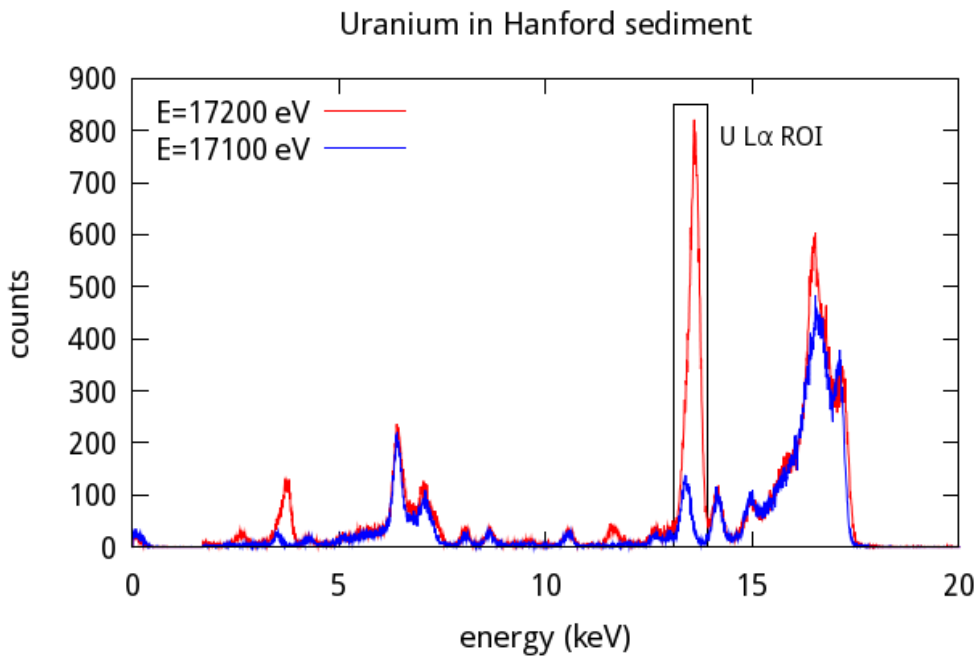


Vortex Si drift detector
1 or 4 elements (currently...)
Peltier cooled

Photo courtesy of Matt Newville.

X-ray fluorescence spectrum





The detector electronically discriminates photons by measuring the amount of energy deposited on the sensor.

Every element in the sample with an absorption edge below the incident energy will fluoresce at its unique energy.

XAS is measured by placing a window, or region of interest (ROI) around the relevant peak.

XRF is then measured as a function of energy.

Total electron yield

A sample holder for electron (Auger) yield measurements with He gas as amplifying media

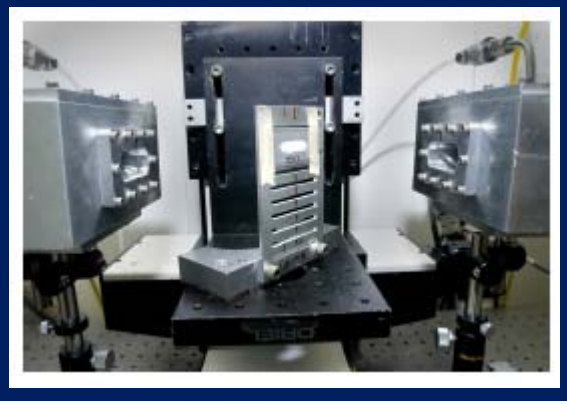
x-rays

Bias voltage ~100 V

Current ~ 100 pA – 10 nA

In situ experiments

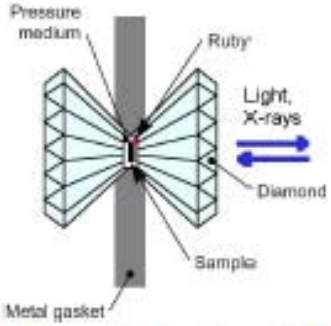
The strength of the EXAFS experiment is that almost anything can go on the sample stage.



Photos courtesy of Matt Newville.

Gas flow reactor for redox chemistry

Tube furnace for high-T XAS



Diamond anvil cell for high-P XAS

Cryostat (ARS Displex)

Combinatorial chemistry (Argonaut Technologies Surveyor)

Peristaltic pump for fluid flow

Cryostream, bio samples (Oxford Cryosystems Cobra)

Tilt stage for grazing incidence

Sample environment

XAS is usually capable of measuring your sample very close to the "proper" state.

Because X-rays are deeply penetrating, an XAS experiment can be made in an appropriate sample environment.

Because XAS is relatively insensitive to the sample matrix, XAS can be measured on almost anything.

Because XAS is element specific, minimal sample preparation is required. Sequential extraction, dessication, and other chemistry-altering procedures can be avoided.

Because XAS has no dependence on symmetry or periodicity, XAS can be measured on matter in all states.

Always remember

A good experiment is a highly relevant experiment!

Choice of standards

How many standards should I measure?

Answer: All of them!

Well, OK ... you can't measure everything. But your standard library should be extensive.

XANES analysis techniques rely upon completeness of standards libraries

Even EXAFS analysis benefits by access to good standards. It is often useful to measure and analyze a known standard as a sanity check on the experimental set-up and on the data analysis tools and procedures

Choice of experimental samples

If you are studying	you should measure
phase transitions	two or more temperature points in each phase
redox chemistry	many different redox potentials
environmental contaminants	samples culled from several different geochemical environments
the effect of a dopant	many different dopant concentrations

The point is ...

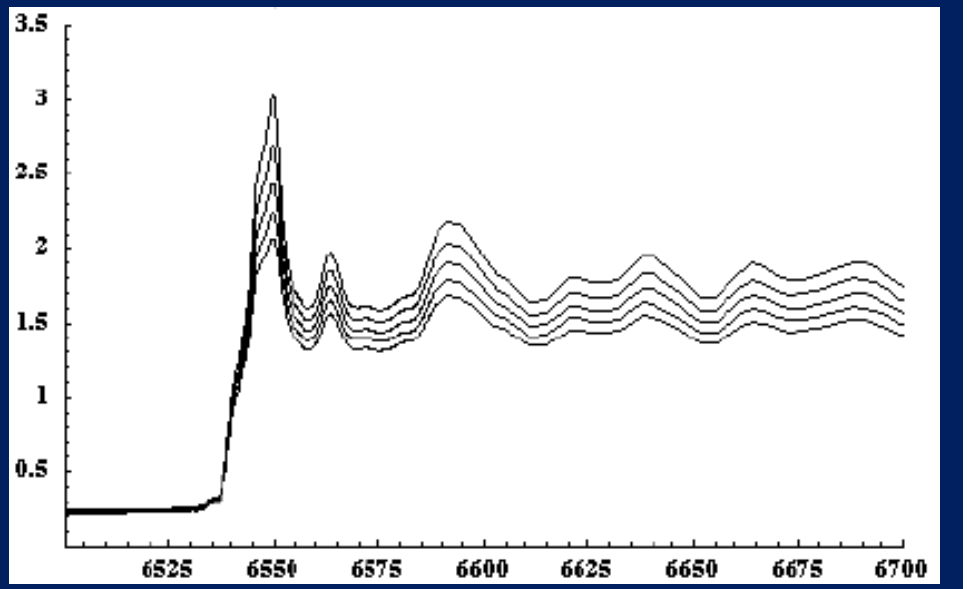
You need to measure enough data to tell the whole story.

Sample preparation

The basic rule of sample preparation

Ideally, the sample is homogeneous so that every ray of light interacts identically with every part of the sample.

If your particles are large compared to an absorption length, then your sample will look something like this:



Some regions are very thick, while other regions have gaps (or leakage). The leakage problem distorts the your data by decreasing white line height and altering the measured σ^2 of the EXAFS. Nonlinearity in response leads to systematically noisy data.

Transmission or fluorescence?

A good transmission sample

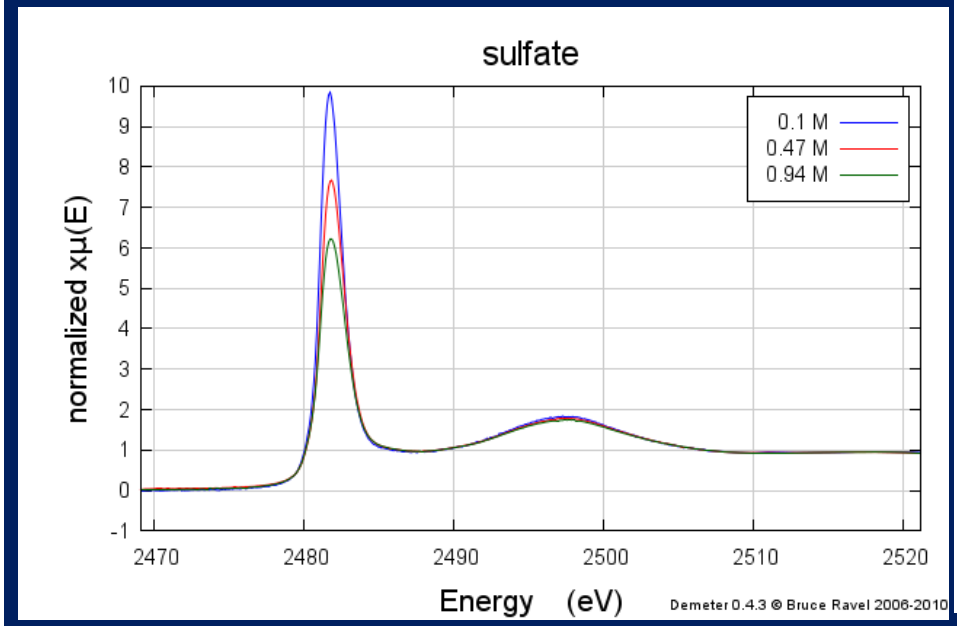
1. Particles are small compared to an absorption length.
2. Particles are homogeneously dispersed so that the sample is of uniform and appropriate thickness *for the energy of the measurement.*
3. The full sample (absorber + matrix) is not so thick that few (or no!) photons make it to the transmission chamber.
4. The edge step is large enough to yield high quality data. An edge step $\simeq 1$ is great, but anything from ~ 0.05 to ~ 1.5 should yield fine data.

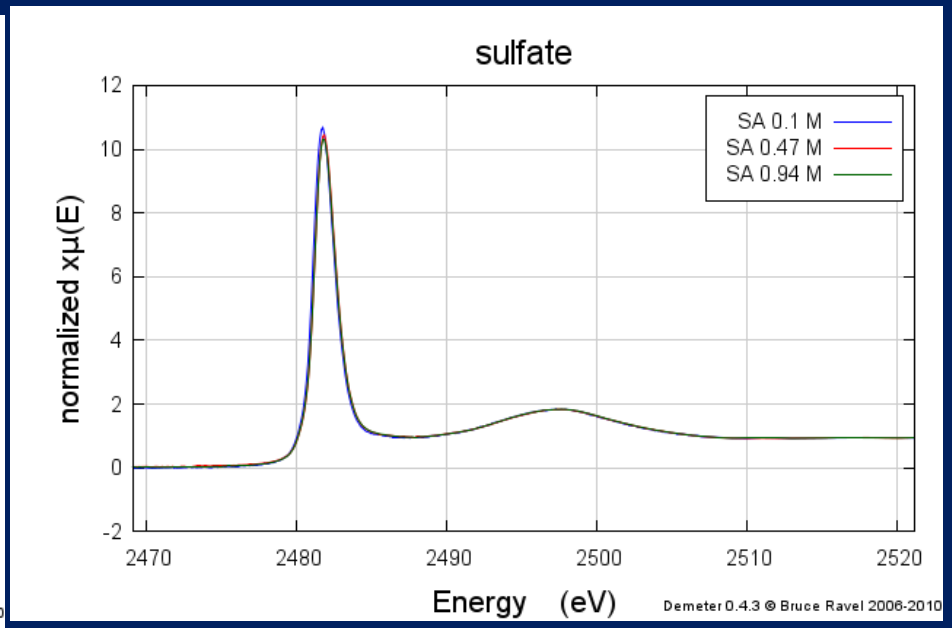
When should a sample be measured in fluorescence?

- your sample is large and cannot be damaged (e.g. a cultural heritage sample or anything else your collaborator expects to get back),
- the absorber is dilute in your sample such that you cannot obtain an edge step > 0.05 in a thin enough sample to pass light to transmission chamber,
- your sample is not dilute but exists in small quantities (e.g. a thin film sample),
- you are measuring a low-energy edge such that preparing a transmission sample is simply impossible,

The effect of self-absorption

If the sample is concentrated in the absorber element, then the penetration depth changes as the scan goes through the edge, the white line, and the oscillations. As the penetration depth changes, the volume of sample probes changes.





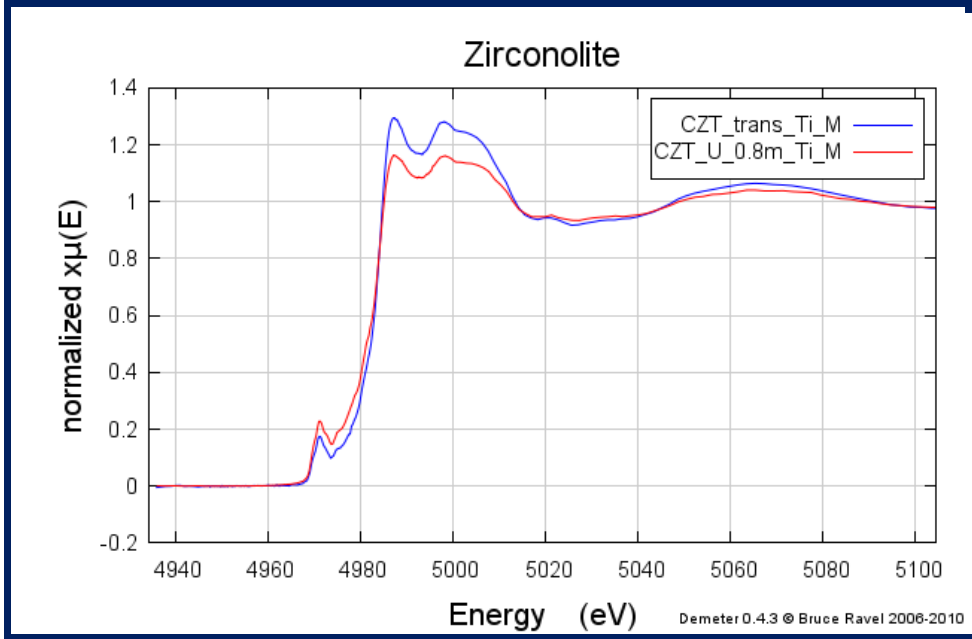
Identical sulfate solutions of 0.1 M, 0.47 M, and 0.94M appear to be different

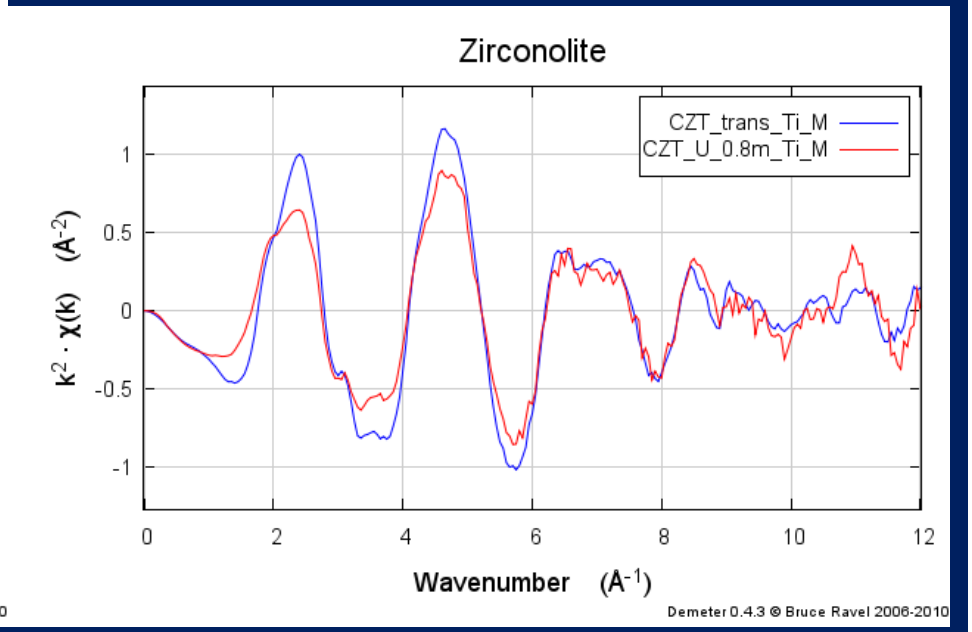
After applying athena's empirical correction the data are the same, as expected

The difficulty of the self-absorption correction

Applying the self-absorption correction requires detailed knowledge of the sample and the matrix, as well as some way of verifying that the correction was applied properly.

Here are data taken in transmission and fluorescence on the Ti K edge of CaZrTi2O7:





Pre-edge features are inflated while the EXAFS is attenuated

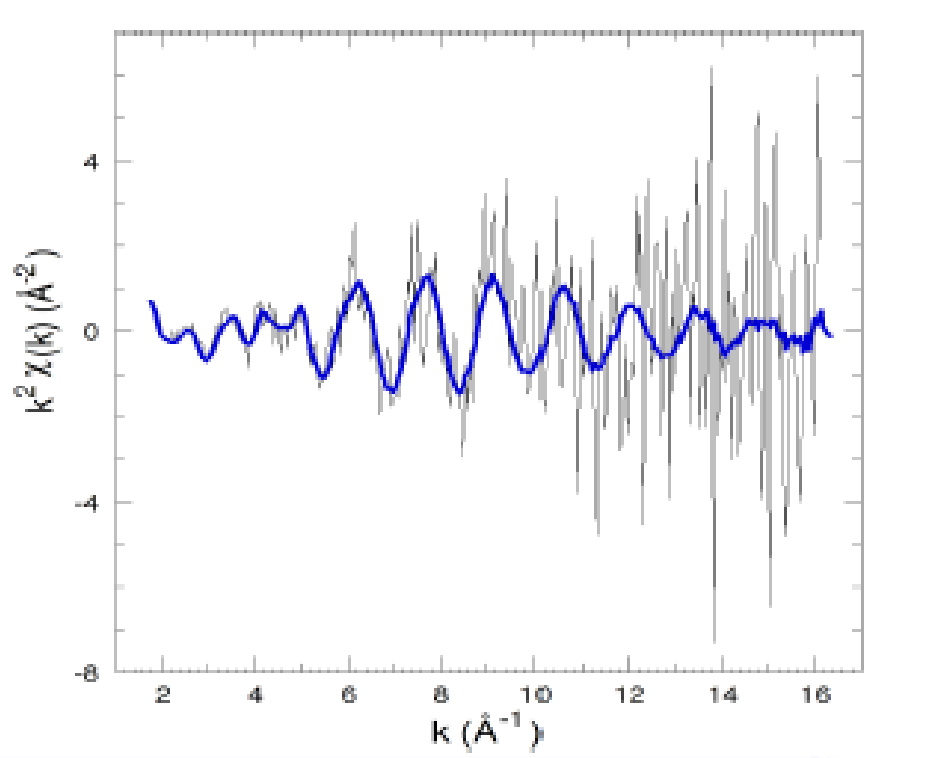
The attenuation of the EXAFS is shown here in χ(k)

In general, one does not have the correct transmission measurement for comparison.

How much is enough data?

In any experiment, there is a tension between time and data quality, between measuring enough samples and measuring each sample well enough.

Ga K edge EXAFS from a 53 Å $Ga_{0.26}In_{0.74}As$ alloy grown on an InP(001) substrate recorded at glancing-incidence. A single scan of ∼ 20 minutes (black) is compared to the merged EXAFS (blue) from the same sample after 4 days of data collection on NSLS X23A2.



If a sample is difficult but important, it is worth spending time on.

Measurement statistics

Data dominated by statistical noise will get better as you measure longer
4× more data → 2× better data.

Data affected by systematic error cannot be improved by measuring longer.

Sensible scan parameters

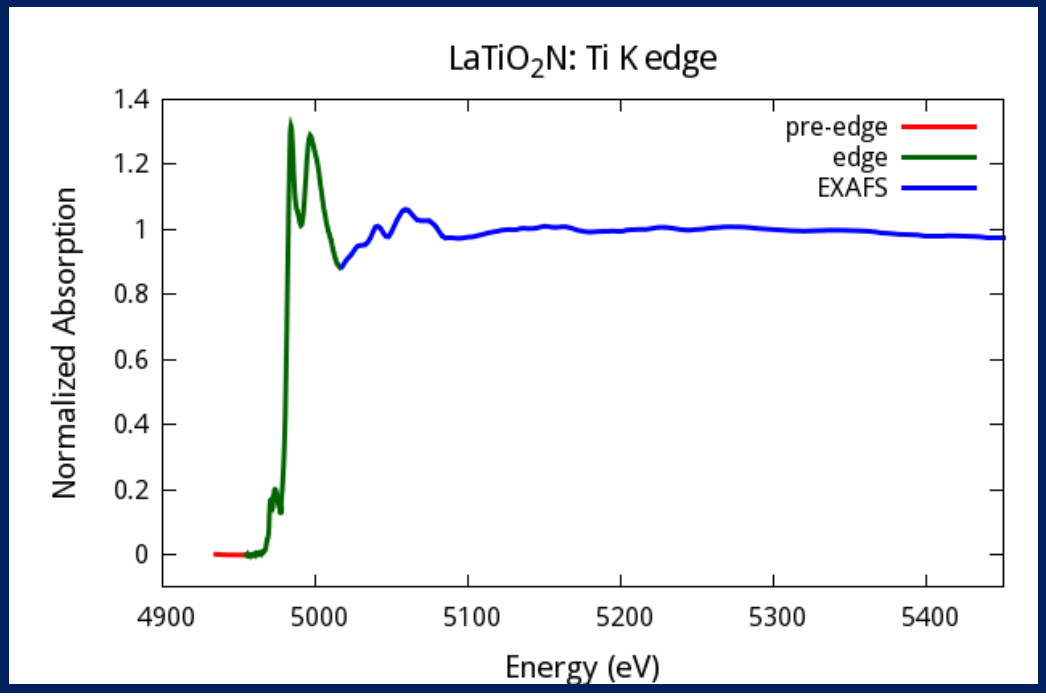
Through the edge, the measurement grid must be very fine to adequately measure the quickly changing data and to determine E0 and the valence of the absorber.

Even in a XANES study, enough of the pre-edge and post-edge must be measured to do a good job normalizing the data.

Steps in the EXAFS region are often even in wavenumber, thus increasing in energy. This is a good time-efficient way to collect data.

Integration time is often increased in the EXAFS region as the signal becomes smaller.

It is usually wise to measure more than one scan.



region	step size
pre-edge	5 eV
edge	0.25 eV
EXAFS	0.05 $Å^{-1}$

0.25 eV is reasonable for 5 keV. A larger step is OK at higher energy, a smaller step might be needed for lower energies.

How many scans is enough?

"It is usually wise to measure more than one scan."

Fine. So how many is enough?

There is no simple answer to that question and it is the reason that even the best beamline automation still requires a human being to be involved with the experiment.

If you plan for one scan and something goes wrong, you have no data.

If you plan for two scans and something goes wrong, you don't know which one is right.

If you plan for three scans and your data is still noisy, you don't have enough data.

It takes data to determine how much data you need.

You need good enough statistics such that the data you intend to analyze is large compared to the level of noise. So, measure enough data such that the statistical noise becomes small compared to $\chi(k)$.

The take-home message

1. Prepare your samples well
2. Think hard about how to measure your data
3. Measure beautiful data

It's that simple!

Thank you for your attention !