Instrumentation for XAS

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

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XAS Instrumentation

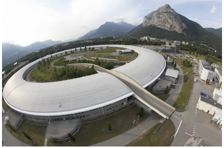
Bruce Ravel

Copyright

5 continents and >20 countries

APS, Chicago, USA

ESRF, Grenoble, France



Australian Synchrotron

Photon Factory, Japan

LNLS, Campinas, Brazil

Diamond, England

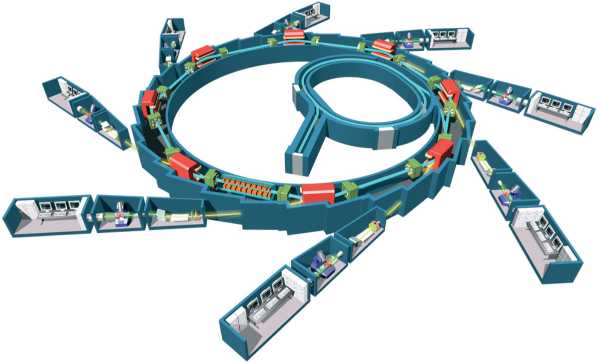
NSLS, New York, USA

Shanghai Synchrotron

SLRI, Thailand

All photos courtesy of the respective synchrotrons.

The floor of a 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.

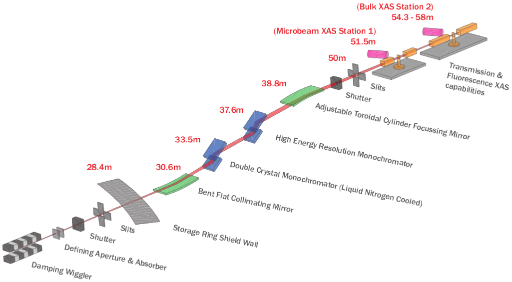
Overview of this talk

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

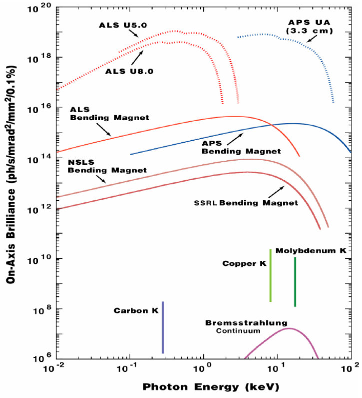
Optics How monochromators, mirrors, and other components conditioning the beam for an XAS experiment.

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.



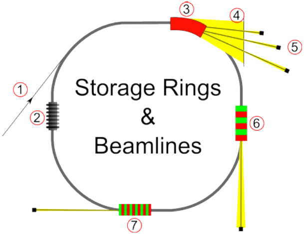
Why build synchrotrons?



Photon properties produced by a synchrotron:

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

The storage ring



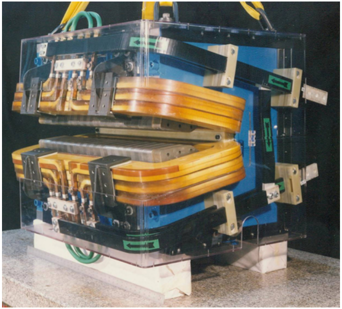
The storage ring is a large, evacuated, polygonal tube for containing relativistic electrons. Along with various kinds of magnets used to condition and shape the stored current, the ring has special magnets which generate useful X-rays as the electrons pass through.

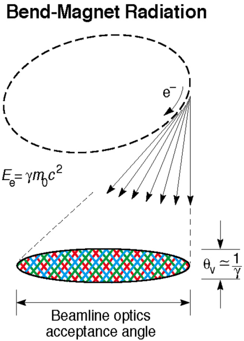
1. Bending magnets
2. Insertions devices: wigglers and undulators

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

Bend magnets

Overview





Bend 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 bend magnet is in a narrow cone.

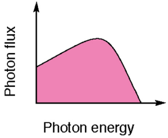
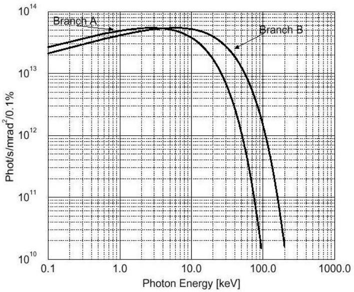


Photo and drawing courtesy of the Advanced Light Source.

Bend magnet

Spectrum



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 bend magnet field strength
- E is the energy of the storage ring

- All bend magnets excel at delivering photons from the IR through the VUV.
- Bend magnets at high energy facilities (APS, ESRF, SPring-8) deliver high flux beyond 100 keV.
- High energy performance be be tuned by increasing field strength, e.g. ALS or SLS superbend devices.

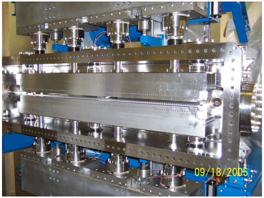
Drawing courtesy of the ESRF BM25.

Insertion devices

Insertion devices periodic magnetic structures designed to improve upon the performance of bending magnets.

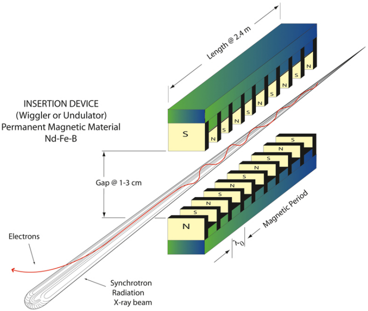
They are inserted into the straight sections of the storage ring.

Insertion devices in use around the world range from the enormous (APS undulator A, $> 2\,\mathrm{m}$, on the left) to the compact (the NSLS X25 minigap undulator, $< 1\,\mathrm{m}$, on the right).



Photos courtesy of the APS and NSLS.

Wigglers



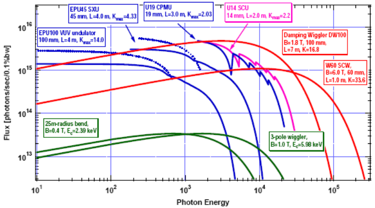


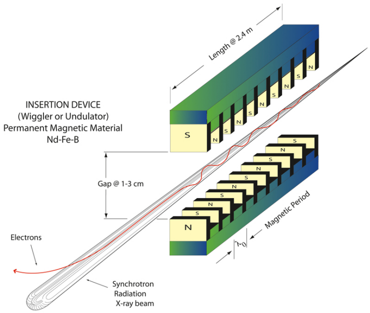
Figure 2. Flux vs. photon energy for various devices at NSLS-II.

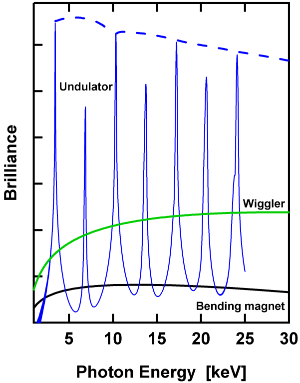
- A wiggler is, in a sense, a sequence of high field dipole magnets. It is an improvement over a bend magnet through a multiplicative effect.
- The profile of the wiggler spectrum is very similar to the BM spectrum, albeit with much higher flux.
- The price a wiggler beamline pays is managing higher heat loads.

Drawing courtesy of the APS, plot courtesy of NSLS-II.

Undulators

Overview



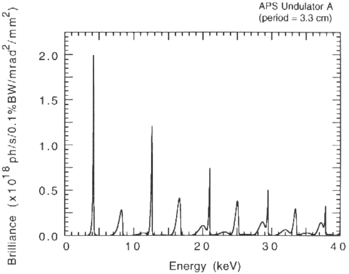


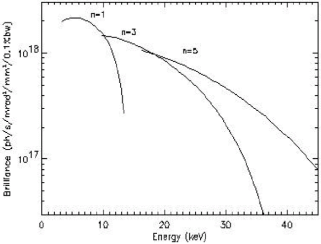
Undulators are much like wigglers, except the magnet period is shorter and the gap is often smaller. The light from each dipole is coherent, resulting in constructive interference at special wavelengths.

Drawing courtesy of the APS, plot courtesy of DESY.

Undulators

Spectrum: On-axis brilliance of APS undulator A





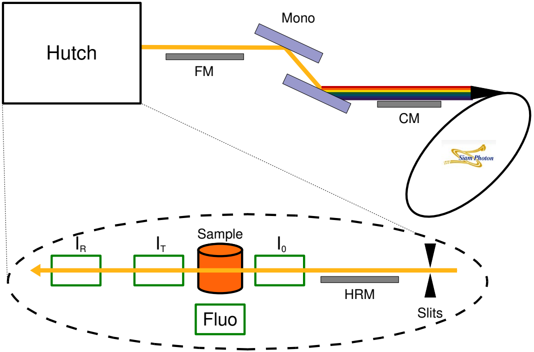
For a given gap, the undulator delivers extremely high intensity at discrete energies. To access other energies, the gap must be scanned.

Undulator XAS beamlines

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

Data courtesy of the APS.

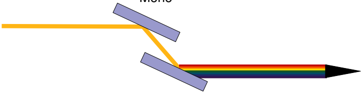
Optics



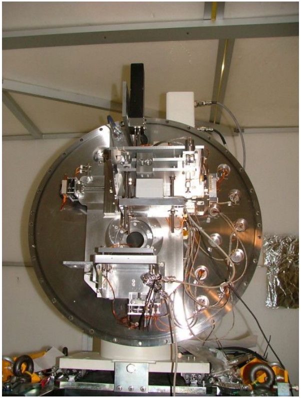
1. Monochromator
2. Mirrors (VCM, TFM, KB)
3. Slits & energy resolution
4. Harmonic rejection (mirror and detuning)

Monochromator

Overview

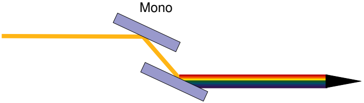


The mono is the device that turns white light (all energies) into monochromatic light (single energy).



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:

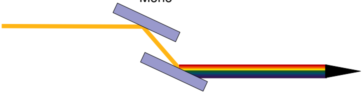
  $$2d\sin(\theta) = n\lambda$$

  At a specific angle θ, photons of a specific energy and with a specific wavelength λ 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.

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

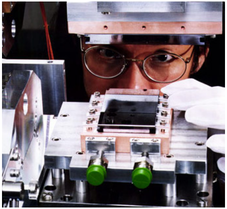


Photo courtesy of the APS.

Mirrors

Overview

- 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....

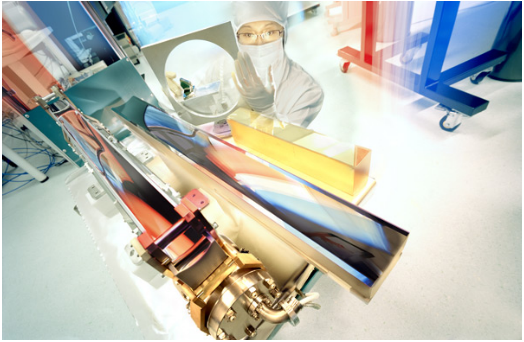
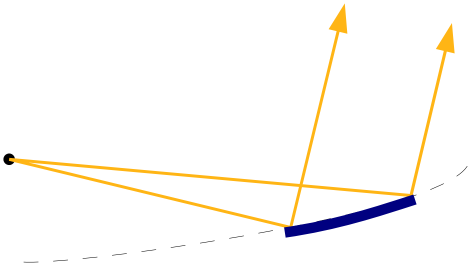


Photo courtesy of the ESRF.

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.



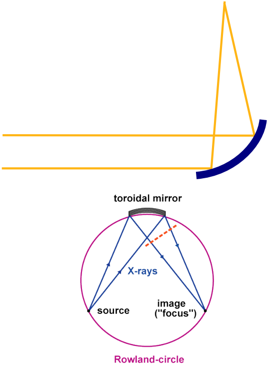
The VCM corrects the divergence of the beam, thus the instrumental resolution is defined by the mono crystal.

Mirrors

Toroidal focussing mirror

Photo courtesy of the ESRF.

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

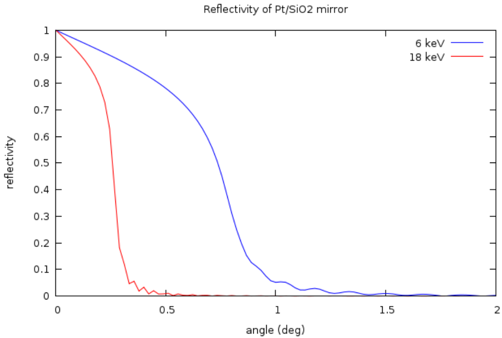


This can easily focus bend magnet radiation to a 500 μm spot.

Mirrors

Harmonic rejection mirror

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



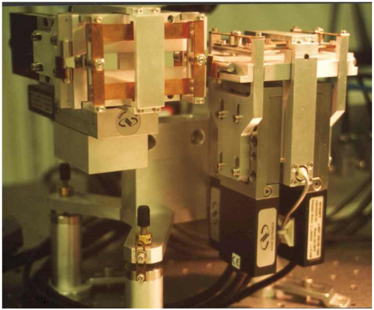
Setting a flat mirror to an appropriate angle (here, 0.5 deg) will pass most photons at 6 keV and absorb most photons at 18 keV.

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

Mirrors

Kirkpatrick-Baez focussing mirror

Kirkpatrick-Baez mirrors are a pair of flat mirrors, both bent into an excellent figure. One mirror focuses vertically, the other horizontally.



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

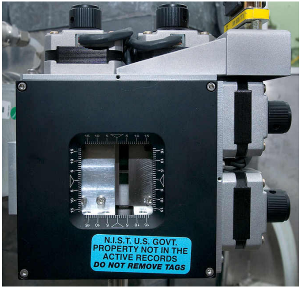
KB mirrors are required for micro-fluorescence, micro-XAS, and micro-XRD.

Photo courtesy of Matt Newville.

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 incident on 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.



Mirror and detuning

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

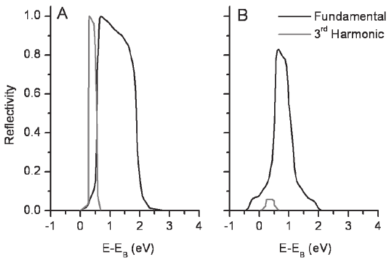


Fig. 14–13. Reflectivity of fundamental energy of 10 KeV and the third harmonic of 30 KeV from a Si(111) monochromator crystal as a change in relative energy from the Bragg energy (E_B) (A) without detuning and (B) with a detuning angle of 3.5 arcsec. The intensity of the third harmonic in B has been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

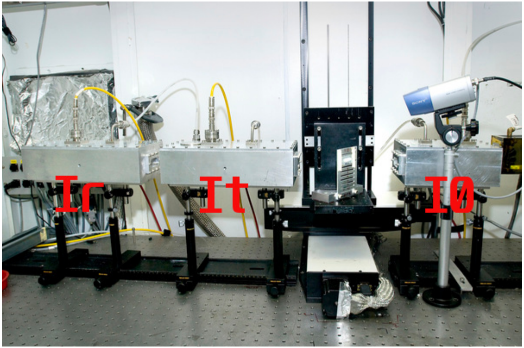
By tilting the second crystal by a few arcseconds relative to the first, the fundamental is attenuated slightly while the harmonic is reduced by more than 2 orders of magnitude.

This is typically done my tilting the second crystal with a piezoelectric actuator.

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), 367

Ion chambers

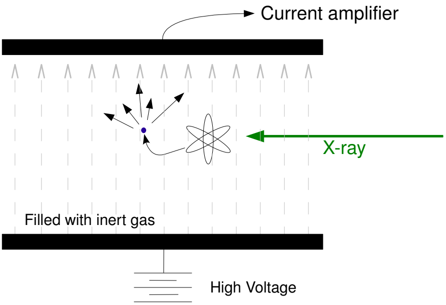
Ion chambers are gas-filled metal boxes with a capacitor inside. X-rays passing through the gas ionize gas molecules. The electrons strike one capacitor plate, inducing a measurable current.



- $\mathbf{I}_0$ Incident detector
- $\mathbf{I}_T$ Transmission detector – direct measure of absorption cross-section
- $\mathbf{I}_R$ Reference detector – precise relative energy calibration

Ion chambers

Count rate

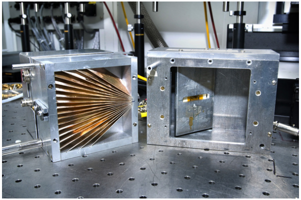


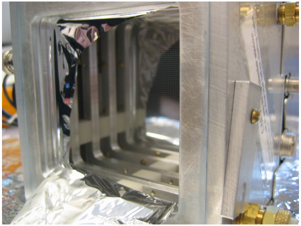
Flux on an ion chamber is easily computed

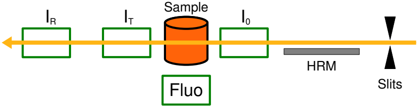
$$V = \frac{eE_\gamma NG}{E_{eff}} \qquad \longrightarrow \qquad N \approx \frac{4 \cdot 10^{20} V}{GE_\gamma}$$

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.

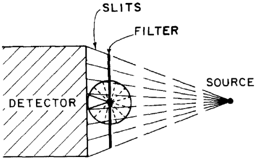
Ion chambers for fluorescence







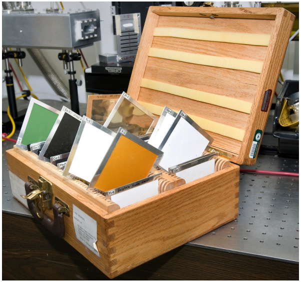
An ion chamber can also be used to measure the fluorescence signal. To increase efficiency (by increasing the signal-to-noise ratio), this detector is often used with a slit assembly and fluorescence filters.

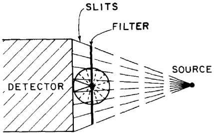


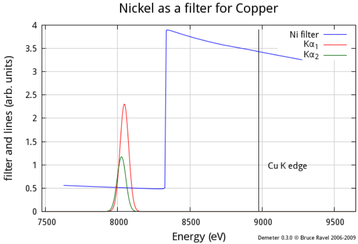
This sort of ion chamber is called a Stearn-Heald detector (diagram from EA Stern & SM Heald, Rev. Sci. Instrum. **50**, 1579 (1979)), also known as a Lytle detector.

Interior photo courtesy of the CLS HXMA beamline.

Fluorescence filters







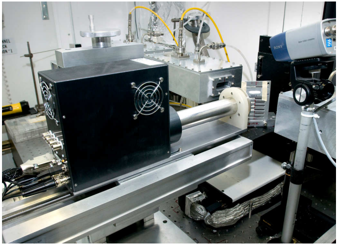
The filter material has its absorbtion edge between the energies of the incident beam and the dominant fluorescence lines of the sample.

The filter preferentially passes the signal and absorbs the elastic and Compton scatter. The slit assembly blocks re-fluorescence and scatter from the filter.

Energy discriminating detection

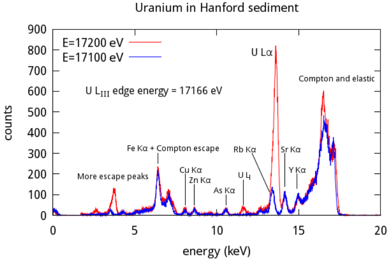
For very dilute or very heterogeneous samples, an energy discriminating detectors offers many advantages over an ion chamber.

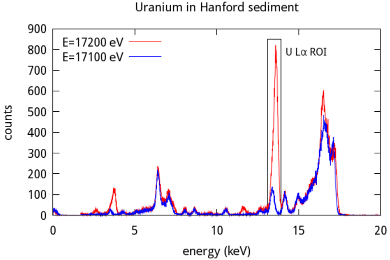
Canberra germanium detector
13 (or more) elements
LN2-cooled



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

X-ray fluorescence spectrum

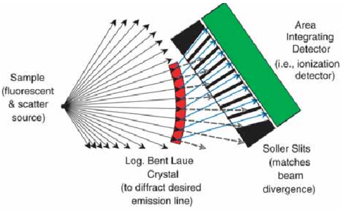


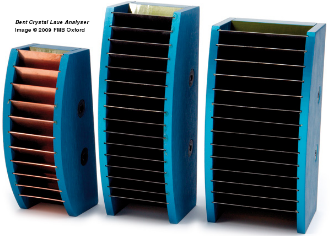


- The detector electronically discriminates photons by measuring the amount of energy deposited on the sensor.
- Every element in the sample with an absorption edge *below* the incident energy will fluoresce at its unique energy.
- XAS is measured by placing a window, or region of interest (ROI) around the relevant peak.
- XRF is then measured as a function of energy.

Wavelength dispersive detection

Another option for discriminating energies is to use a crystal analyzer to spatially separate energies by Bragg or Laue diffraction.

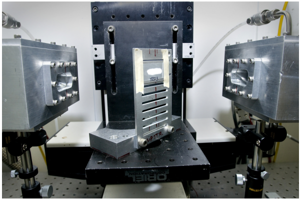


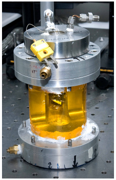


The bent Laue analyzer uses a thin silicon wafer bent over a frame. Rays of different energies Laue diffract in different directions from each other and from the transmitted rays. A filter assembly prevents all but the rays of the chosen energy from passing to the detector.

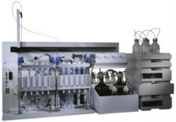
Hutch

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

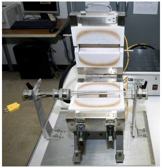




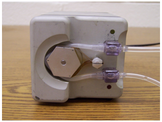
Gas flow reactor for redox chemistry



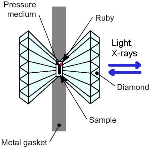
Combinatorial chemistry (Argonaut Technologies Surveyor)



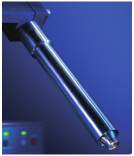
Tube furnace for high-T XAS



Peristaltic pump for fluid flow

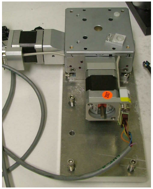


Diamond anvil cell for high-P XAS



Cryostream, bio samples (Oxford Cryosystems Cobra)

Cryostat (ARS Displex)



Tilt stage for grazing incidence

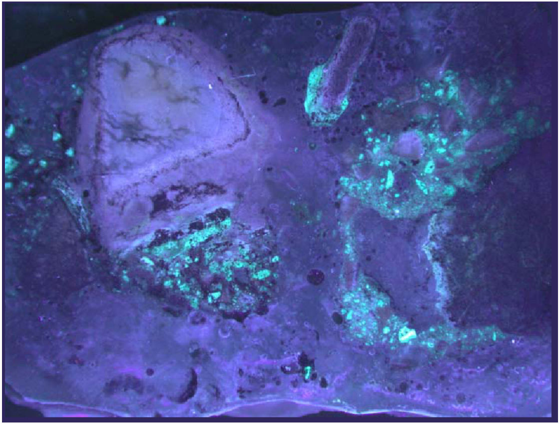
MicroXAS in an environmental science context

- Used a Cenberra 13 element germanium energy discriminating detector
- Horizontal focussing using a mirror with an APS undulator source
- XRF mapping by rastering a sample using an XY motorized stage
- Sample containment for radiological saftey which the X-rays pass right though
- EXAFS performed on different regions of the sample

Gravel Contaminated with U

Gravel embedded in epoxy with a polished surface

Under a UV lamp, U glows greenish.

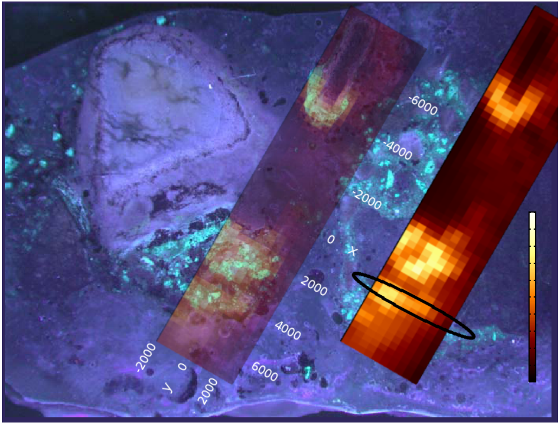


D Phillips, DB Watson, SD Kelly, B Ravel & KM Kemner, Environ. Sci. Technol. (2008) **42**:19, pp 7104-7110

Gravel Contaminated with U

Gravel embedded in epoxy with a polished surface

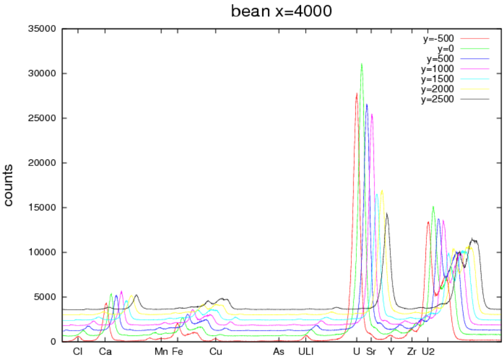
UV photo + superposed U map — 200 μm probe at APS 10ID.



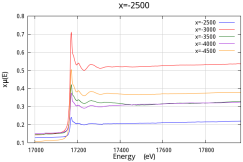
D Phillips, DB Watson, SD Kelly, B Ravel & KM Kemner,
Environ. Sci. Technol. (2008) **42**:19, pp 7104-7110

XRF Spectra at each Position

Here are a few of the XRF spectra from the marked area on the U map from the previous page.



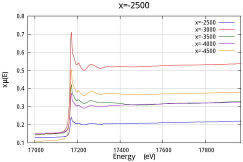
μ-EXAFS

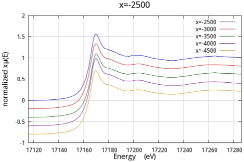


- High quality XAS data is measured with the 200 μm probe. We can see the variation in U quantity under the spot in the XAS step size.

D Phillips, DB Watson, SD Kelly, B Ravel & KM Kemner, Environ. Sci. Technol. (2008) **42**:19, pp 7104-7110

μ-EXAFS

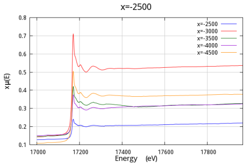


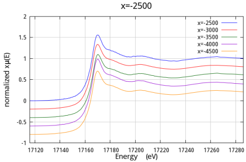


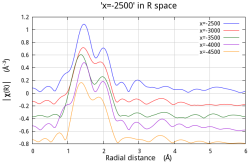
- High quality XAS data is measured with the 200 μm probe. We can see the variation in U quantity under the spot in the XAS step size.
- Normalizing the data, we see variability in the XANES, indicating spatial heterogeneity in U speciation.

D Phillips, DB Watson, SD Kelly, B Ravel & KM Kemner, Environ. Sci. Technol. (2008) **42**:19, pp 7104-7110

μ-EXAFS







- High quality XAS data is measured with the 200 μm probe. We can see the variation in U quantity under the spot in the XAS step size.
- Normalizing the data, we see variability in the XANES, indicating spatial heterogeneity in U speciation.
- The EXAFS is of high quality and can be analyzed to uncover the different structural environments around the U at the various locations.

D Phillips, DB Watson, SD Kelly, B Ravel & KM Kemner, Environ. Sci. Technol. (2008) **42**:19, pp 7104-7110

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- Some information was cribbed from a presentation by Steve Heald
- The μXRF and μXAS data are from an experiment I performed along with Shelly Kelly, Max Boyanov, and Ken Kemner.