National Synchrotron Light Source II

Brookhaven National Laboratory

U.S. DEPARTMENT OF ENERGY

Sample preparation and sample environments

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XAS 2025: Fundamentals of XAS Data Analysis: A Hands-on Tutorial, March 11th, 2025

Why talking about sample preparation?

1. Over a half of lost time during synchrotron beamtime is due to the sample quality deficiencies
2. If you do not recognize how sample quality affects the XAS data, you will collect and potentially publish misleading results

This presentation does not include math: see, e.g., http://gbxafs.iit.edu/training/XAFS_sample_prep.pdf for more quantitative explanation of the underlying phenomena

Best approach

Speak with beamline staff!

Sample preparation – victim of XAS popularity

XAS is versatile: almost anything can be measured (solids, liquids, gases, soil, dust, batteries, fuel cells, meteorites, wastewater, colloidal suspensions, protein solutions etc)

Your **specimen** must be transformed into a **sample**!

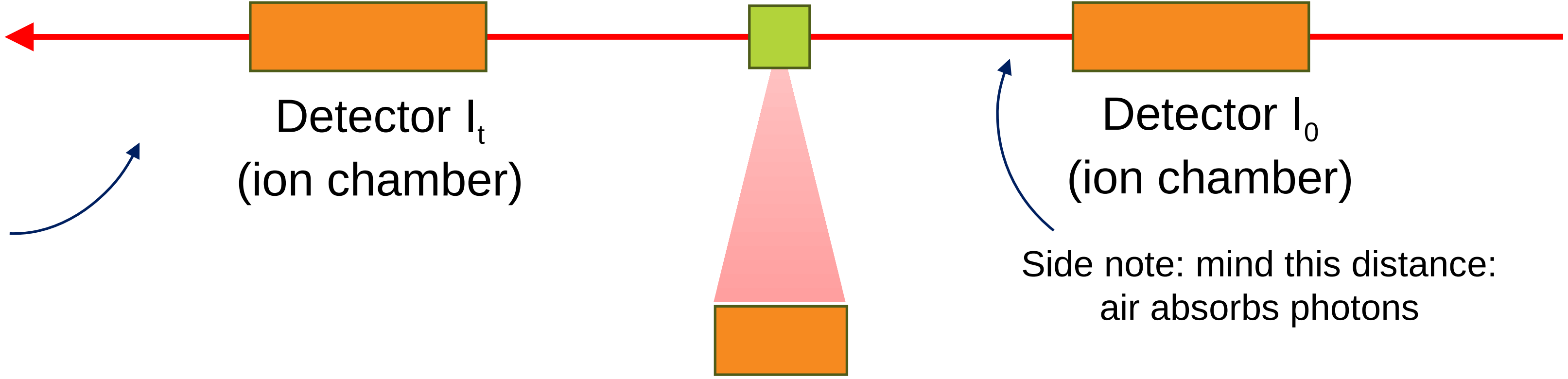
What are the characteristics of a good sample?

1. Concentration compatible with one of the common detection methods
2. Doesn’t introduce spectra distortion
3. Can be handled ㅆ

Oftentimes, the samples are just what they are…

Detection methods: transmission vs. fluorescence

Transmission: photon flux detected upstream of the sample and downstream of the sample



Sample

Detector I_t
(ion chamber)

Detector I_0
(ion chamber)

Side note: we often put a corresponding metal foil and another detector for energy calibration

Side note: mind this distance: air absorbs photons

Fluorescence detector

Fluorescence: emitted photons are collected by the detector placed on the side of the sample

For transmission absorbance (per Beer-Lambert law) is $\mu = -log(I_t/I_0)$

For fluorescence, in thin dilute sample approximation, intensity is proportional to μ

Sample size

Considerations:

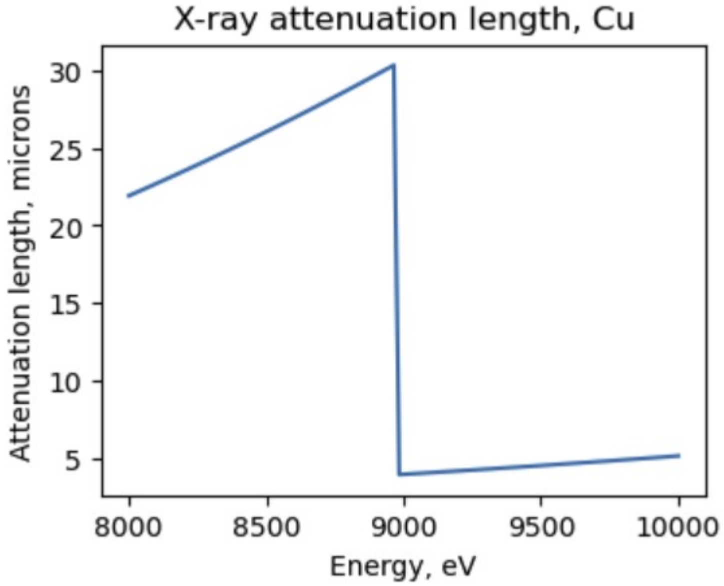
1. Beam size at a specific beamline
   - ISS: 1 mm (H) x 1 mm(V) or 50-100 μm (FWHM).
   - QAS: 10 mm(H) 1.5 mm(V) x 10 mm(H), or ~0.5 mm (FWHM),
   - BMM: 8 mm (H) by 1 mm (V) or 300 μm (FWHM).
2. Standard holder
3. Ease of handling

Uniformity is the key!!

Basic rule of sample preparation: sample shall be made **homogenous** so that every X-ray photon interacts identically no matter what area on the sample it hits.

Attenuation Length:

The depth into the material measured along the beam where the X-ray flux falls to 1/e of its value at the surface.



To be homogenous enough means particles shall be **smaller** than the attenuation length

Disclaimer: sometimes you cannot make smaller particles, e.g., certain sieve fraction of a catalyst to prevent gas flow blockage.

Uniformity is the key!! (cont.)

Imagine your sample looks like that

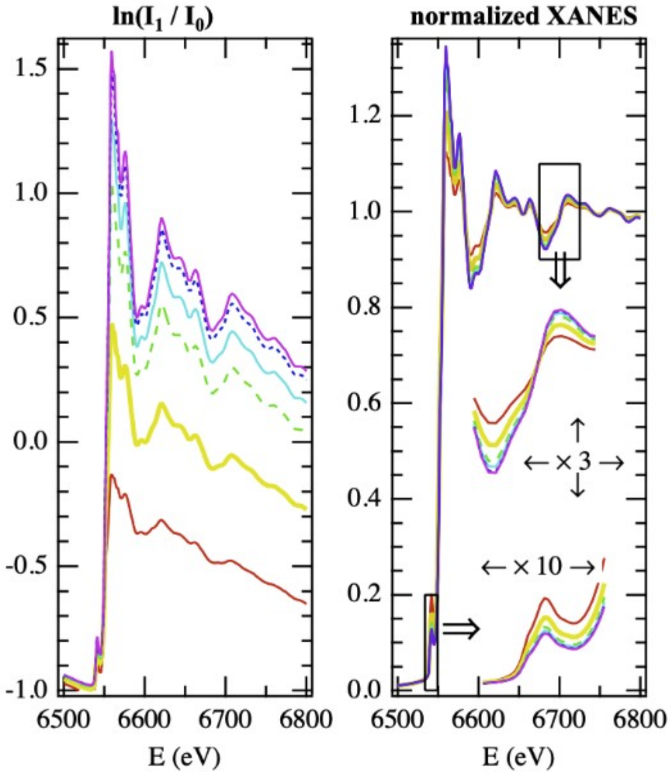
There are regions of varying density and pinholes: the X-ray leakage problem leads to spectra distortion:

1. White line intensity decreases
2. Photons seeing different effective thicknesses create a “disorder” that manifests itself in artificially exaggerated [2]
3. Noise in the data increases

Takeaway

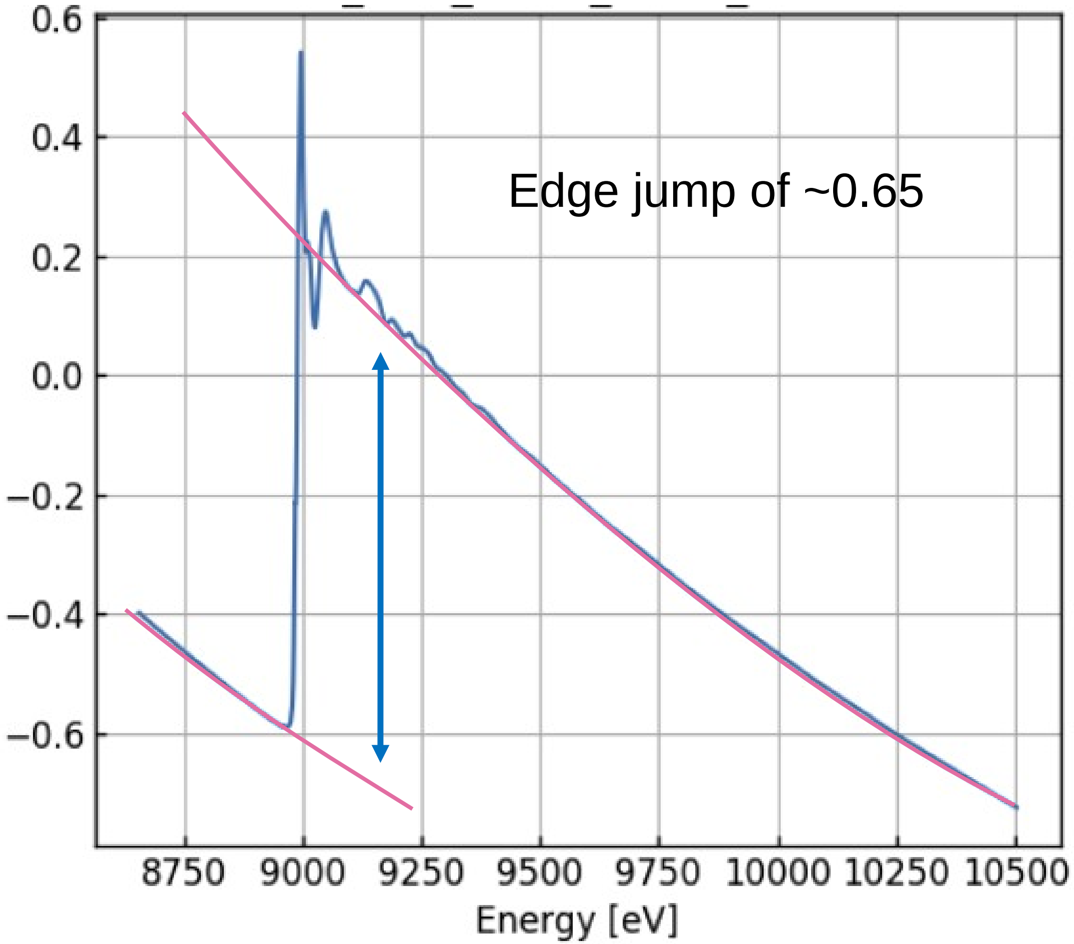
Particles shall be smaller than attenuation length and uniformly dispersed over the sample

Simulated spectra for particle sizes from 30 um to 0.3 um



Sample preparation for transmission experiments

It is recommended that the sample for transmission measurements has an edge step of 1-1.5 (however, 0.1-1 can be acceptable if the sample is of good quality)



Sample preparation for transmission experiment

Finding right amount of sample with Hephaestus

List of typical materials

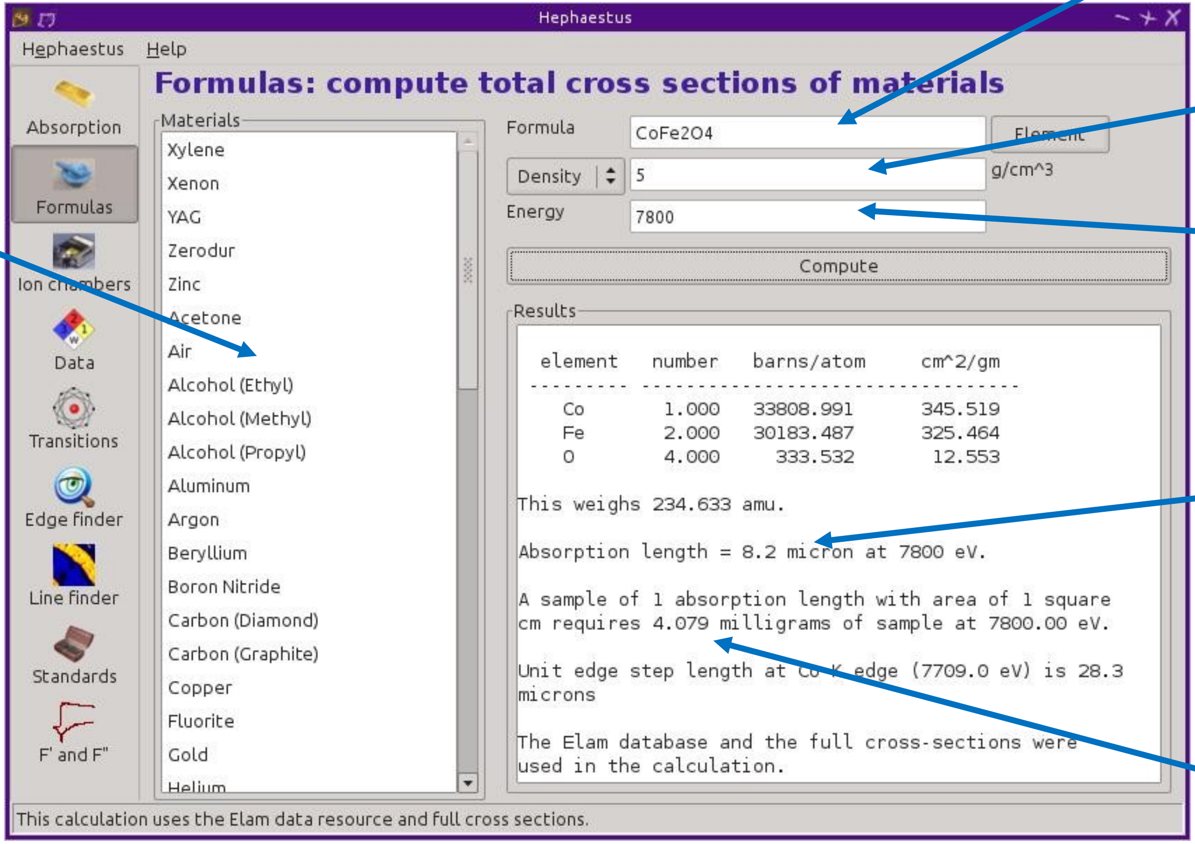
Chemical formula

Density

Energy (100 eV above the edge energy)

Absorption length

Amount of material/cm^2 for the edge jump of 1



Formulas: compute total cross sections of materials

Materials
- Xylene
- Xenon
- YAG
- Zerodur
- Zinc
- Acetone
- Air
- Alcohol (Ethyl)
- Alcohol (Methyl)
- Alcohol (Propyl)
- Aluminum
- Argon
- Beryllium
- Boron Nitride
- Carbon (Diamond)
- Carbon (Graphite)
- Copper
- Fluorite
- Gold
- Helium

Formula: CoFe2O4

Density: 5 g/cm^3

Energy: 7800

Results

```
  element   number   barns/atom     cm^2/gm
 --------- ----------------------------------
    Co       1.000   33808.991      345.519
    Fe       2.000   30183.487      325.464
    O        4.000     333.532       12.553

This weighs 234.633 amu.

Absorption length = 8.2 micron at 7800 eV.

A sample of 1 absorption length with area of 1 square
cm requires 4.079 milligrams of sample at 7800.00 eV.

Unit edge step length at Co K edge (7709.0 eV) is 28.3
microns

The Elam database and the full cross-sections were
used in the calculation.
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This calculation uses the Elam data resource and full cross sections.

Making pellets

Most reliable ex situ sample preparation method is making pellets made using a hydraulic (or hand) press (similar to IR pellets)

Inert binder/dilutant may be added to maintain correct concentration

Rule-of-thumb 1 Total amount of sample+binder >100 mg (for ease of handling)

Rule of thumb 2 Grind as long as you can… and then some

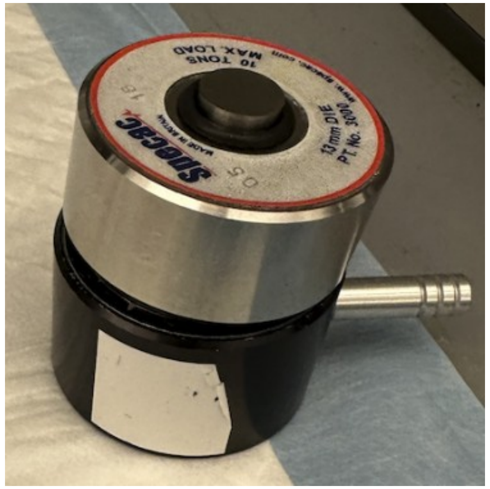
Rule of thumb 3 Sample+binder mixture color shall be uniform

Note on binders

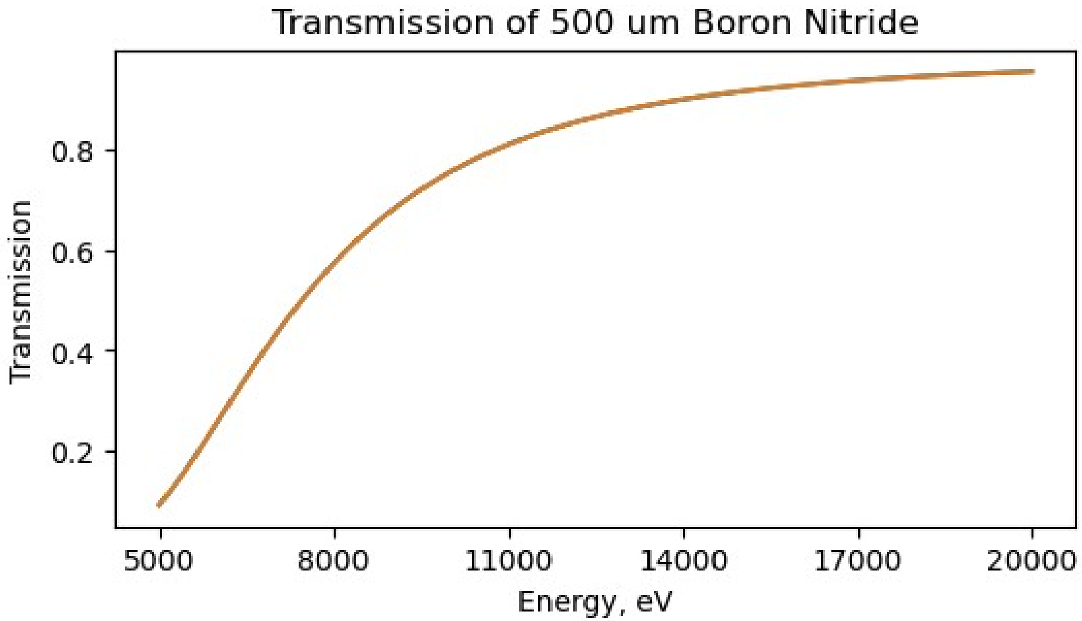
BN, cellulose, zeolite, polyethylene glycol (Inert is a relative term: BN catalyzed methane oxidation, zeolites are catalysts, PEG polymerizes under pressure…)

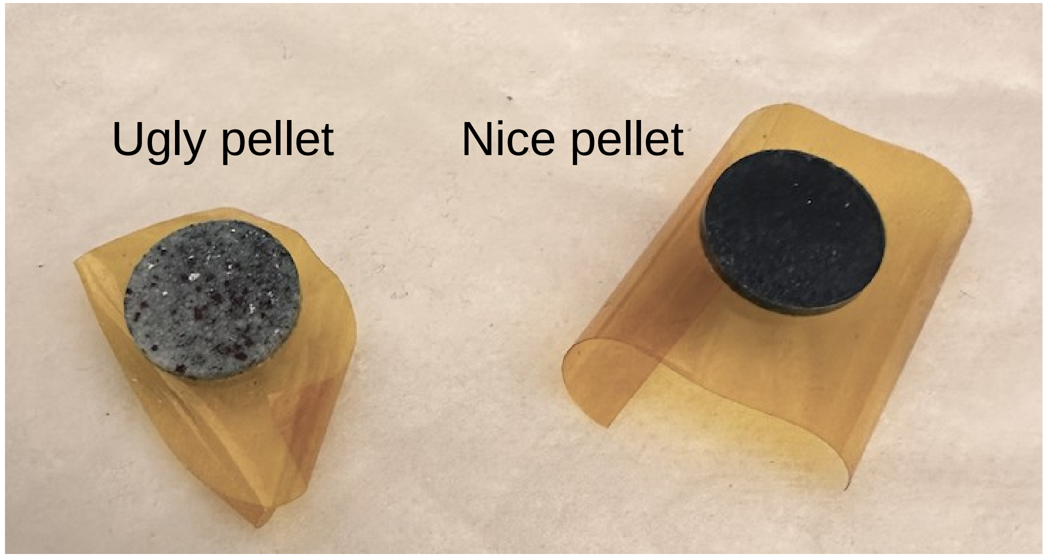
Making pellets

Equipment



Mind binder absorption





Other sample prep methods

- Capillaries

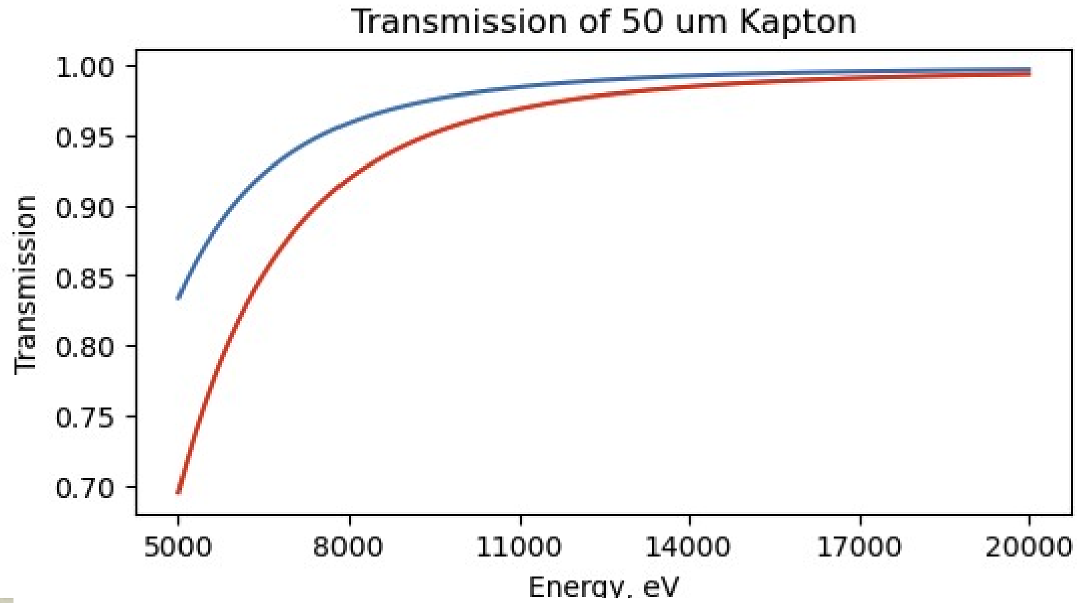
Typical materials – borosilicate glass, quartz, Kapton

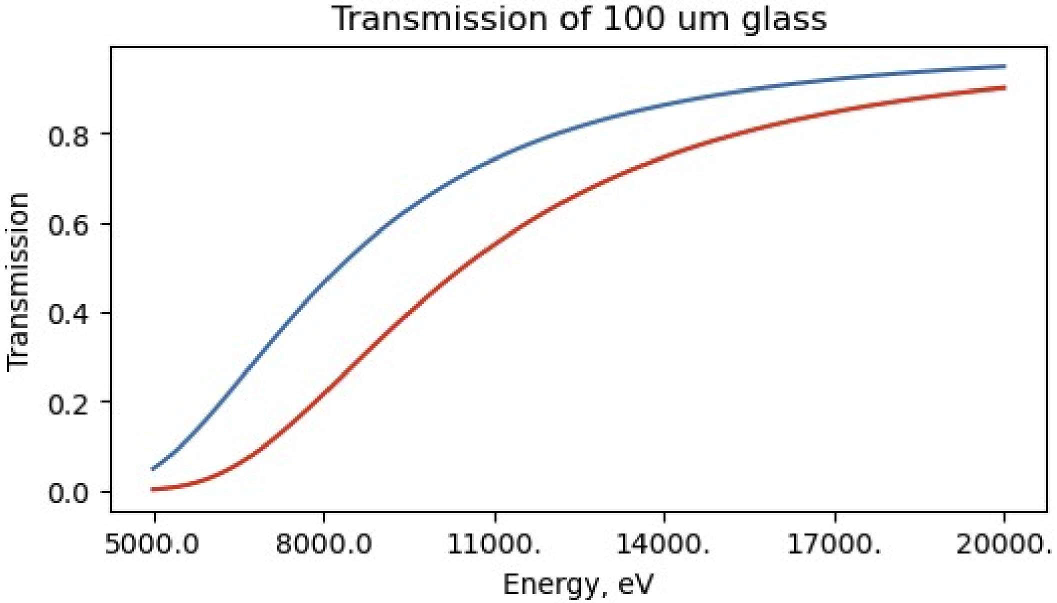
Mind the wall thickness: attenuation can be strong

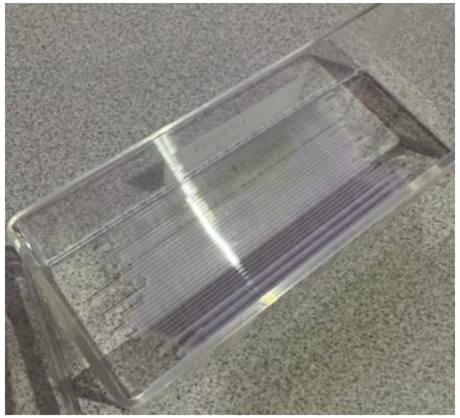
Even though *in situ* comes later:

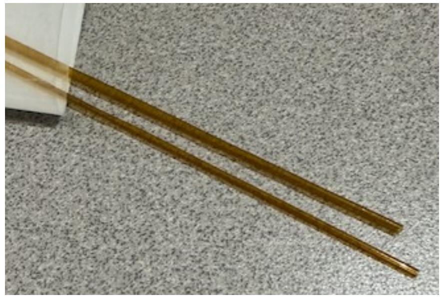
If heating is involved:

1. Glass – up to 600 ºC
2. Quartz – up to ~ 1300 ºC (becomes brittle)
3. Kapton – up to 300 ºC



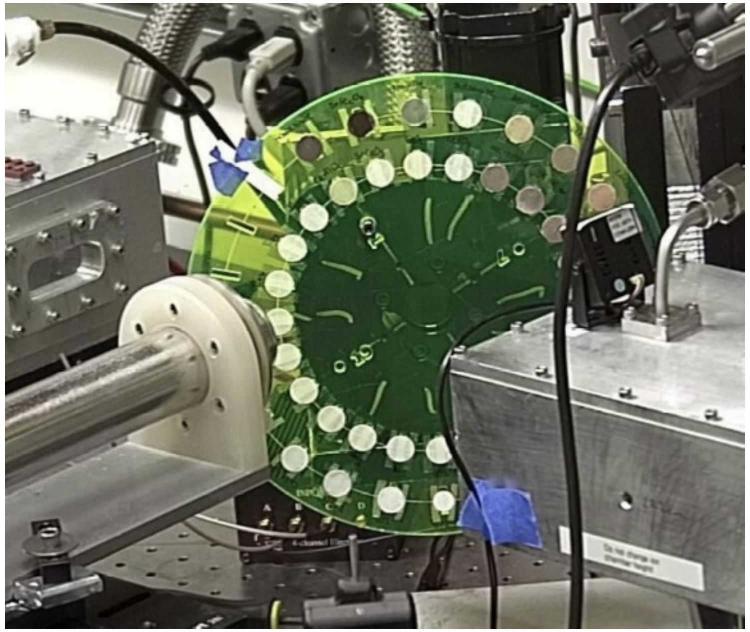






Capillaries can be sealed with epoxy, quartz wool or wax

Other powder sample prep methods



- Fill the wells in the sample holder with powder

- Sample on adhesive tape

My personal opinion: It shall not be done

If you have absolutely no choice, the powder shall be ground and spread as thin as possible, and the tape folded

- Always take the spectrum of the tape – you might be surprised
- Mind the absorption of the tape - may be critical at lower side of the spectra

When to measure in fluorescence

1. Sample has low loading yielding edge jump of 0.1 or less
2. Sample is supported on opaque substrate (thin film on Si wafer)
3. It is undesirable or impossible to manipulate the sample (art object, meteorite etc.).
4. Low energy edges cannot be measured in transmission

A good fluorescence sample:

- Homogenous – while effects of leakage and non-uniformity are not as severe as in transmission, it is still desirable.

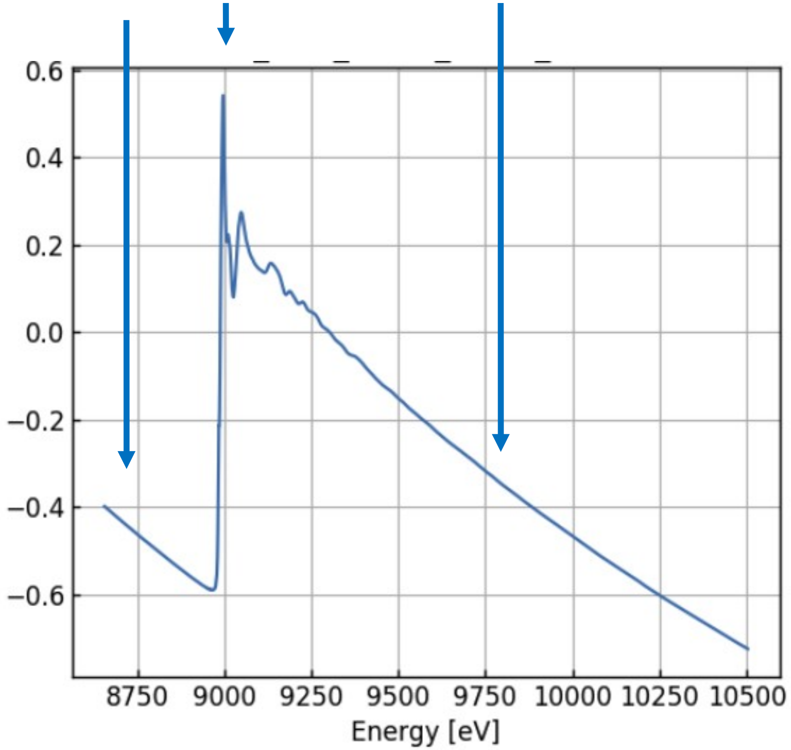
Self-absorption in fluorescence measurement

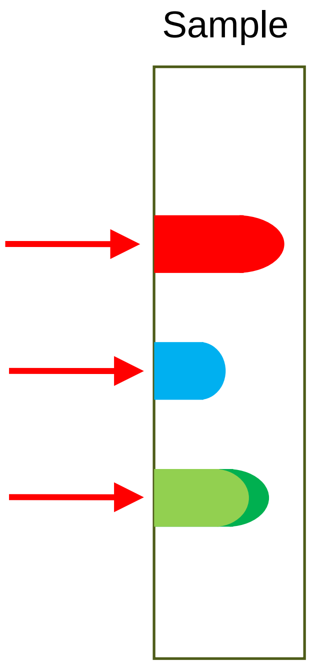
Spectral distortion (reduced white line and EXAFS wiggles) is the result of changing penetration depth of X-ray beam when scanning through the edge

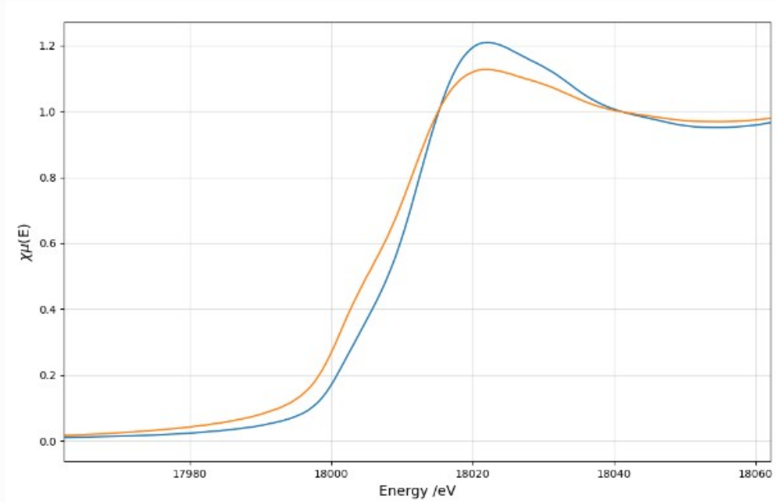
No absorption

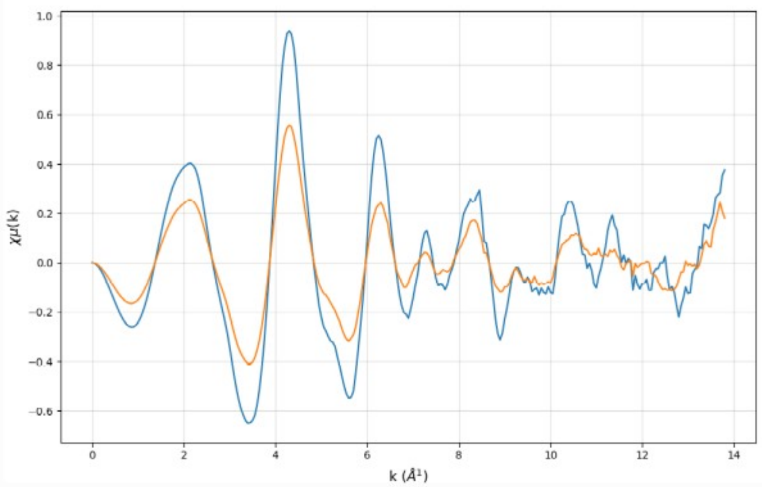
Strong absorption

Varying absorption





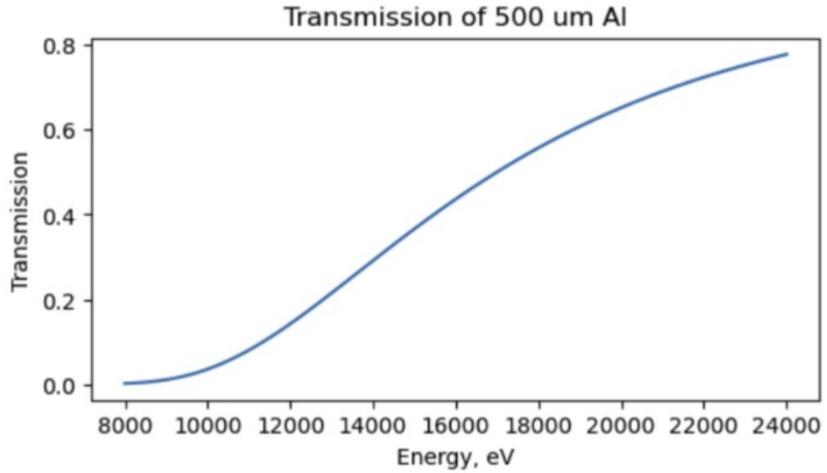




Fluorescence measurements best practices

This is particularly important for dilute sample

- Avoid sample holders/sample environments made of same or neighbor elements (and mind overlap between 3d K edges and 4f and 5d L edges)
- Check windows/tapes/capillary sealing materials for the element of interests (very low levels of Mn, Zn in Mylar, Fe in Kapton have been found)
- Avoid fluorescence from in-line calibration foil getting fluorescence detector. Use apertures upstream of the reference foil.
- When compounds containing lighter elements are used to support heavier elements (e.g., Pd/CuO), non resonance fluorescence from the support obscures the signal from the element of interest (energy discriminating detector is not always a solution). Use Al foil for reducing lower energy signal.



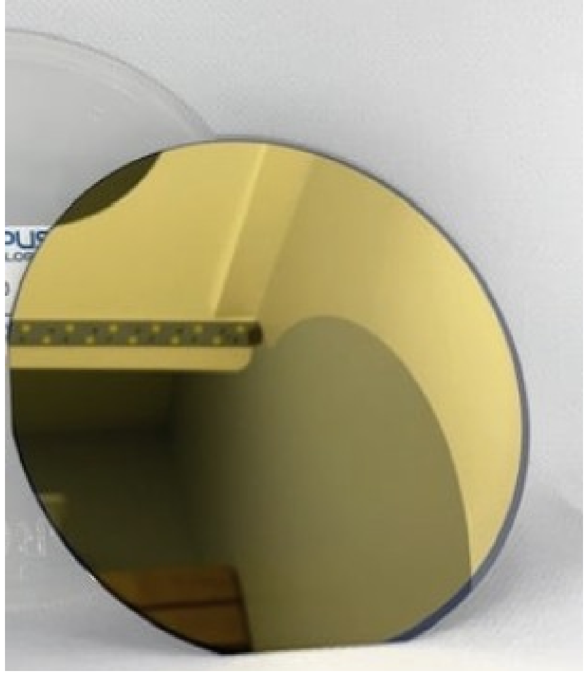
In the past lead tape was used extensively for *ad hoc* shielding. It’s banned now due to health and safety reasons. Tin foil ca be used instead – not as blocking but as pliable.

Thin films

Thin films are supported on a substrate

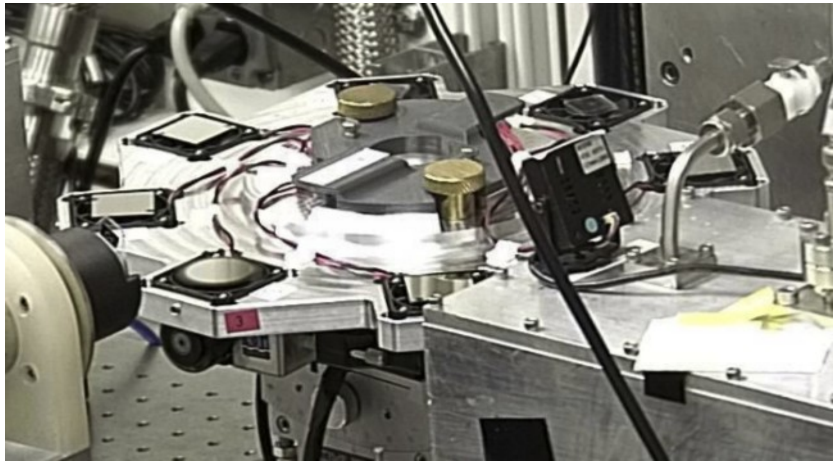
Measured in fluorescence mode

Films are positioned at grazing or near-grazing incidence angle to the beam to spread the beam over a larger surface and increase surface sensitivity



Substrate and films are often crystalline, leading to Bragg peaks hitting the detector.

We often spin the samples to “smear” Bragg peaks



Liquid samples

Naturally homogenous (unless they are suspensions)

Appropriate containment

1. Capillaries sample
2. Sample holders with wells or holes sealed with adhesive tape

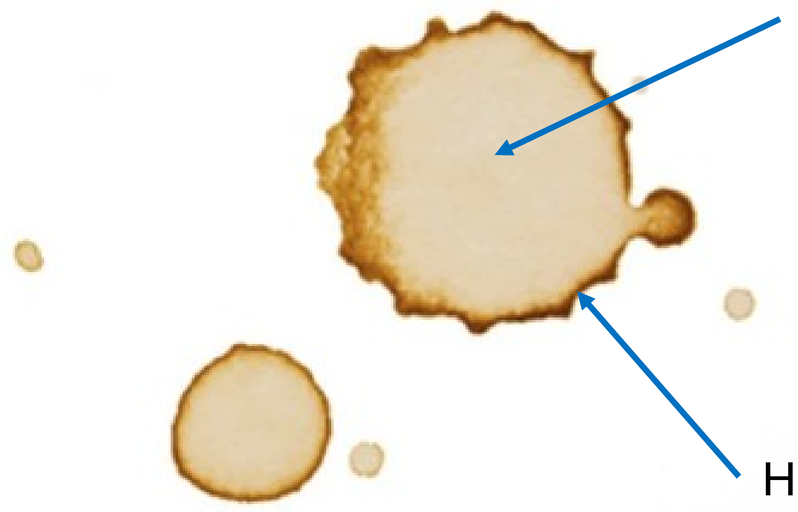
Beware of beam damage (more on it later)

Drop casting

A method to deposit catalyst slurry onto a porous flat substrate, e.g., carbon paper.

Common in electrocatalysis/fuel cells

Usually produces highly inhomogeneous samples due to ”coffee stain” effect



Lower concentration = weak spectra

High concentration gradient
= noisy spectra

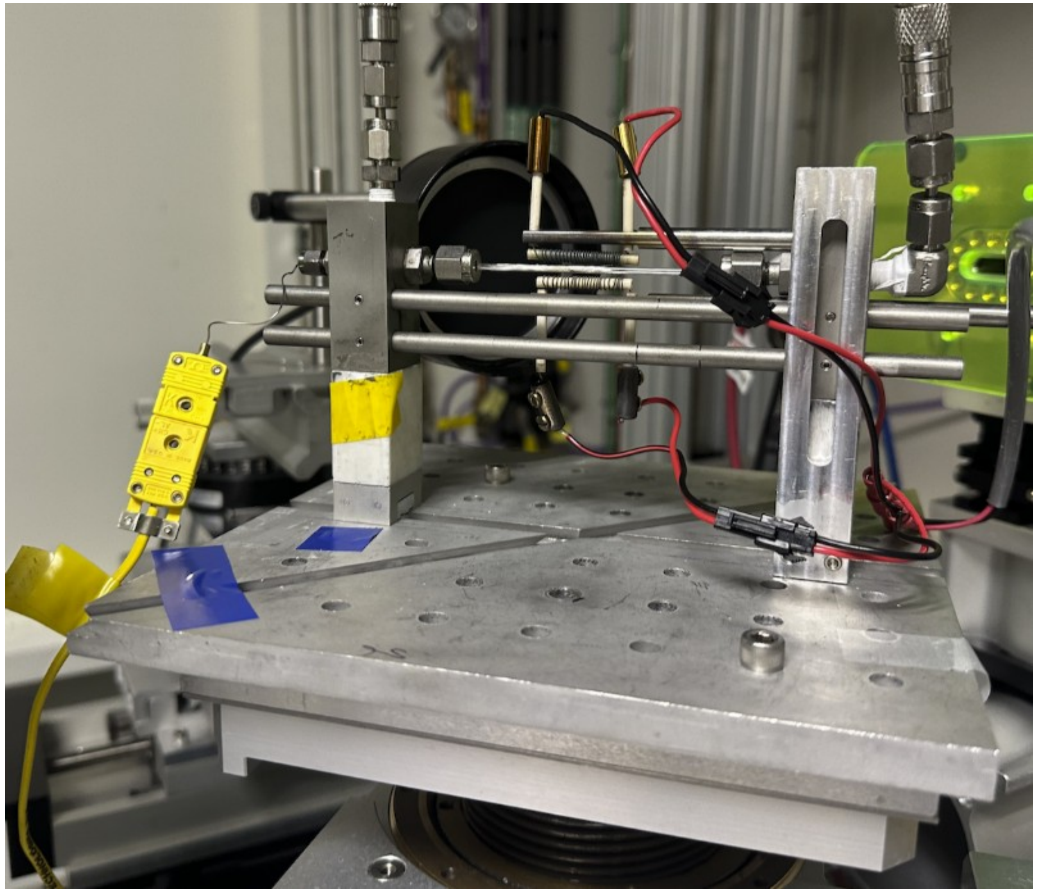
Sample environments

What we want to expose the sample to:

1. Temperature
2. Reactive gases /pressure
3. Reactive liquids
4. Pressure
5. Voltage/current
6. Magnetic field

We also want to keep the sample intact (limit exposure to X-rays/minimize X-ray beam damage

Klausen (capillary) flow cell



Advantages:

- Compatible with different capillaries
- True plug flow catalytic reactor
- Fast cooldown

Disadvantages

- Hard to do operando - low catalysis amount, and low gas flow rates are needed to observe conversion
- Temperature profile is poorly defined

Another capillary flow cell

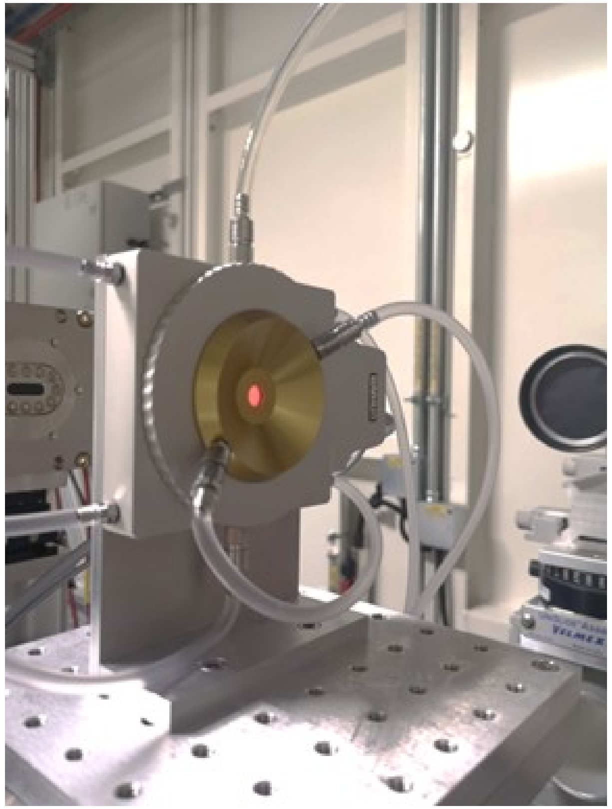
Advantages:

- Compatible with different capillaries
- True plug flow catalytic reactor
- Better temperature stability
- ~~Fast cooldown~~

Disadvantages

- Hard to do operando - low catalysis amount, and low gas flow rates are needed to observe conversion
- ~~Temperature profile is poorly defined~~

Other temperature cells (commercia

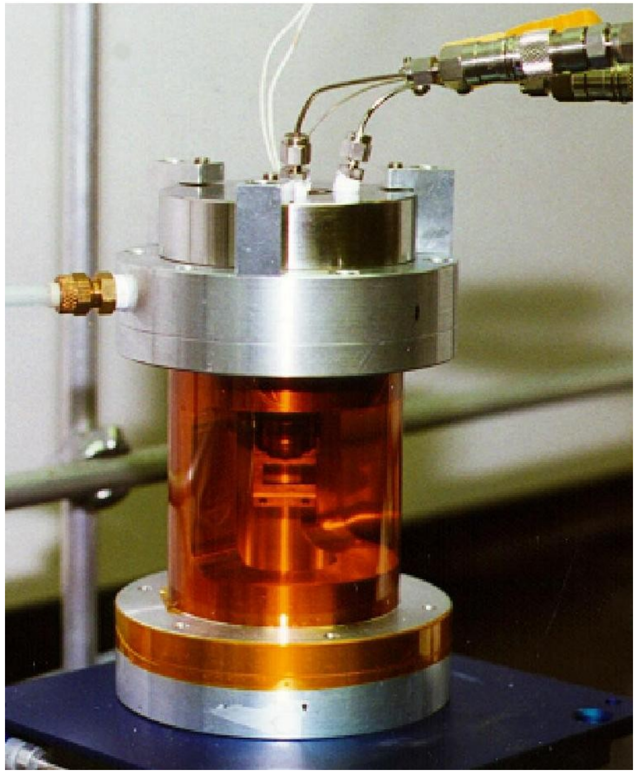


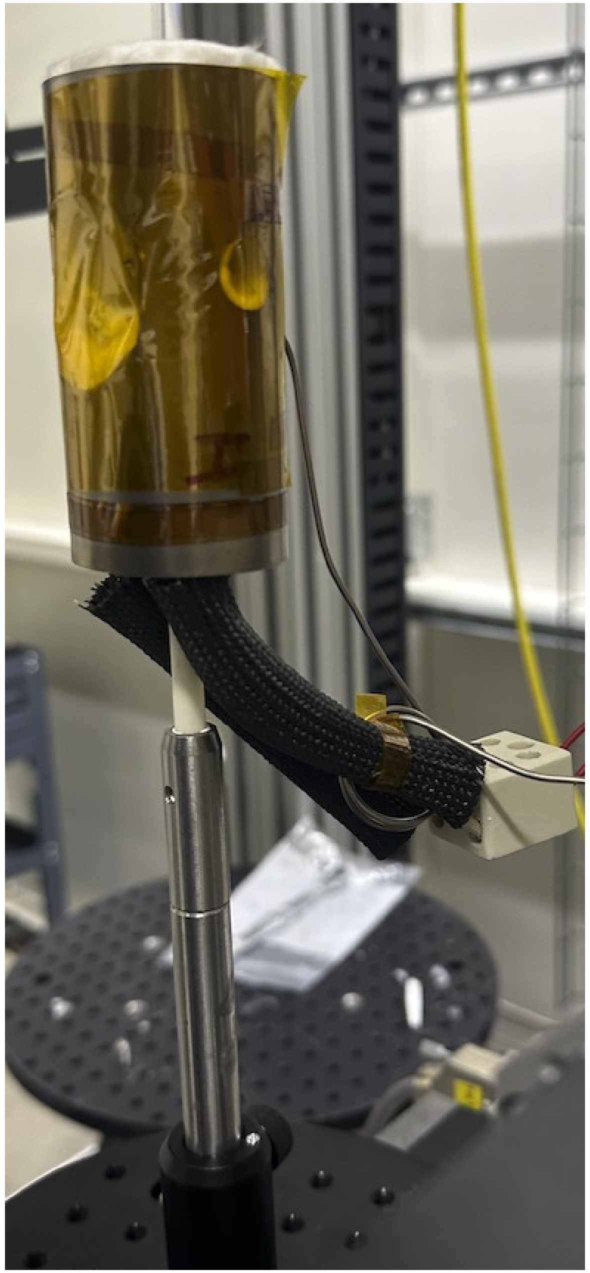
Commercial designs originally for optical microscopy

- Temperatures up to 1500 C
- Some design allow cooling
- While OK for gas treatment, not suitable for catalysis due to large dead volume.
- Some design allow cooling to -195 C

Other temperature cell

Users are allowed to design their own cells, as long as they are safe and have windows/openings for the all/preferred detection methods.

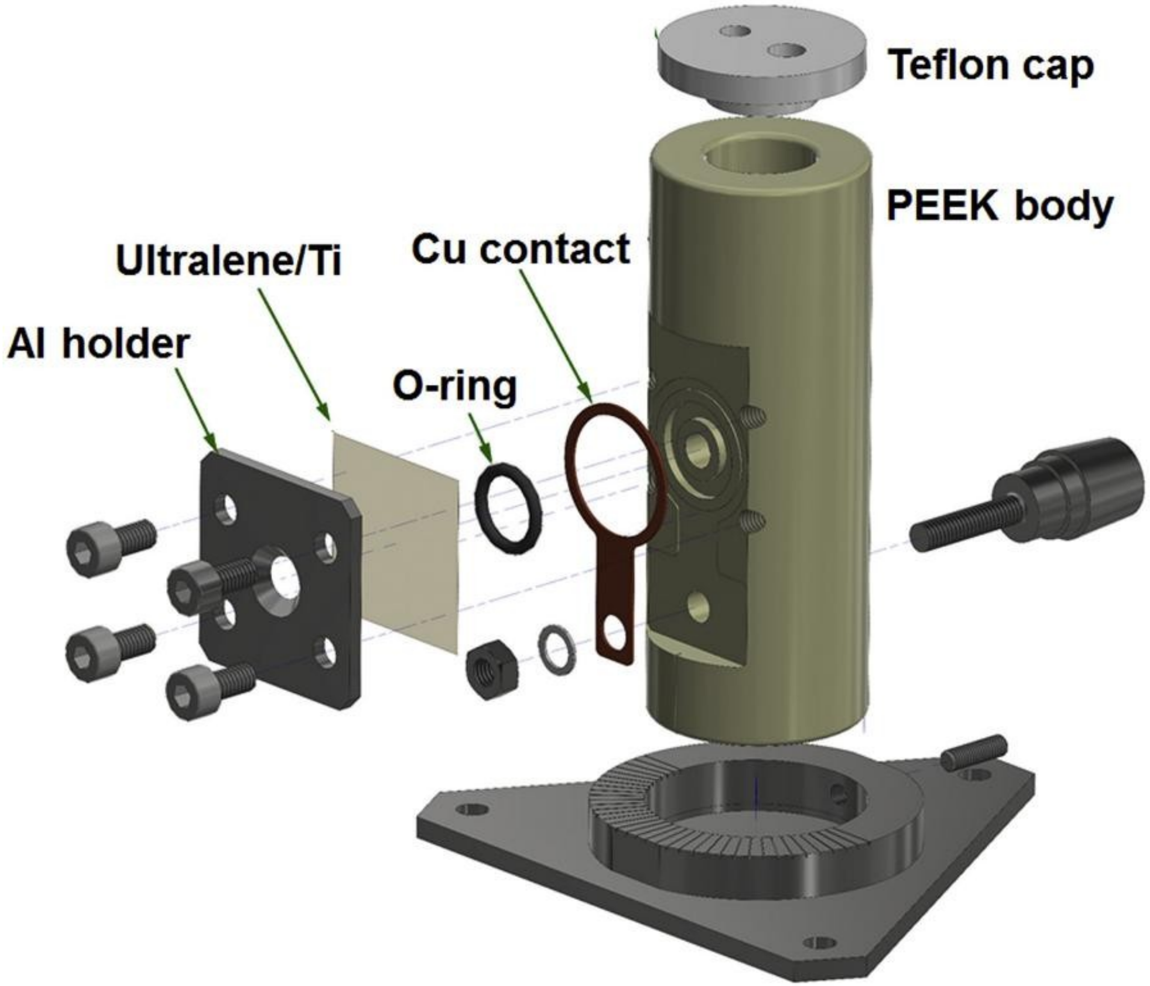




Electrochemical cells

Typically user designed:

- Accommodate variable number of electrodes
- Location of electrode being investigated is important (due to electrolyte absorption)
- Bubble formation is sometimes inevitable
- These cells leak!!



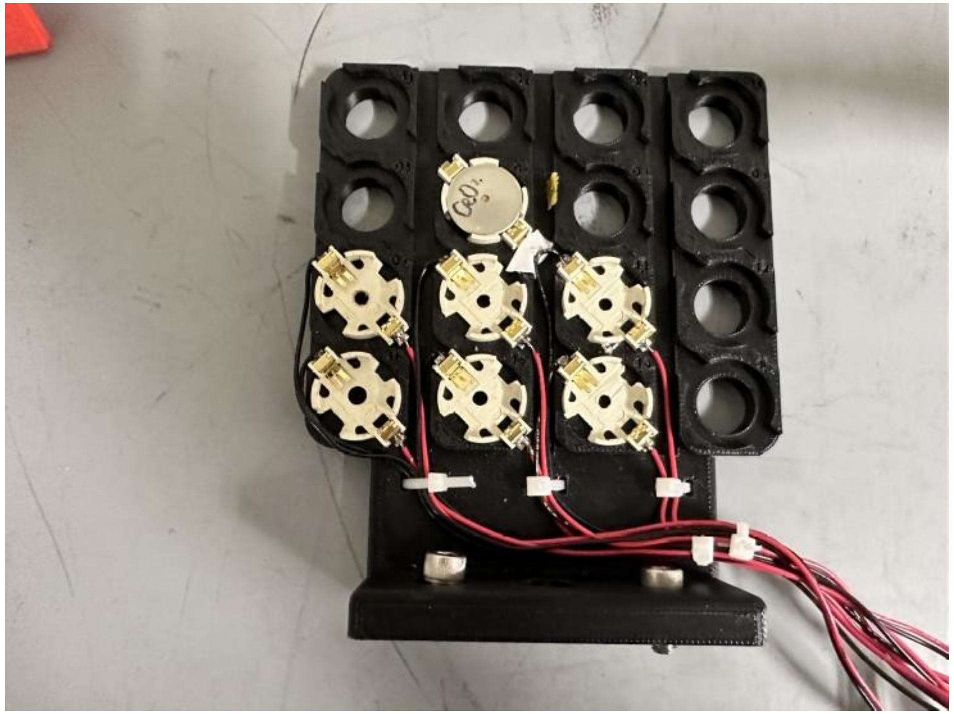
Electrochem. Comm., 94, 2018, 14-17

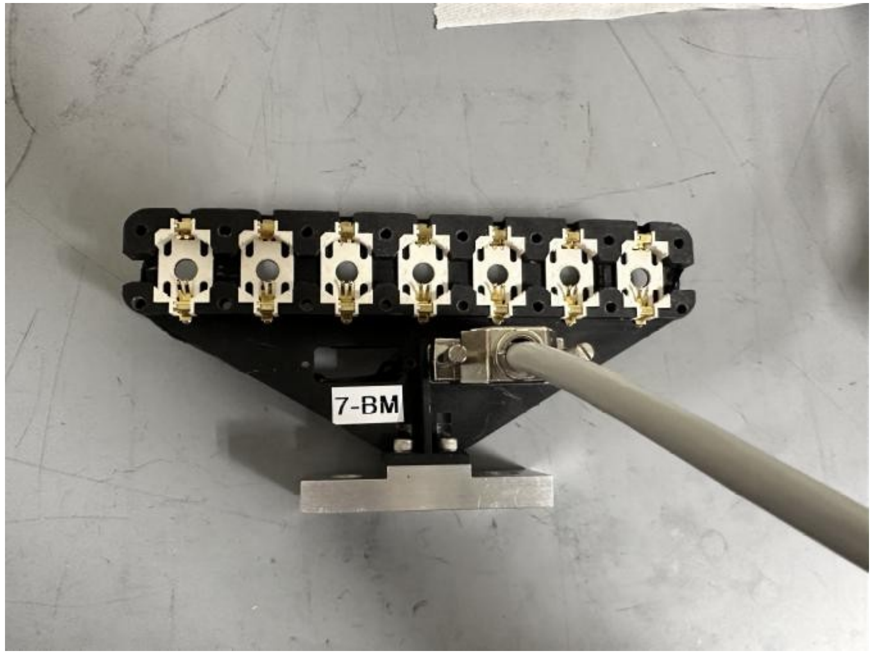
Battery holders

While not sample environments by themselves, they make battery cells handling much easier.

Allow for high throughput measurements

Side note: adding X-ray transparent windows to a coin cell may change field distribution and chemistry

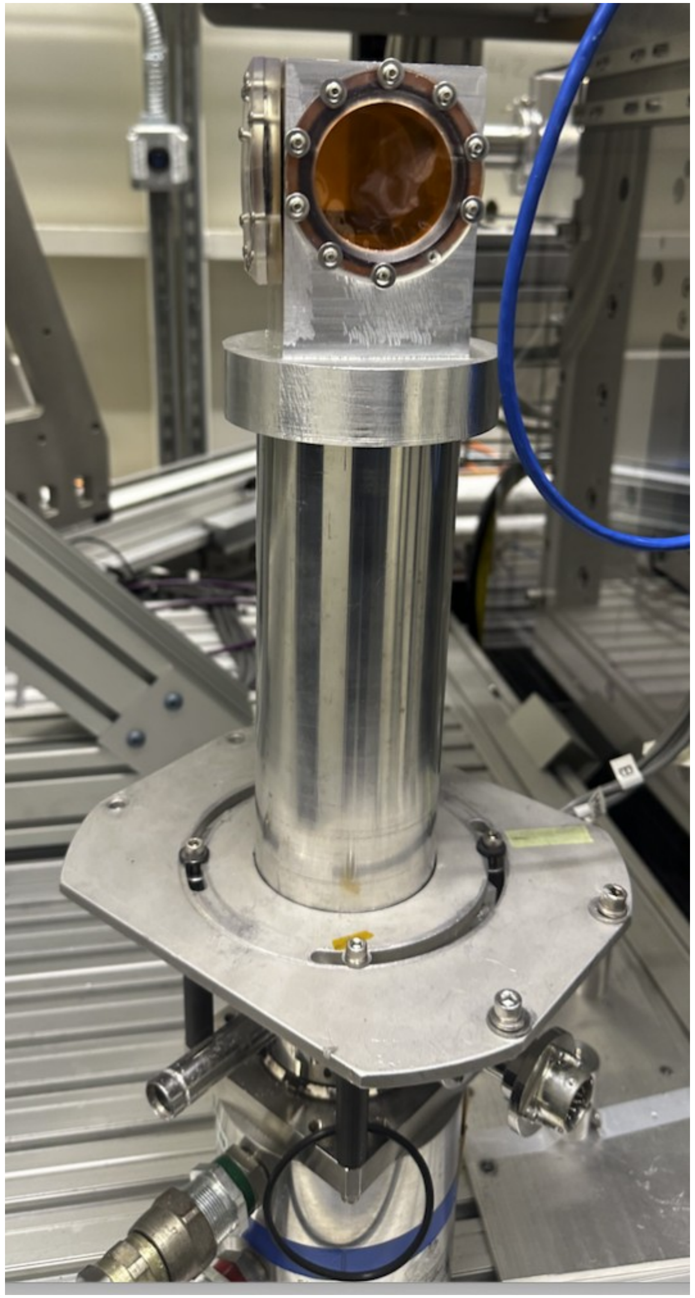




Cryostats

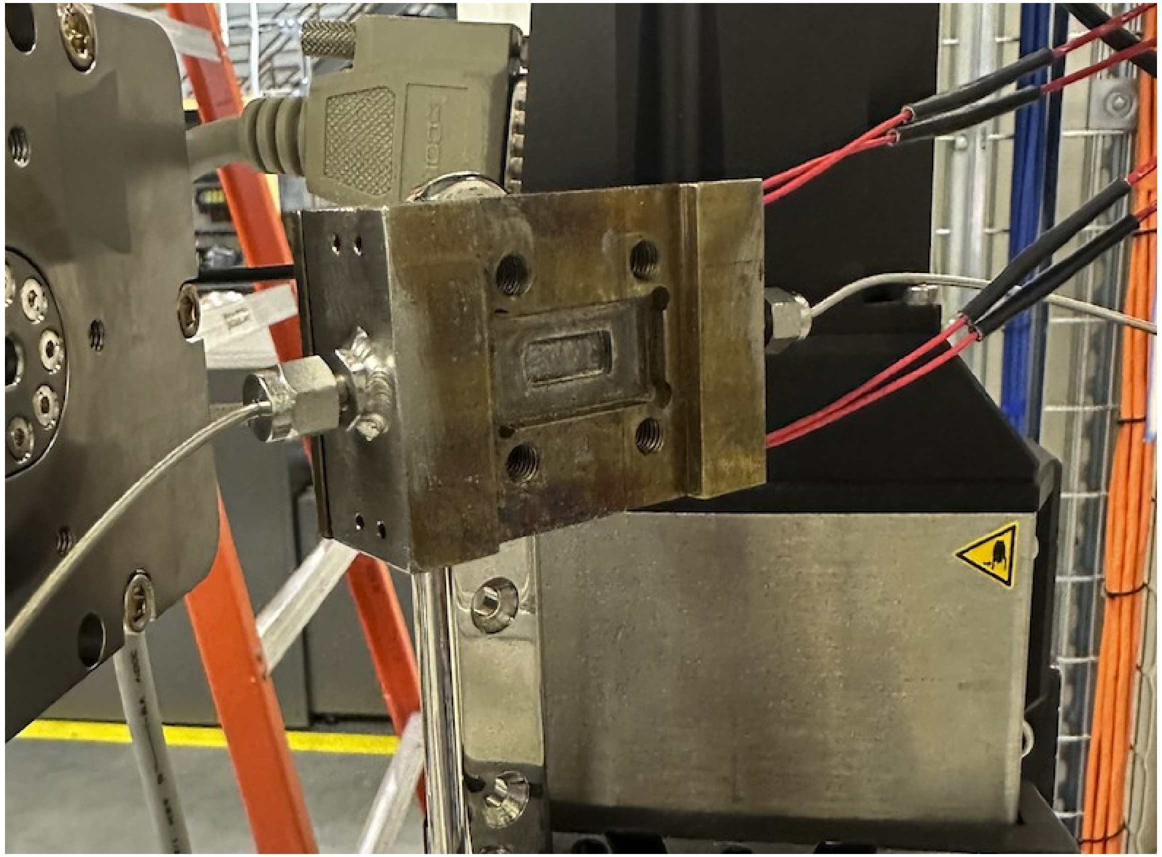
Allow for low temperature measurements down to a few K

- Thermal motion decreases, and EXAFS can be recorded up to higher k.
- Improves sample radiation sensitivity
- Cooling is slow (can be >1h)
- Sample handling is difficult, especially if samples need to be mounted frozen



High pressure gas and liquid cells

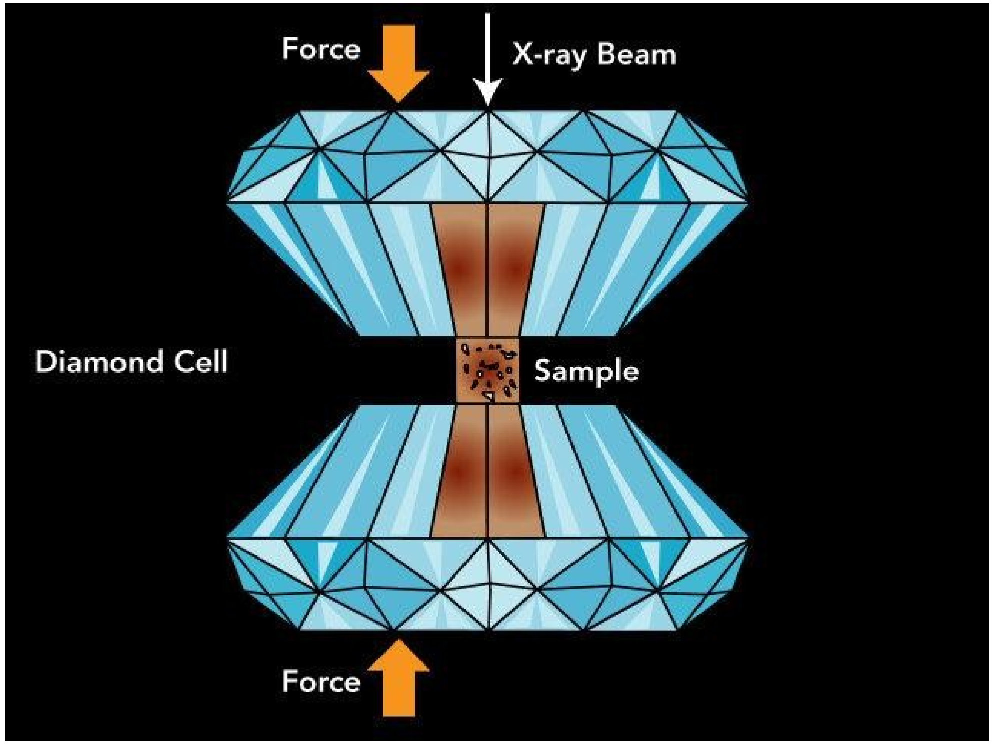
When catalytic (or other) experiment requires reactant pressures above ambient, custom cell are required.



Really high pressure cell

Diamond anvil cells allow to create pressures up to 700 Gpa (usually below 200 Gpa)

- Recreate the pressure existing deep inside planets and to synthesize materials and phases not observed under normal ambient conditions.
- Diffraction from diamonds can (and does) lead to very intense spikes in the spectra

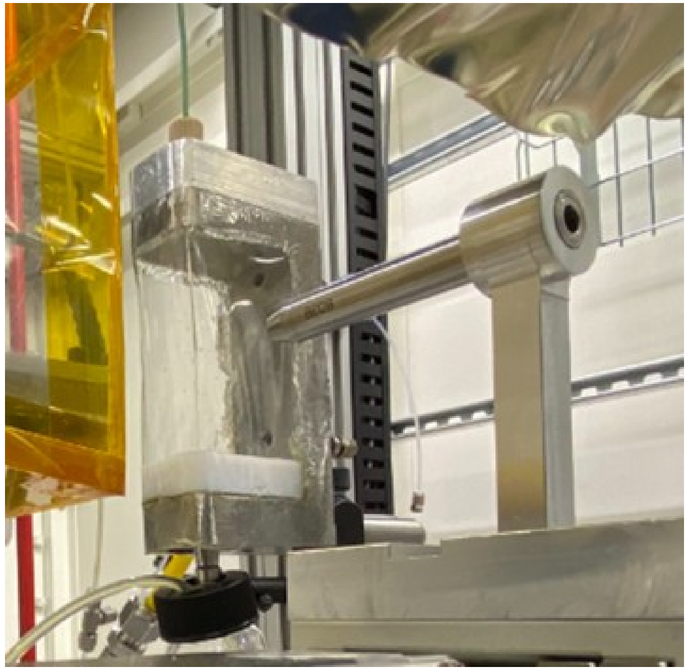


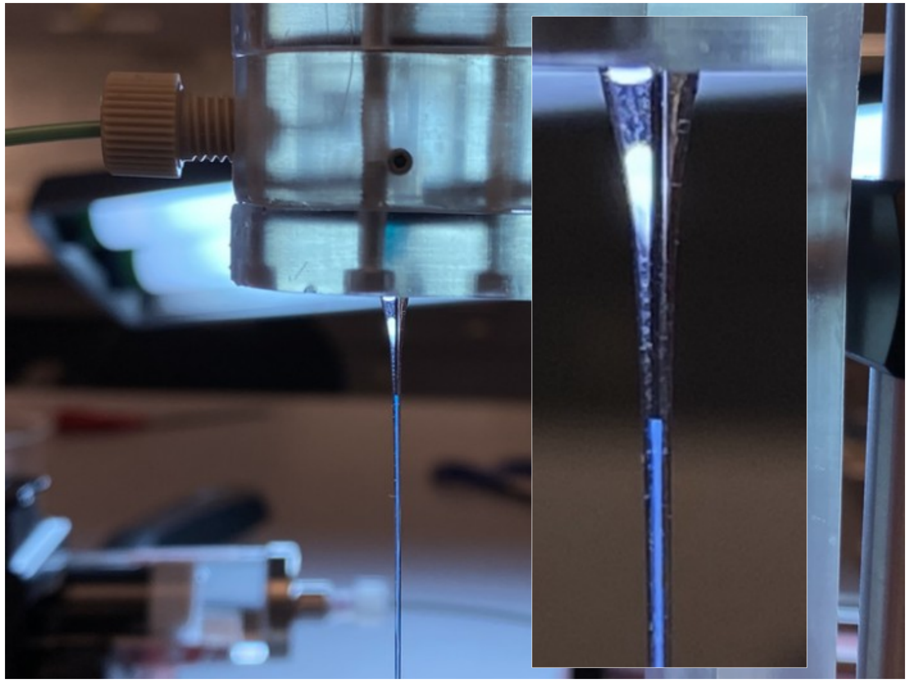
Liquid jet

To prevent sample damage in liquids, the sample needs to be constantly exchanged.

The liquid is pumped with syringe or/peristaltic pump through a nozzle

One can protect air sensitive liquids by enclosing it within another fluid in a "coaxial" jet





Conclusions

1. Sample preparation should be considered in the early stages of experiment planning
2. Discuss detection method(s) with beamline staff and tailor the samples and sample environment(s) to them.
3. Discuss how to mount the sample environment if you bring your own.

Best approach

Speak with beamline staff!