Brookhaven National Laboratory

U.S. DEPARTMENT OF ENERGY

# Sample Preparation and Environments

## Getting the most out of your science

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ISS Beamline

XAS 2026: fundamentals of XAS Data Analysis, 10 March 2026

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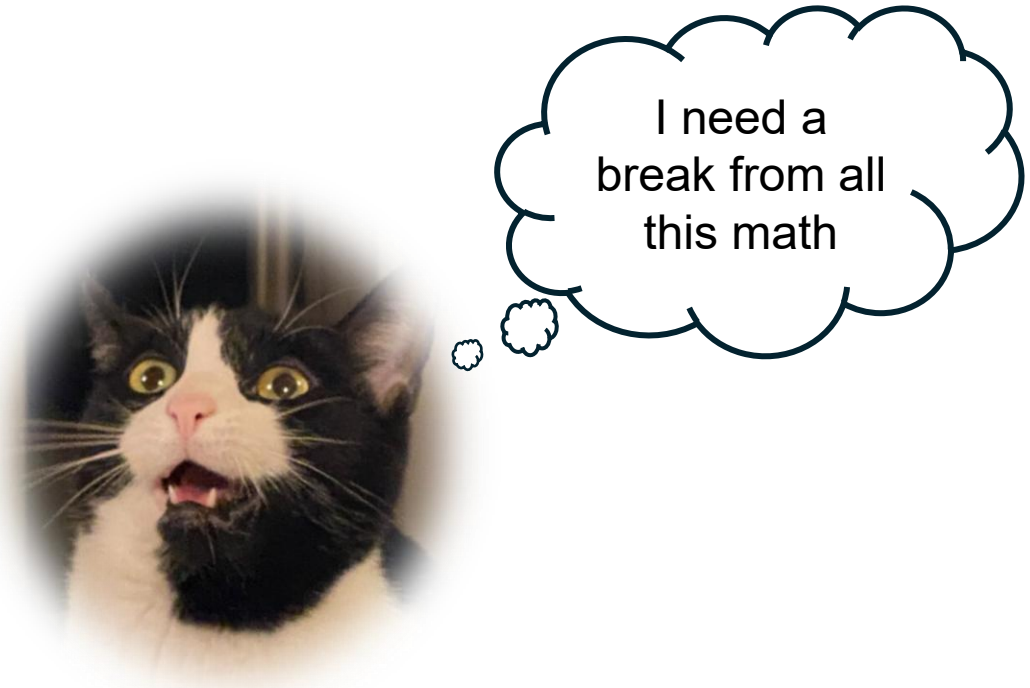
# Before We Begin…

## XAS has both quantitative AND qualitative aspects!

**We will discuss very little math in this presentation**
For a more quantitative discussion of the underlying phenomena,
see e.g. https://gbxafs.iit.edu/training/XAFS_sample_prep.pdf



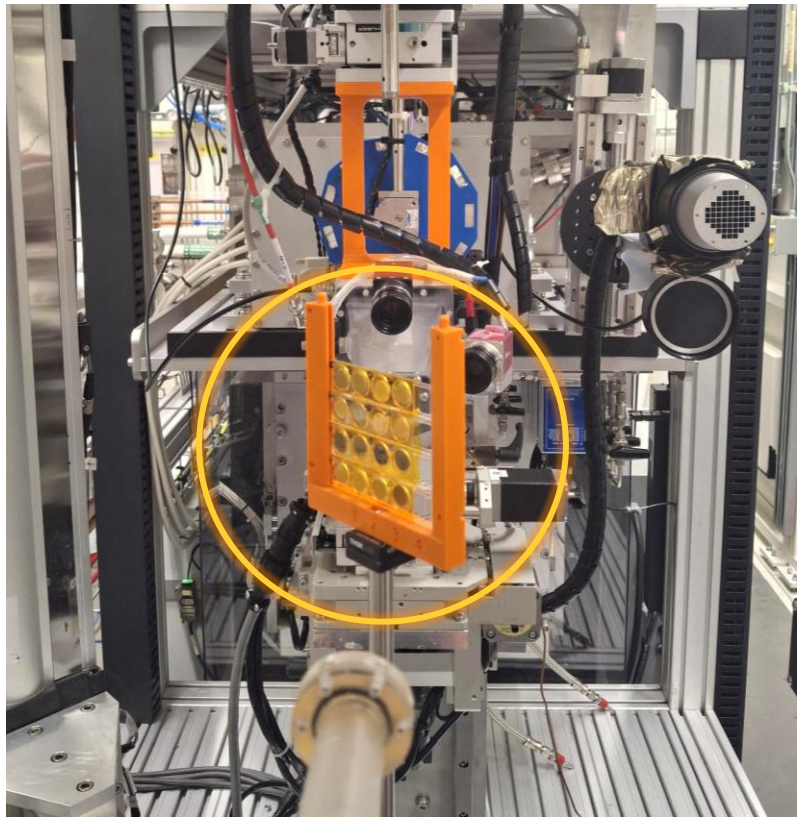
# Why are we talking about sample preparation?

1. **Sample quality deficiencies account for <u>over half</u> of lost time during synchrotron beamtime**

2. **If you do not recognize the impact of sample quality, you may collect and even publish misleading results!**

**Refer back to these slides when you're making your samples, so you don't look like this during beamtime**

# What will we talk about today?



How we measure your samples

How to prepare your samples

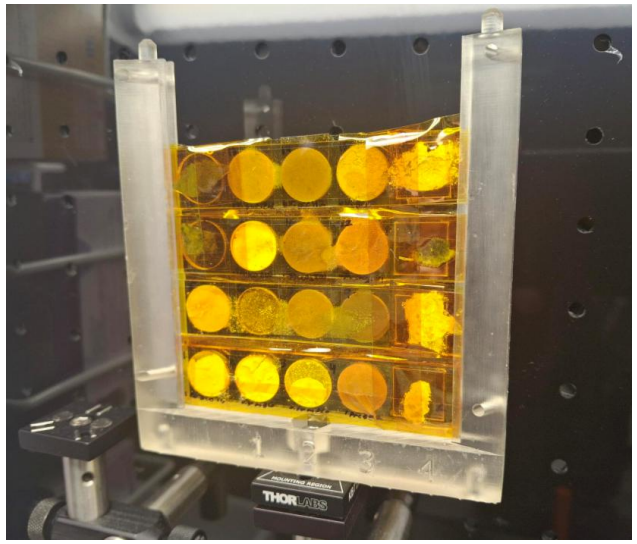
What we **can** do at the beamline

How to avoid <u>common mistakes</u> at the beamline

**Unsure of something before your experiment? Talk to us!**

# What is a sample?

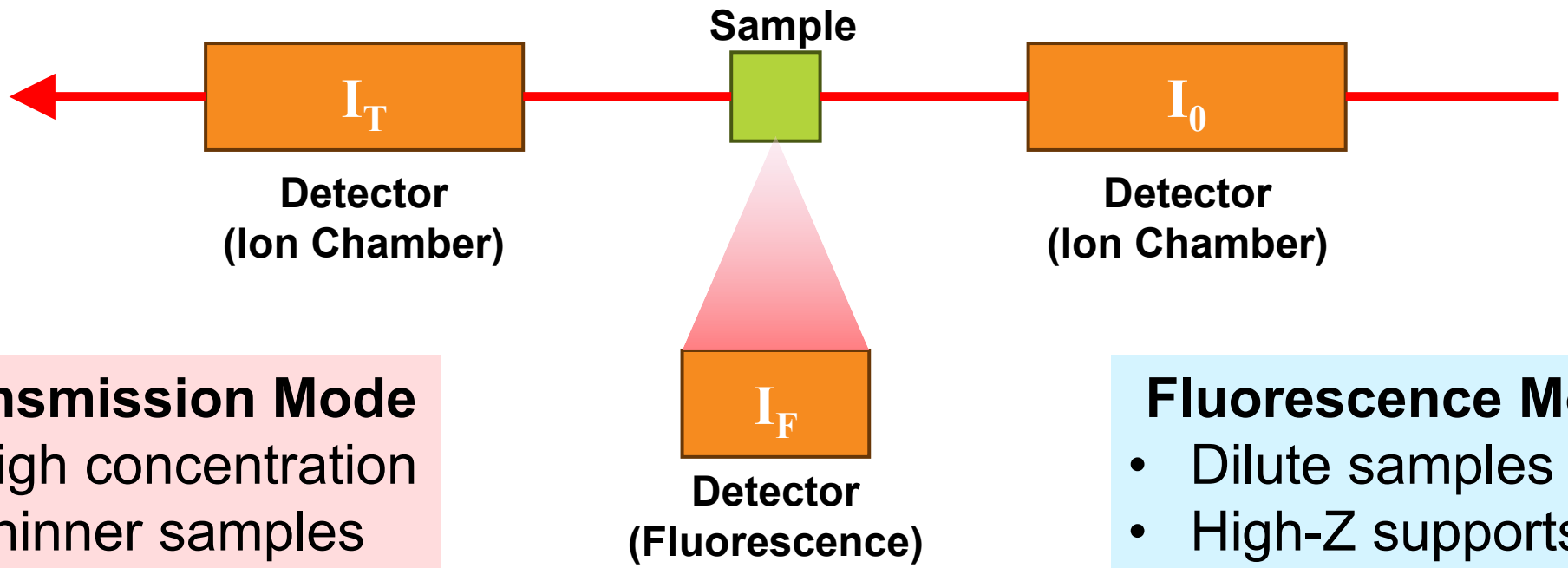
your **material** ≠ your **sample**



**Making a good sample from your specimen:**

- The right concentration for the detection method
- Doesn't introduce spectra distortion
- **Can be handled**

# Detection Methods




**Transmission Mode**

- High concentration
- Thinner samples
- Hard X-rays

$$\mu = -\log(I_T/I_0)$$

**Fluorescence Mode**

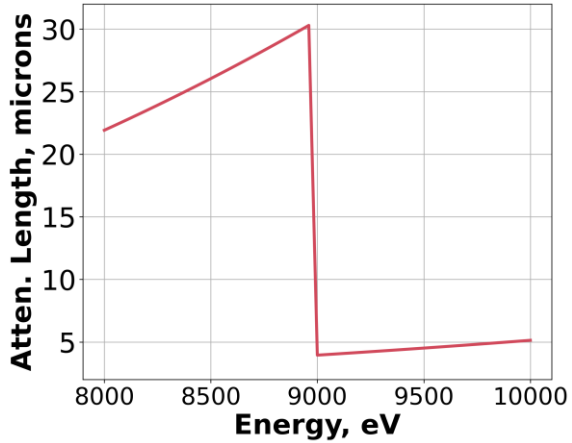
- Dilute samples
- High-Z supports
- Soft/Hard X-rays

$$\mu \sim (I_F/I_0)$$

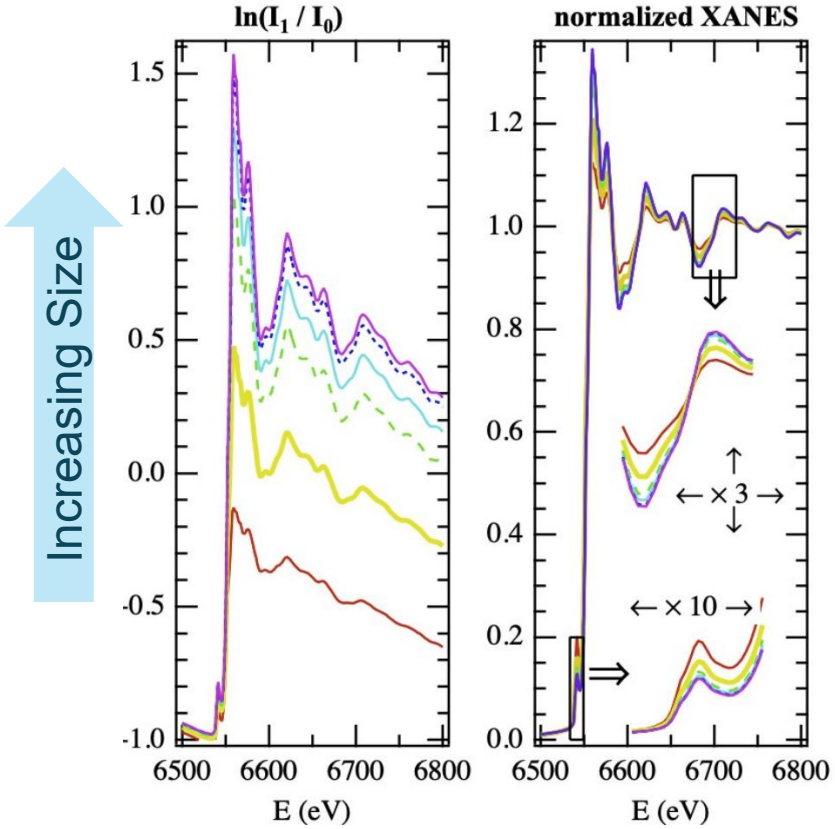
# Uniformity is Key

The most important factors to sample preparation:

- Samples should be as **homogeneous** as possible!
  - Similar makeup, similar **size**, similar density
- Smaller particle size is better (where possible)
  - Too small during gas-flow experiments may create blockage
- **Attenuation Length**
  - Depth of material where X-ray flux falls to 1/e of its value at the surface (~37%)
- Be consistent!




Simulated spectra for particles 0.3 μm to 30 μm



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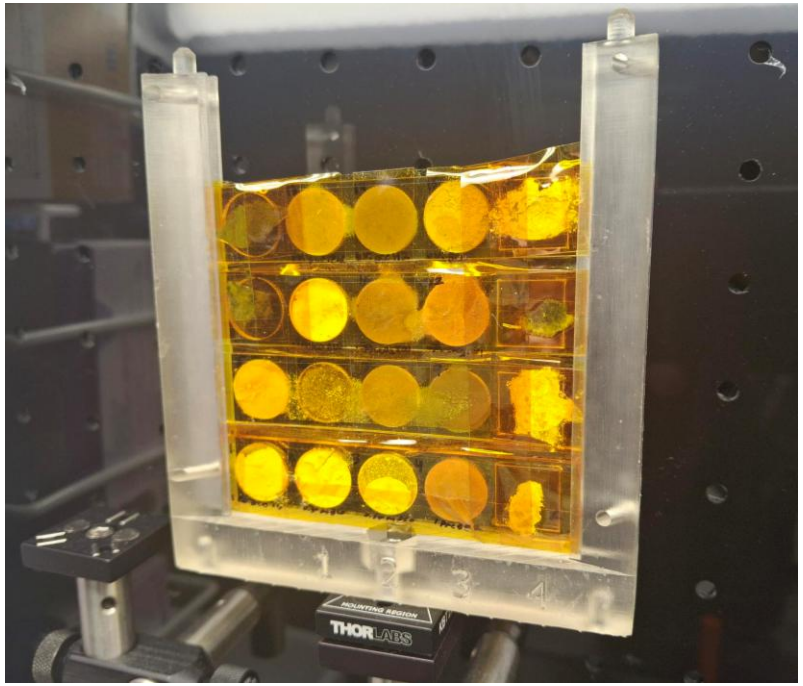
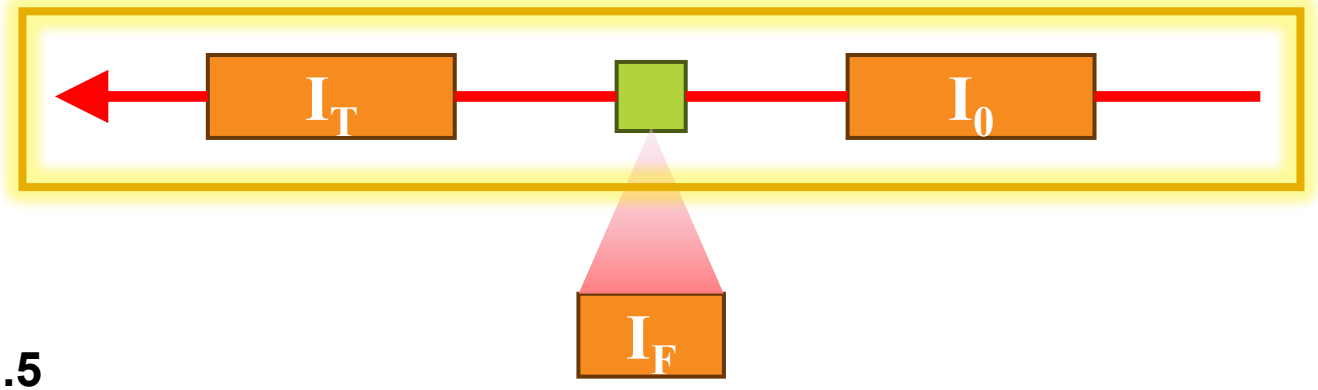
# What makes a good sample?

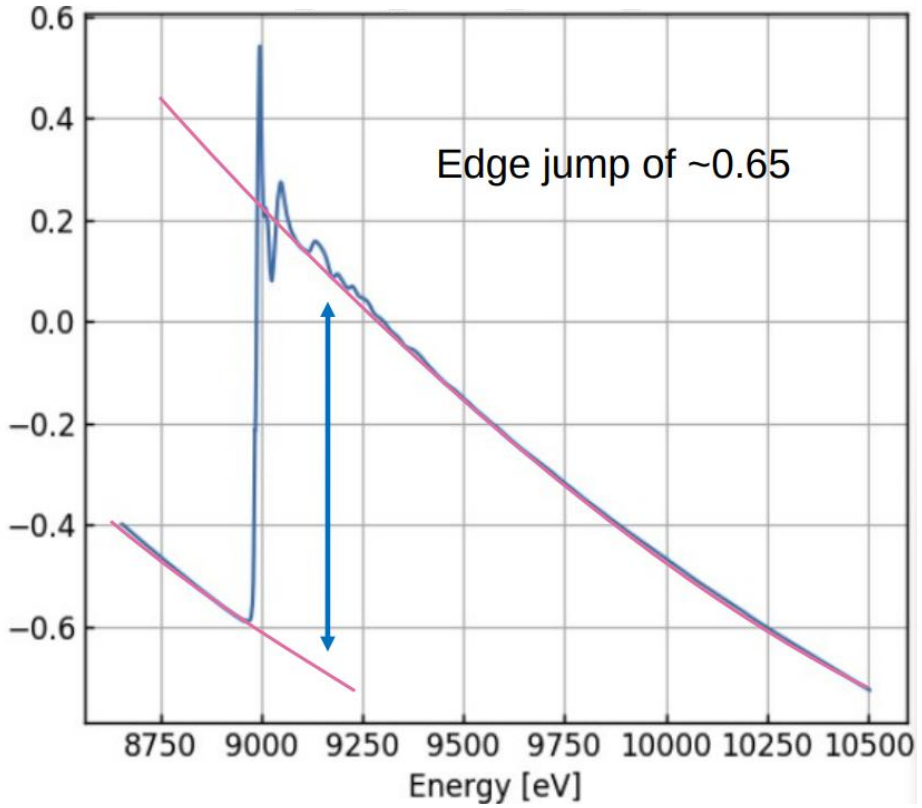


# Transmission Sample Prep

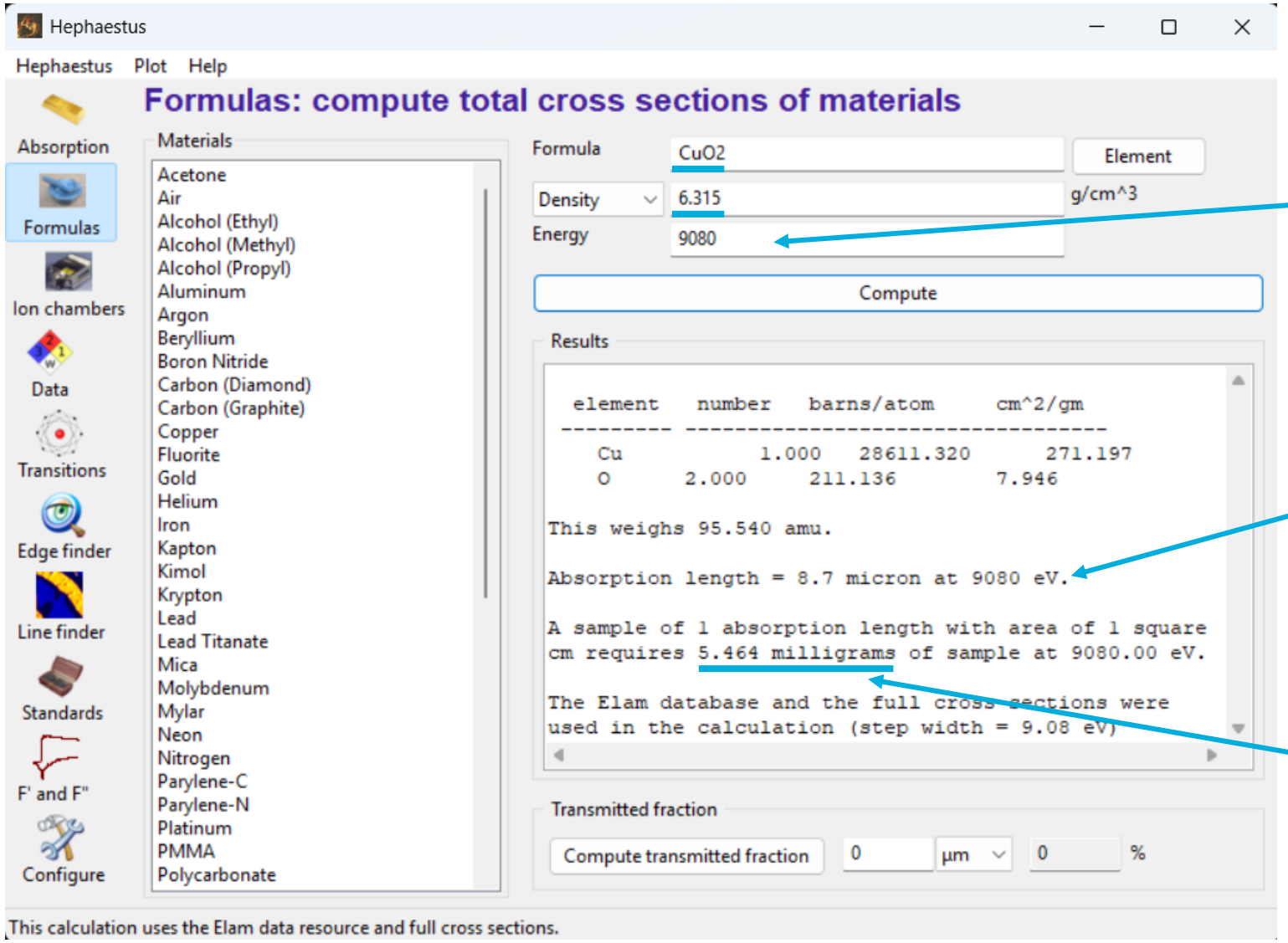



- Ideal edge jump for transmission mode is **1.0 – 1.5**
- Lower edge jump (0.1 – 1.0) is still viable if the sample quality is good
  - May take more scans for higher quality, high-k
- Higher edge jumps (1.5 – 2.0) indicate too concentrated or too thick
  - High concentration can dampen signal, especially >2.0
- **If edge jump is below 0.1, use fluorescence mode**

**So how do we know how much to add?**



# Using Hephaestus for Sample Prep




Energy
(~100 eV above edge)

Absorption length

Material (in g/cm$^2$)
for an edge jump of 1

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# Pelletizing Samples

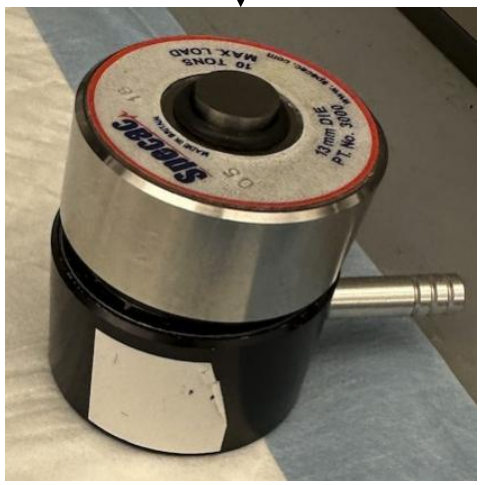
1. Add appropriate ratio of binder + material (“inerts” like boron nitride, silica, etc.)
2. Grind mixture in mortar
3. Add ground mixture to pellet die
4. Press the pellet, then seal pellet if necessary

Similar process to pressing IR pellets, tutorials are available online for optimizing your pressure settings

Unbound nanomaterials may fuse at high pressures!


Pellet Press

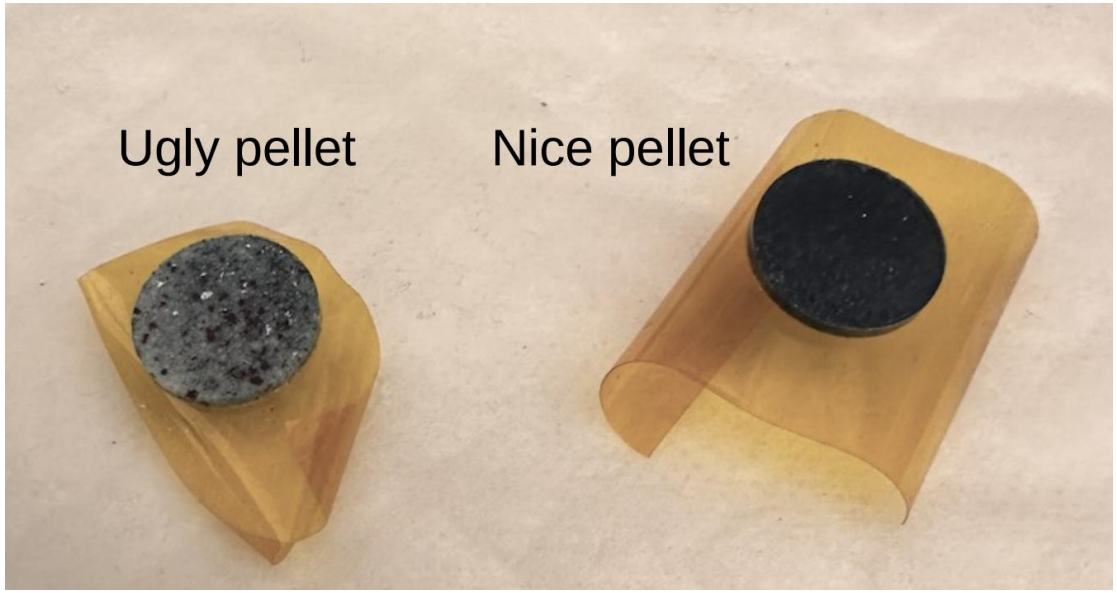
Pellet Die




# Pelletizing Samples

*Some helpful tips for making good pellets*

- **Sample + Binder > 100 mg**
  - Easier to handle, less breakage
- **Samples must be well-ground**
  - Grind as long as you can…and then some
- **Sample + Binder mixture should be uniform**

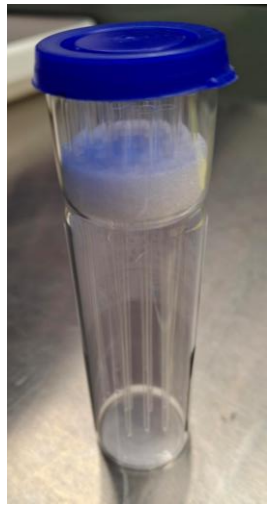


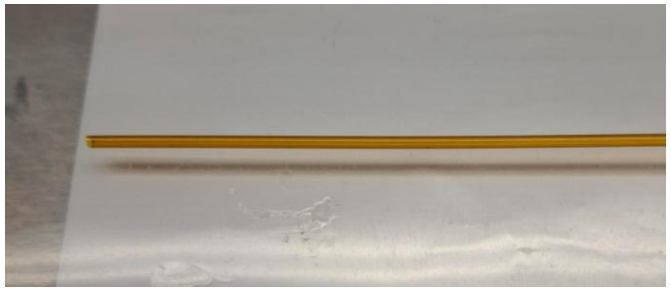

**Some common binders are NOT inert in certain situations**
i.e. zeolites are catalytic, boron nitride catalyzes methane oxidation, PEG polymerizes under pressure

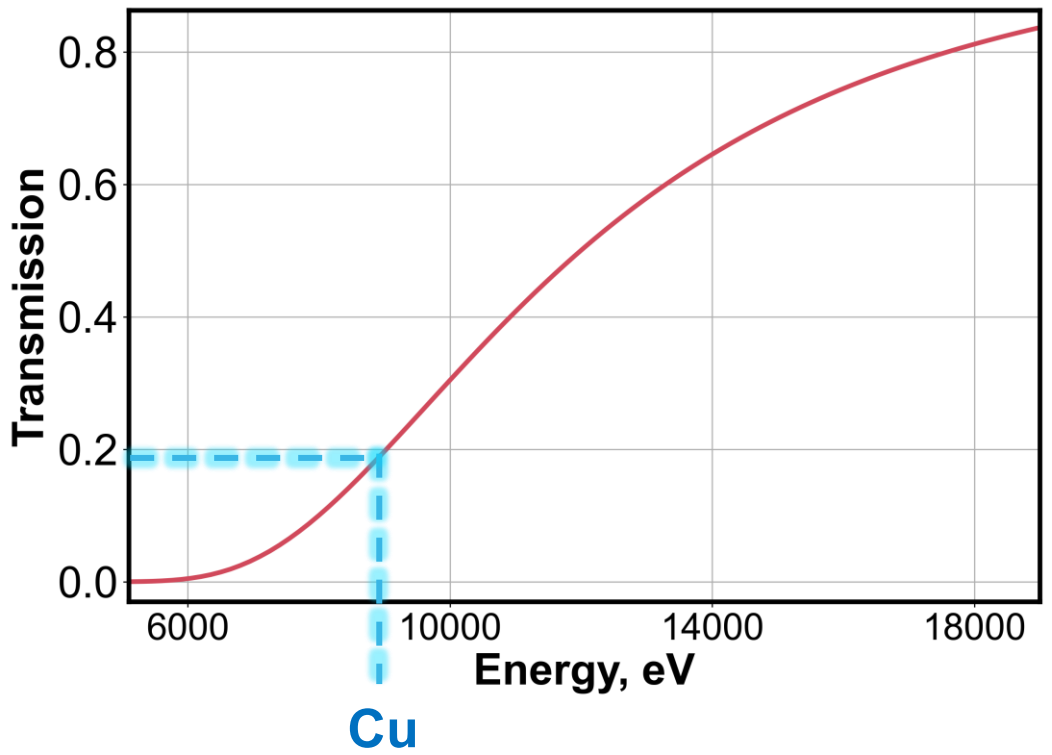
**Some binder/sample combos and ratios may not pelletize easily**
Plan for some trial-and-error getting your pellets to “stick”

# Capillary Samples

- **Kapton** – up to 300°C
  - Highest transmission
- **Glass** – up to 500°C
  - Borosilicate
- **Quartz** – up to 1300°C
  - Can become brittle








A quartz capillary (300 μm wall thickness) cuts **80%** of photons when measuring Cu

Some samples/conditions need thin, fragile capillaries
**Plan ahead with beamline staff!**

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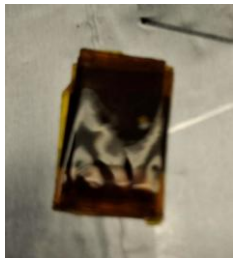
# Other Sample Prep Methods

**Samples on Adhesive Tape**
This seems to be a popular method but…

**Advantages**
- Fast? (I'm not so sure…)
- Somewhat ok for tight size distributions
  - i.e. colloidal nanoparticles

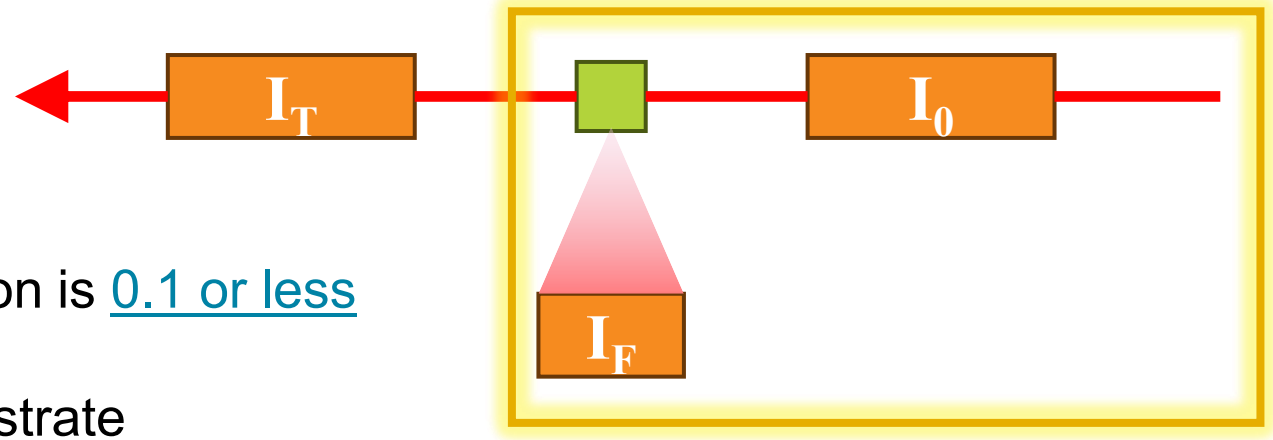
**Disadvantages**
- Heterogeneous, forms pinholes
- Adhesives can affect chemistry
- Sticky surfaces are easily contaminated!
- Tapes often have a background
- At low energy, tape can block signal
- Loose nanoparticles = special waste disposal
- Etc. etc.

**If you absolutely must:**
- Grind it as much as possible
- Spread thin, brush off excess
- Fold it up (and count!)
- Bring a blank tape sample to scan the background

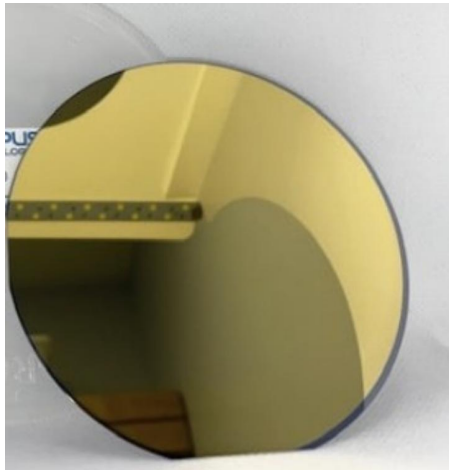


Sample folded eight times

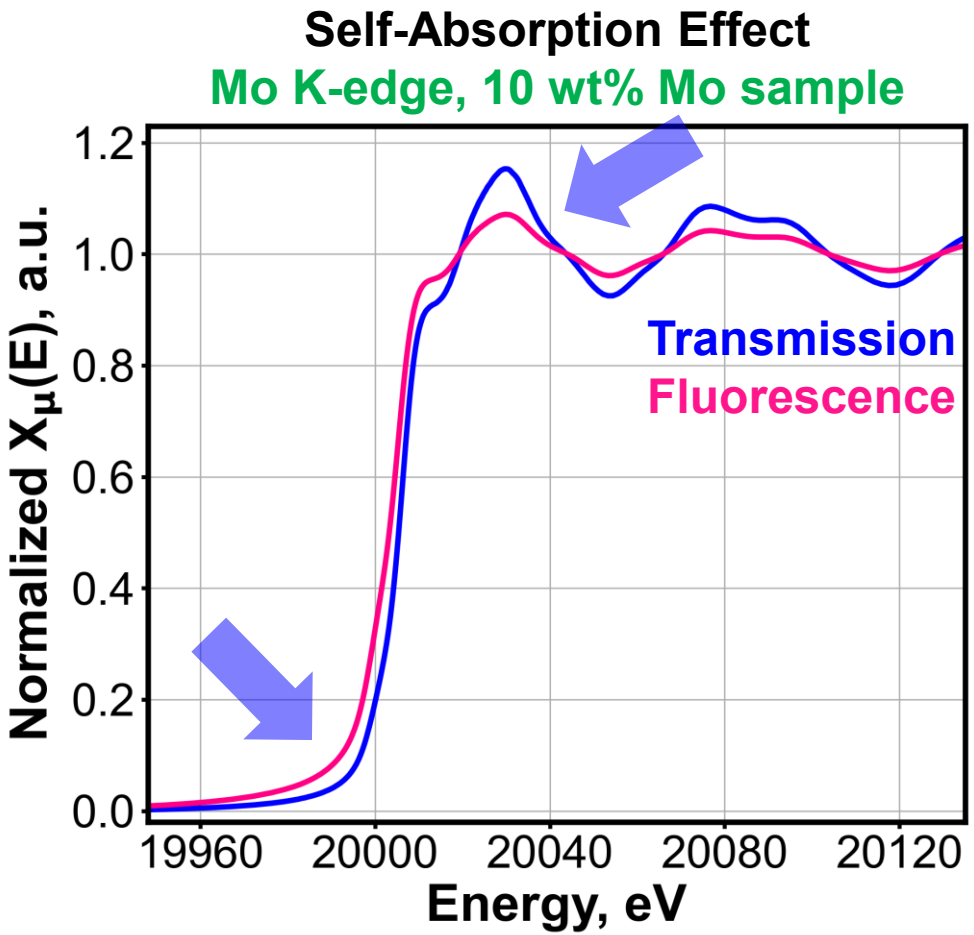
# When to use Fluorescence




- **Dilute samples** – edge jump in transmission is 0.1 or less
- Target element is on a thick or opaque substrate
  - Films on thick Si, catalysts on ceria, etc.
  - Cerium K-edge is 40 KeV!
- Thick samples (especially at low energy)
  - Samples that can't be altered – meteorites, art objects, etc.

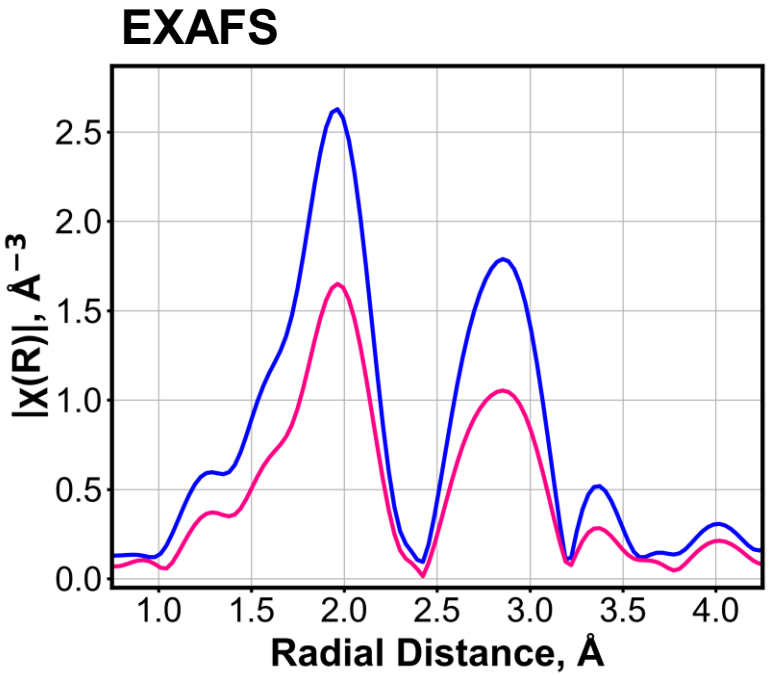


# Fluorescence Sample Prep




Distortion of XANES, loss of amplitude at high concentration measuring fluorescence

- Self-absorption changes with energy as you scan, so it can't easily be "corrected" for a single scan
- Makes EXAFS fitting difficult due to shifting, inconsistent amplitudes

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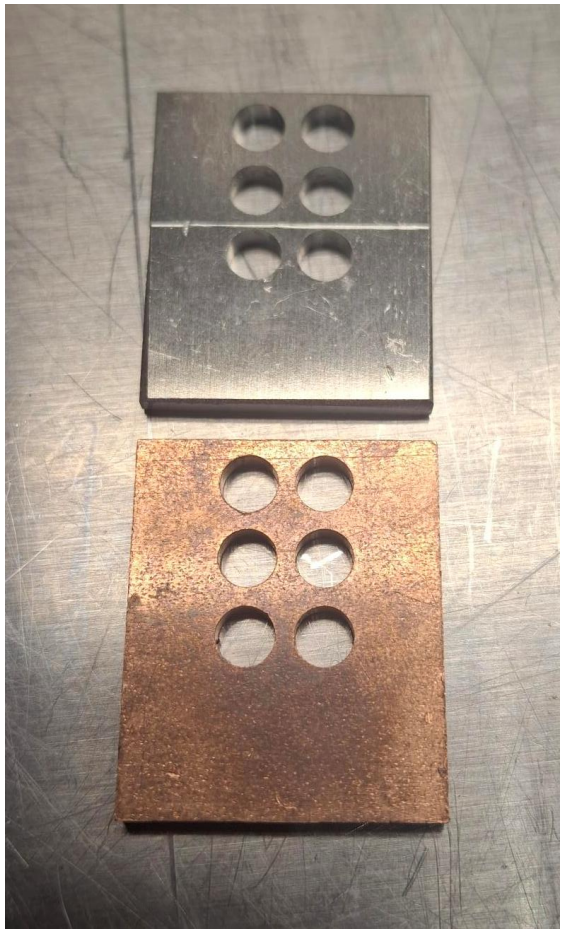
# Fluorescence Sample Prep

**Additional tips for fluorescence samples:**

- Avoid sample holders, materials with edges near your target element
  - Check the K-edge and L-edges of your material and the holders

- Fluorescence is far more sensitive to contaminants, small amounts
  - Kapton windows may have trace amounts of **Fe**
  - Mylar windows may have trace amounts of **Mn**, **Zn**

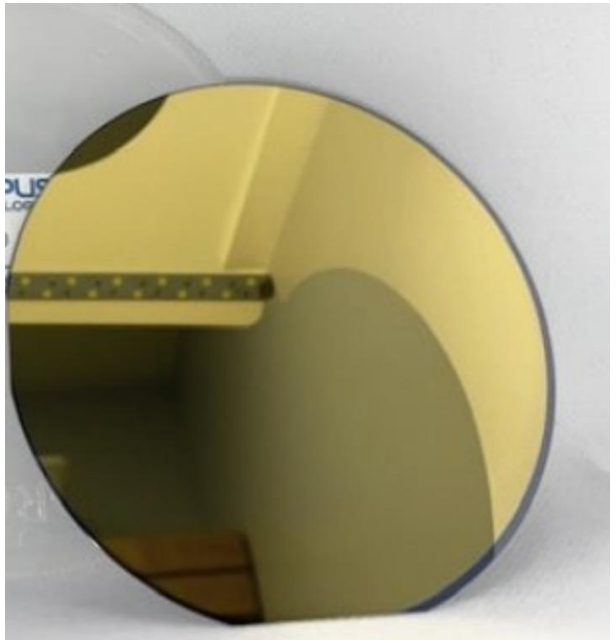
- Lighter elements (i.e. Cu in Pd/CuO) may interfere with signal of heavier elements by non-resonance fluorescence
  - Filters, tin foil shielding can be used



# Other Sample Types

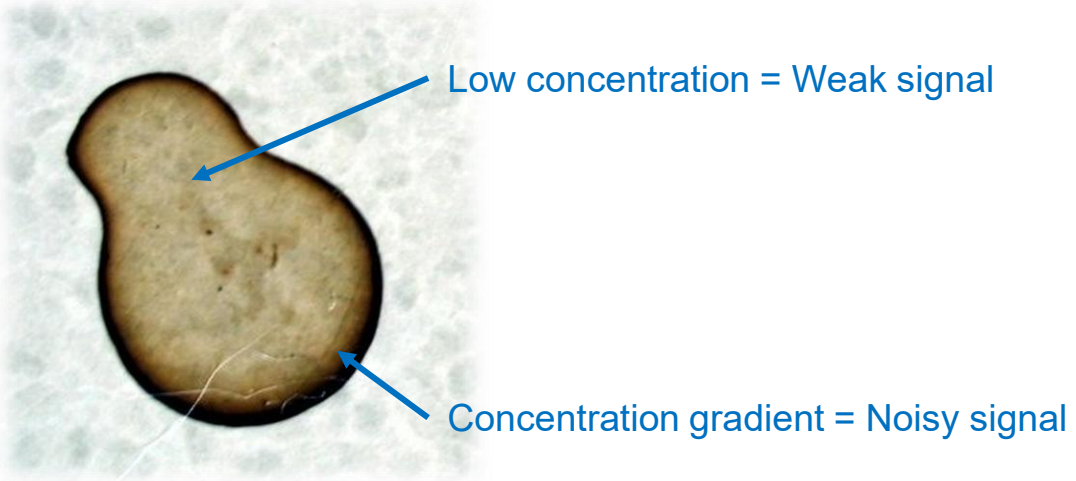
## Thin Films

- Measured in fluorescence mode
- Grazing angle to maximize surface area on beam
- Crystalline materials may cause Bragg peaks
  - We can spin samples to “smear” these peaks



## Dropcast Films

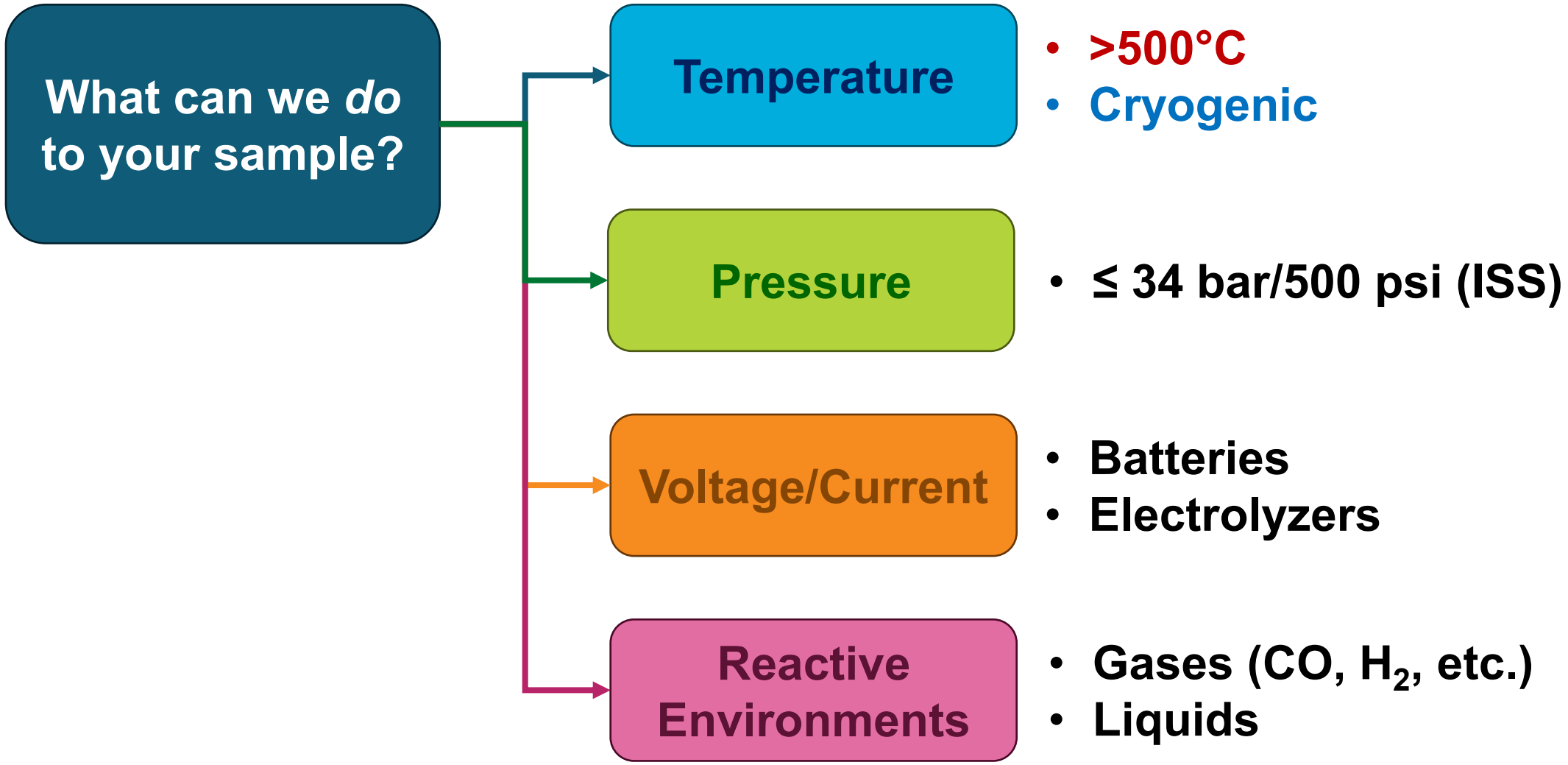
- Depositing dry material from a liquid slurry
  - Common in electrocatalysis & fuel cells
  - Often on flat substrate or carbon paper
- Concentration varies greatly across surface
- Creates a “coffee stain” effect



# Liquid Samples

- Naturally homogeneous, but suspensions may settle
  - Depending on energy, water can attenuate beam
- Requires good containment
  - Sealed capillary
  - Sample holder with wells sealed by tape
- Solutions may be susceptible to beam damage
  - More on this later!
- In solid/liquid systems (i.e. catalysis), introducing liquid phase can dampen solid material signal

# Sample Environments



# Flow Cells

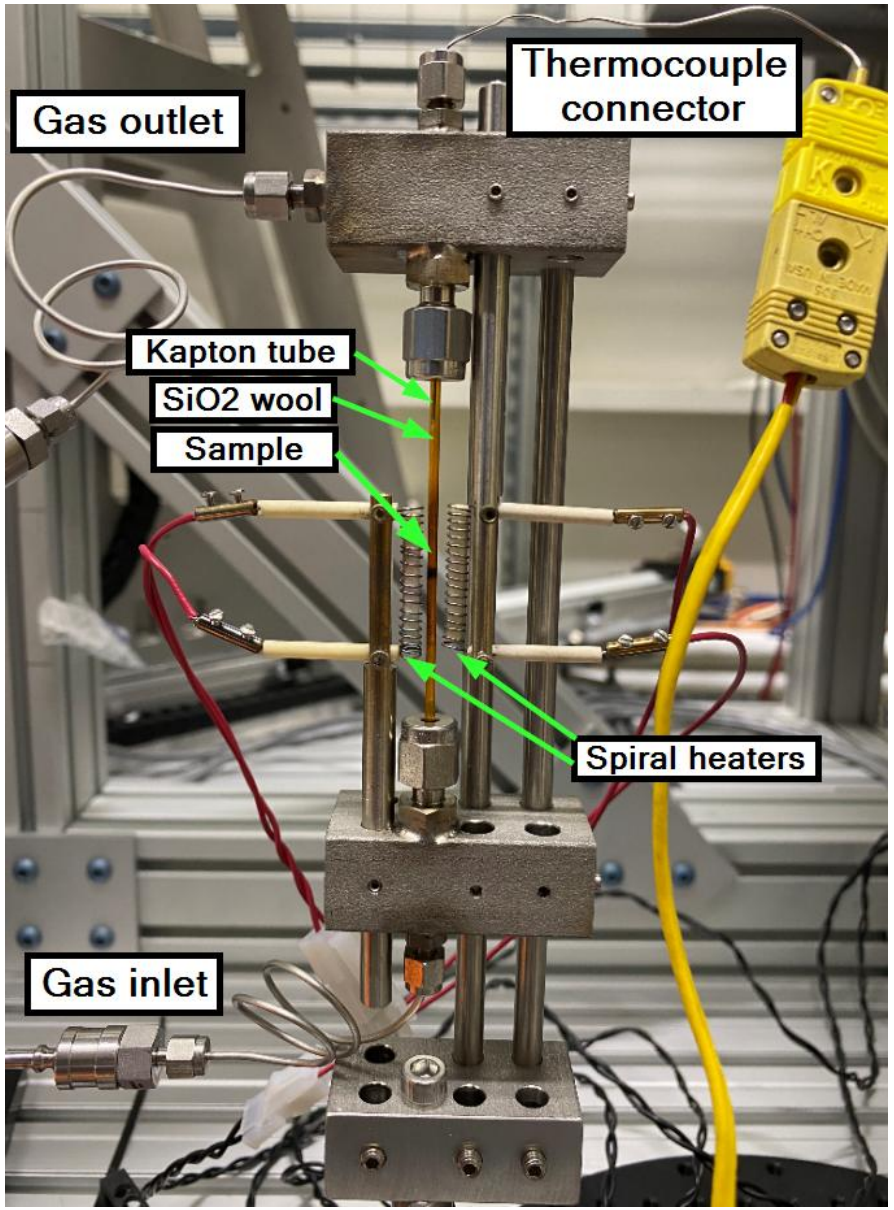
## Advantages

- Compatible with different capillaries
- True plug flow for catalytic reactions
- Rapid temperature control and cooling

## Disadvantages

- Low catalyst amount, hard to do *operando*
- Need very low flow to see products
- May not represent reactions at scale

Remember: capillaries can attenuate the beam and reduce signal!



# High Pressure Cells

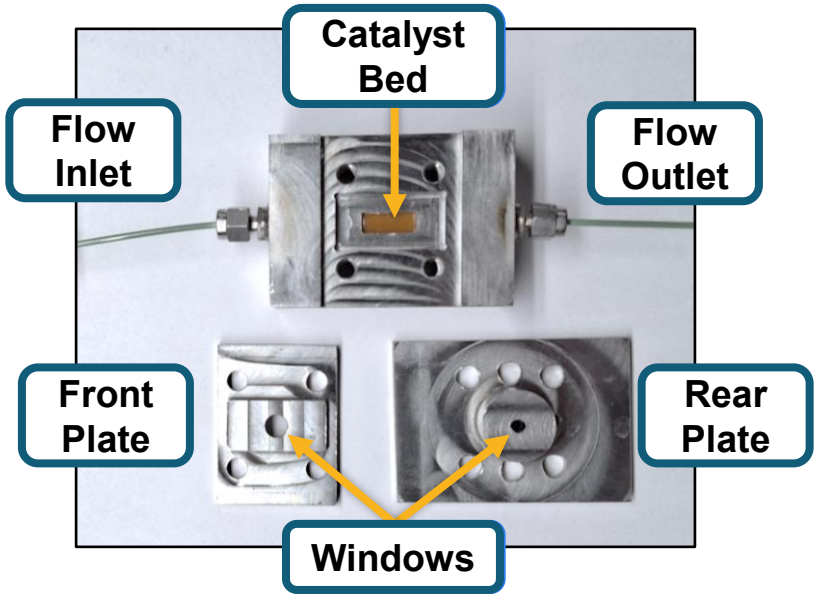
## Advantages

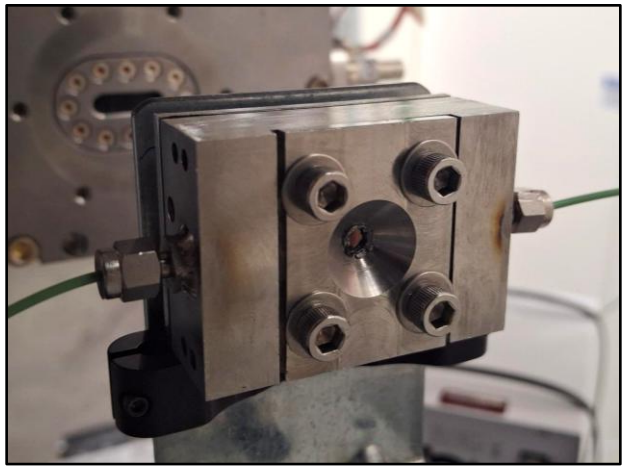
- Can hold up to 34 bar (500 psi)
- Can reach up to 600°C
- Compatible with batch or flow systems
- Good for ambient liquid flow, too!

## Disadvantages

- Pressurization takes time
- Not a true plug flow
- Fluorescence may be limited depending on cell material (Steel contains Fe, Mo, Ni, Cr etc).

Custom setup may be required, contact beamline staff ***before submitting your proposal!***



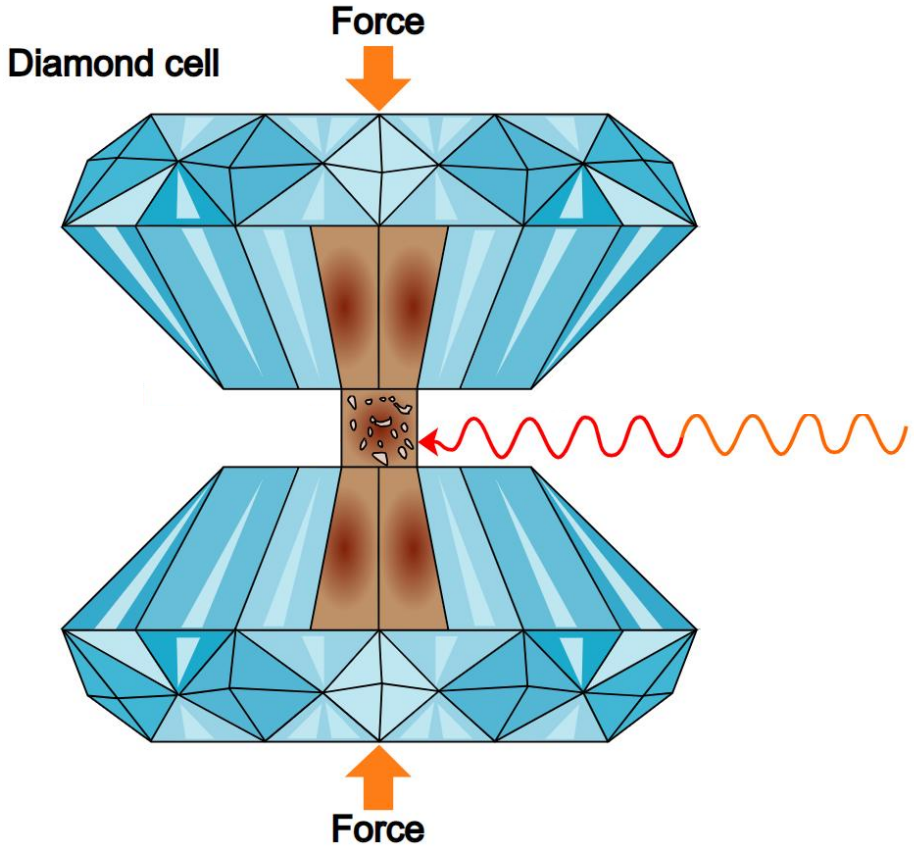



# Very High Pressure

**Primarily for high pressure materials systems**

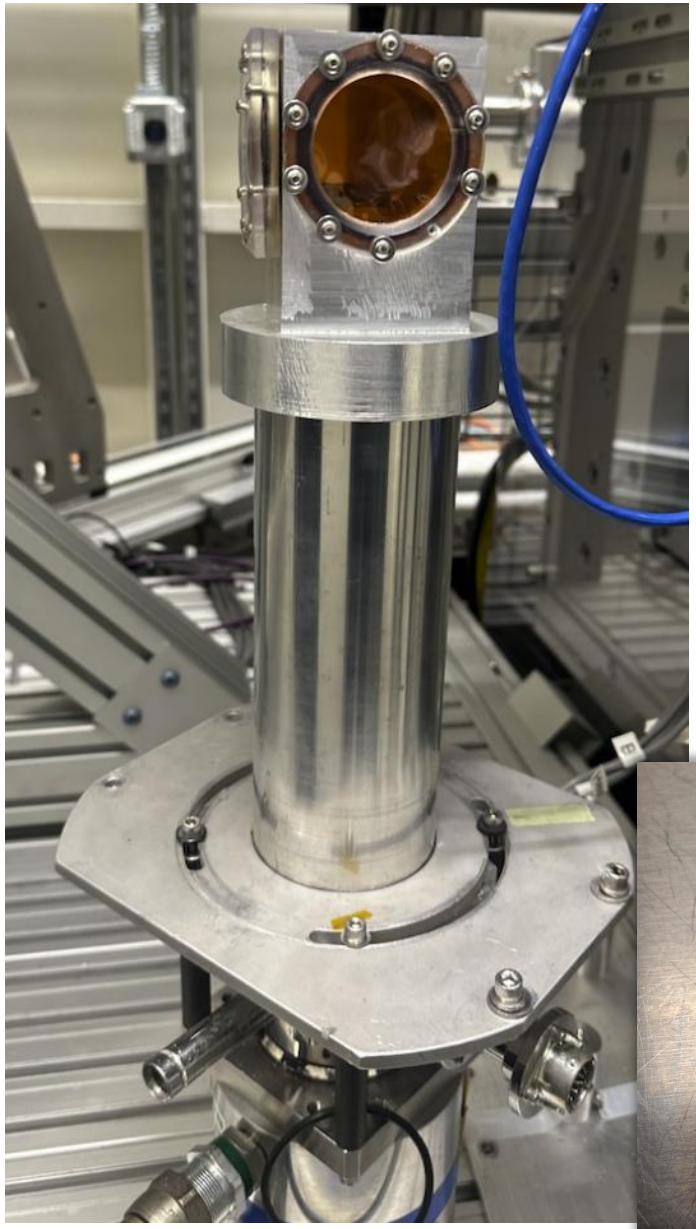
- Simulating pressures deep within planets
- Synthesizing materials and phases that can't be achieved at ambient pressure

Diamond anvil cells typically measure up to **200 GPa** but can create up to **700 GPa**

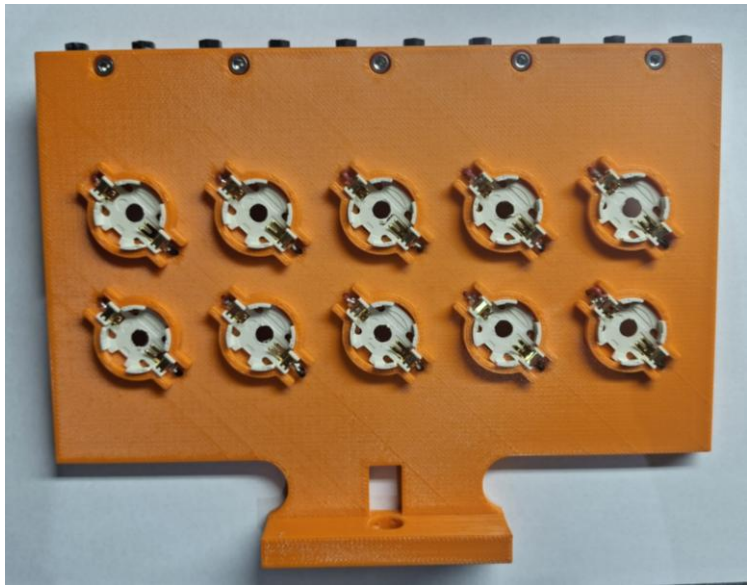


# Cryostats

- Extreme cooling – down to a few Kelvin
- Ideal for biological samples or those sensitive to beam damage
  - Higher signal-to-noise from reduced phonons
  - Improves radiation sensitivity
- Cooling is slow - > 1hr for some samples
- Sample preparation and transfer can be difficult, especially for samples that are loaded frozen

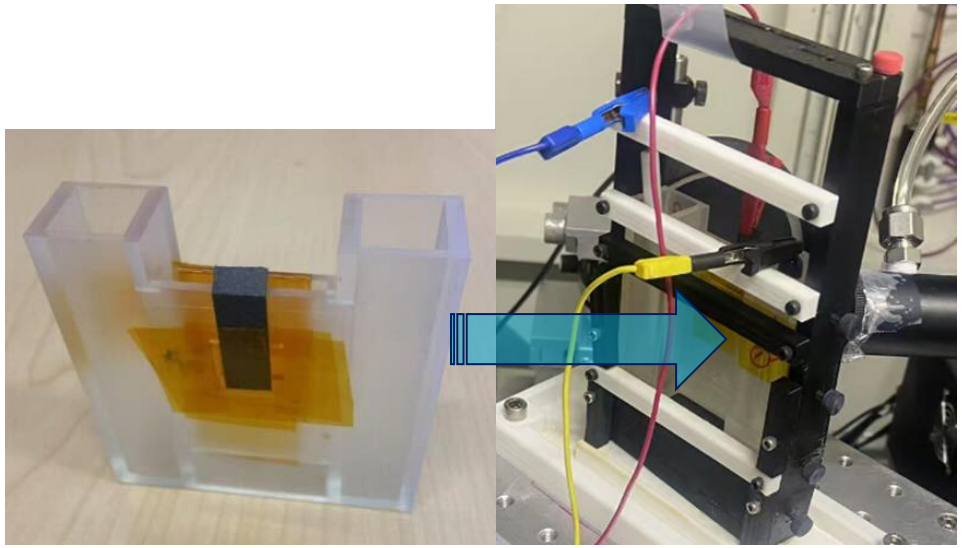


# Batteries and Electrochemistry



**High-Throughput Cell Module**

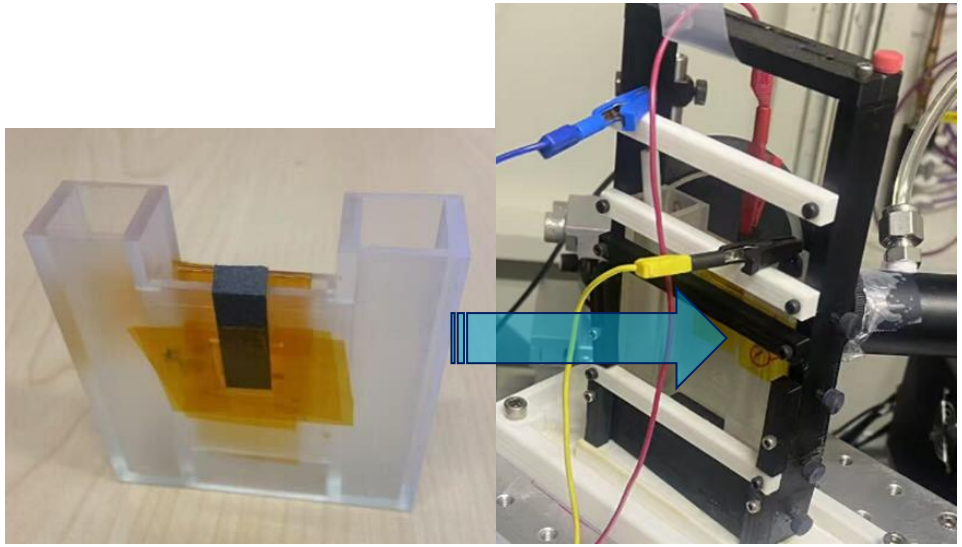

**Potentiostat**



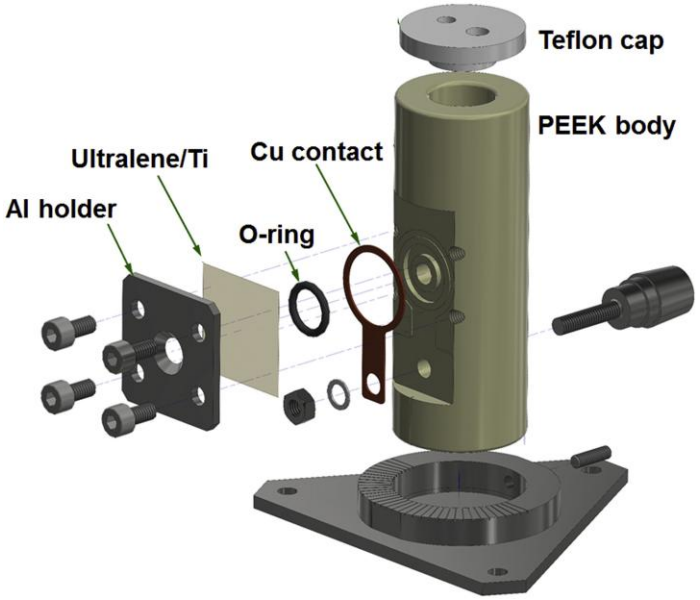
**Electrochemical “H”-Cell**

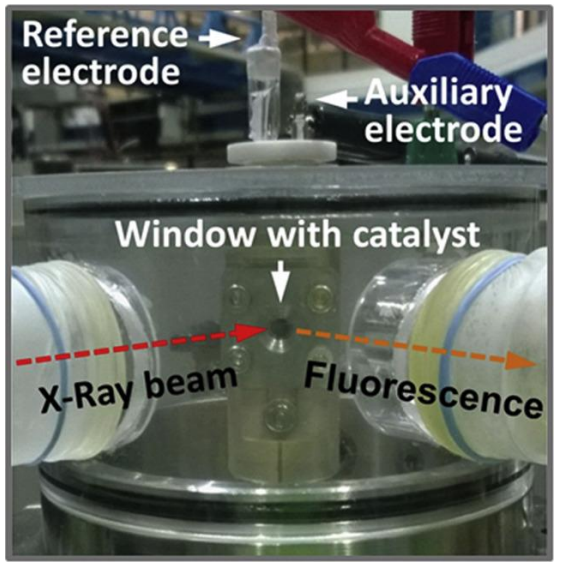
- Cycling multiple battery cells in parallel for high-throughput *operando* measurements
- Note: Adding X-ray transparent windows to cells may change field distribution and chemistry!

# Batteries and Electrochemistry



**Electrochemical “H”-Cell**



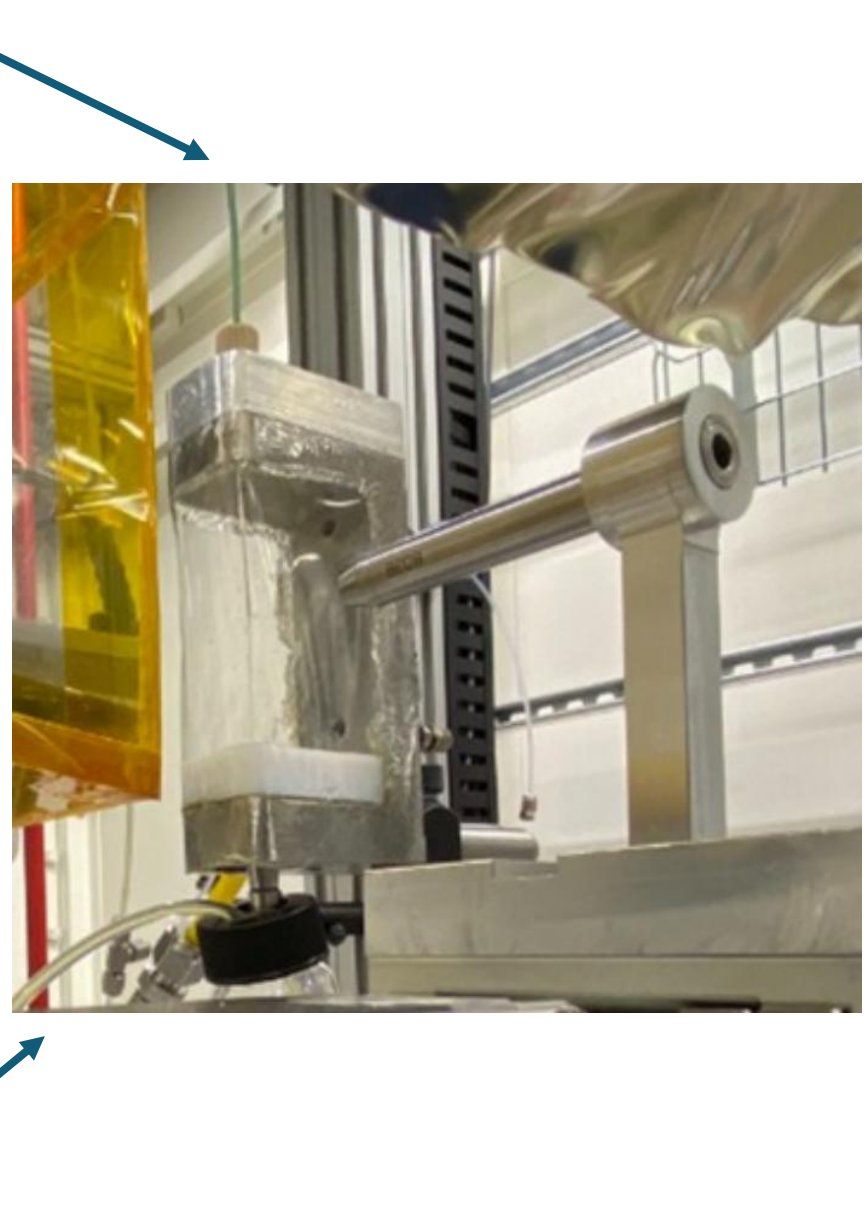




Villullas et al. *Electrochem. Comm.* (2018) 94, 14-17.

- These cells are typically user-designed
- Electrolytes can absorb X-rays and bubble formation may affect signal
- **These cells leak!!!**

# Liquid Samples

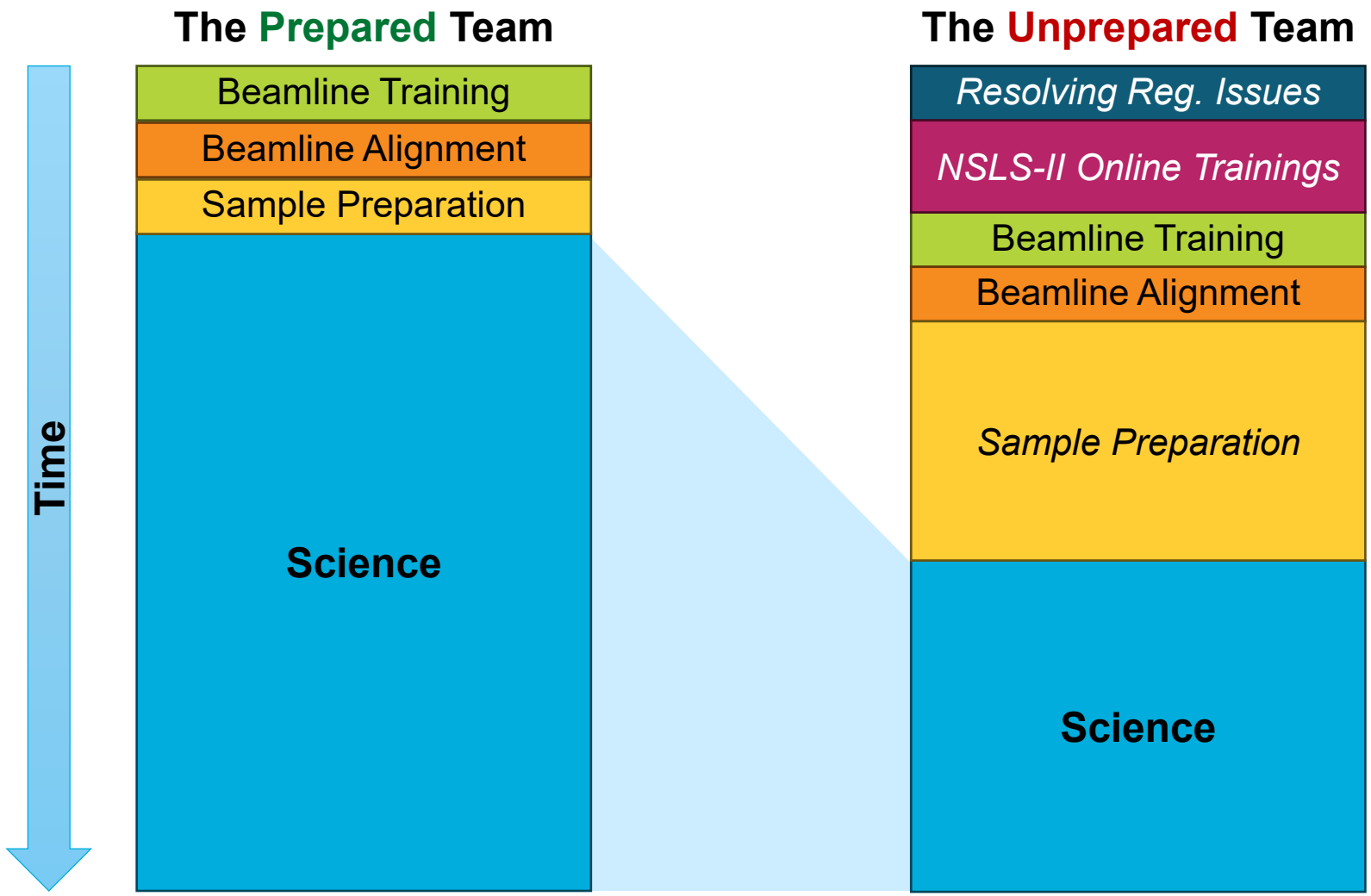
- Liquids are sensitive to “beam damage”
  - Changes to sample imparted by the beam itself
- A “liquid jet” may be used to reduce damage
  - Circulated by a peristaltic/syringe pump
- For air-sensitive liquid samples, we can enclose it in another liquid
  - “Co-axial jet”



# Preparing Yourself

- NSLS-II operates 24 hrs a day…but humans do not!
  - Have a plan, have a place to sleep, **have a team**
- Prioritize your samples!
  - Acts of nature, beam dumps, sample issues
  - **Don’t save the best for last**
- Check your status – is everyone’s registration active?
  - Don’t get turned away at the gate!
  - Complete online trainings ahead of time
- Submit your Safety Approval Form (SAF) on time!
  - Minimum **45 days** before your experiment
  - **If its not on your SAF, you can’t measure it**

# Preparing Yourself



# In Summary

- Knowing your sample prep will save time at the beamline
- Refer to these slides whenever you're preparing samples
- Unsure of something before your experiment? **Talk to us!**
  - **Before you submit a proposal** to know capabilities
  - **Before you start your experiment** if unsure of sample prep

**Acknowledgements:**
- Eli Stavitski (NSLS-II) who originally presented on this topic and from whom I have adapted this talk
- And to you all, for showing a keen interest in XAS and for lasting through this talk…

…now please enjoy your dinner!