Sample Prep Guide for Remote Operation at PIPOXS

Calculating sample and BN masses needed for XAS samples

For XAS experiments—transmission, fluorescence, and HERFD—it's important that the concentrations of your samples are not too high, otherwise your spectra will be distorted. For most compounds, the neat material will be too concentrated to measure directly and you will need to dilute your sample with a material that doesn't absorb x-rays very strongly, such as boron nitride (BN), to get to an acceptable concentration. A good introduction to sample prep can be found in Grant Bunker's tutorial here: http://gbxafs.iit.edu/training/XAFS_sample_prep.pdf

There are two steps needed to determine how to best prepare a sample. The first is to determine the attenuation length of your sample material; if the results of that calculation look promising, then you can calculate how much you need to dilute your material to make a good XAS sample. We'll go through both steps here.

Step 1: Determining path length

Grant's slides walk through how to calculate the attenuation length, but we'll do it here, too, for good measure. There are a few pieces of information you'll need:

1. The chemical formula of your material
2. Your material's density
3. The absorption cross sections (σ) of every element in your material at an energy just above the edge

Items 1 and 2 should be easy to determine, and item 3 can be found in tables such as these: http://www.csrri.iit.edu/periodic-table.html. For our example, we'll use Fe_2O_3 as the sample of interest and do our calculations for collecting data at the Fe K-edge. The density of Fe_2O_3 is 5.24 g/cm^3 and, since we're planning for the Fe K-edge (energy = 7112 eV), we can find the cross sections for an energy around 7150 eV. From the table linked above, we can find that the cross sections for Fe and O at 7150 eV are:

- σ(Fe) = 400 cm^2/g
- σ(O) = 15.3 cm^2/g

To calculate the overall cross section for Fe_2O_3 we need to multiply the atomic cross section of each element by the mass percent of that element in the compound. For example:

FW(Fe_2O_3) = 159.7 g/mol
σ(Fe_2O_3) = 400 cm^2/g * (111.7 g Fe / 159.7 g Fe_2O_3) + 15.3 cm^2/g * (48.0 g O / 159.7 g Fe_2O_3)
σ(Fe_2O_3) = 284 cm^2/g

From here we just need to multiply the cross section by the density to get the calculation absorption at 7150 eV.

$\mu(7150) = (284\ cm^2/g) * (5.24\ g/cm^3)$

$\mu(7150) = 1488\ cm^{-1}$

This tells us that, for a 1 cm thick sample, the absorption value would be 1488. To determine the path length—the thickness of sample for which μ(7150) = 1, we can simply invert this answer to get a path length of:

$1 / 1488\ cm^{-1} = 0.00067\ cm = 6.7\ microns$

This result, that to get an absorption of 1 we need only 6.7 μm of Fe_2O_3, is really important, since it tells us that every individual particle of Fe_2O_3 should be 6.7 μm or smaller. For reference, an 800 mesh powder has particles about 15 μm in size, so this sample needs ***very*** small particles to give good data. For path lengths smaller than 10 μm or so, careful thought needs to be given to how to prepare samples, since getting particles this small can be a highly nontrivial task. If you have questions about any of this, don't hesitate to reach out.

Step 2: Calculating required dilution with BN

Once you've established that you can prepare your sample with small enough particles, the next parameter to determine is how much dilution the sample needs. The sample cells used at PIPOXS are 1 mm thick, and the results above indicate that a sample of pure Fe_2O_3 needs only to be 13.4 μm thick to have μ(E) = 2, so we definitely need to dilute this sample in order to be able to measure it. For this we typically use a low Z material like boron nitride (BN) or graphite (C) since these materials dilute the highly absorbing sample without being very absorbing themselves. To determine the amounts needed, using a tool like this (https://www-ssrl.slac.stanford.edu/smbin/mucalwebnew.pl) is probably the easiest way to go.

Most of the fields here are self-explanatory, but it's important to make sure that the "total mass of diluted sample" is 0.03 grams (30 mg) and the "area for the cell window" is 0.22 cm^2 since that's the correct number for the PIPOXS sample cells. When you're ready, hit "Submit" and the page will generate results after a few seconds.

XAS Powder Sample Weight Calculator

Enter the chemical formula for the sample: Fe2O3

Note: Entries are case sensitive, parentheses are ok, e.g. "Fe2(SO4)3"

Enter the chemical formula for the diluent: BN

Note: Entries are case sensitive, parentheses are ok, e.g. "Li(CO3)"

Enter the total mass of diluted sample: .03 g

Enter the element symbol (for edge energy): Fe

Choose the edge: (•) K Edge ( ) L1 Edge ( ) L2 Edge ( ) L3 Edge ( ) M Edge

Enter the area for the cell window: 0.22 cm^2

Note: 0.5927cm^2 is the area of a standard SMB/XAS powder plate window

Choose the desired absorption or transmission at the edge: (•) Absorption ( ) Transmission

2

Submit Reset

Mucal, a subroutine created by Pathikrit Bandyopadhyay that calculates X-ray absorption cross sections, was used in the creation of this perl script. The source can be found here.

The most important part of these results is listed in bold at the top: for a μ(E) = 2, you need 0.79 mg Fe_2O_3 diluted with 29.21 mg BN. What's critical here is the weight **ratio** of sample to BN. In other words, you can safely double or triple the amounts of sample and BN and still be ok; e.g. using 1.58 mg sample and 58.42 mg BN, or 2.37mg sample and 87.63 mg BN would both be fine since the ratio between the two components is the same as the calculation.

XAS Powder Sample Weight Calculator

Breakdown of sample: || Fe: 2 || O: 3 ||
Breakdown of diluent: || B: 1 || N: 1 ||

0.79 mg of sample (Fe_2O_3) and 29.21 mg of diluent (BN) is ideal.

The edge energy for Fe at the K Edge is 7.112 keV.

Sigma(Fe_2O_3) is 290.080 at the edge and 41.335 before the edge.

Sigma(BN) is 7.250 at the edge and 7.253 before the edge.

Sigma(total) for this sample composition is 14.667 at the edge and 8.147 before the edge.

The total absorption is 2.000 at the edge and 1.111 before the edge.

Calculate spectrum for an energy range:

6.912 keV to 8.112 keV

Note: Default values are for a typical XAS scan to K=16 for the chosen edge.

Compute data for 100 intervals.

Graph Data | Download Data | Reset

Note: For 100 data intervals, this calculation takes about 5 seconds.

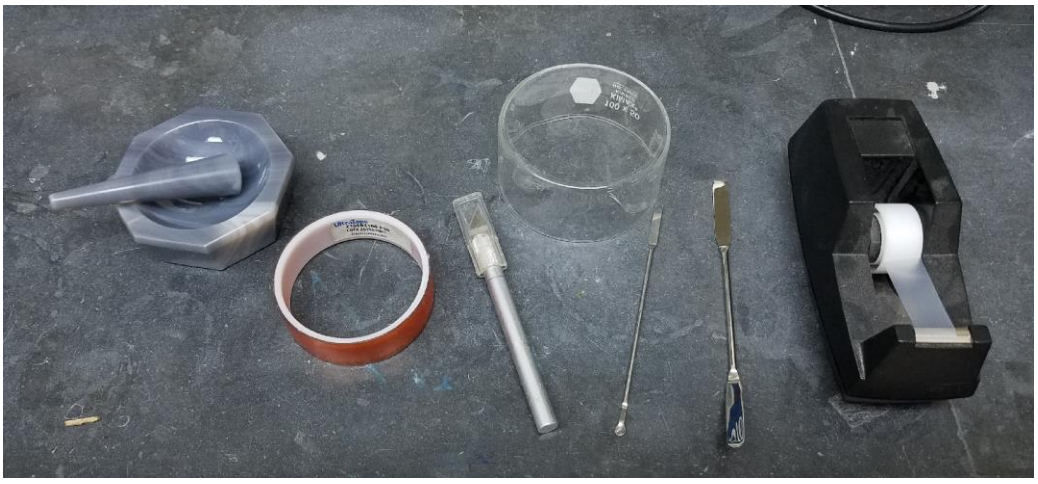
Appendix 1: How to load the aluminum sample cells

The aluminum sample cells to be used at PIPOXS this fall are simple and versatile, being compatible with both XAS and XES experiments. The basic idea behind these cells is to fill the hole in the plate with your powdered sample and then to seal the cell with two layers of Kapton tape. Important criteria for preparing these samples are:

- The sample (together with boron nitride, if needed) is ground to a fine and uniform powder. For some samples, this means particle sizes on the order of 10 µm!
- The hole in the cell is completely and uniformly filled with sample; i.e. there are no holes or large thickness variations in the sample.
- The sides of the cell are clean and free from sample.
- Both faces of the cell are well-sealed with Kapton tape.

For this process you'll need:

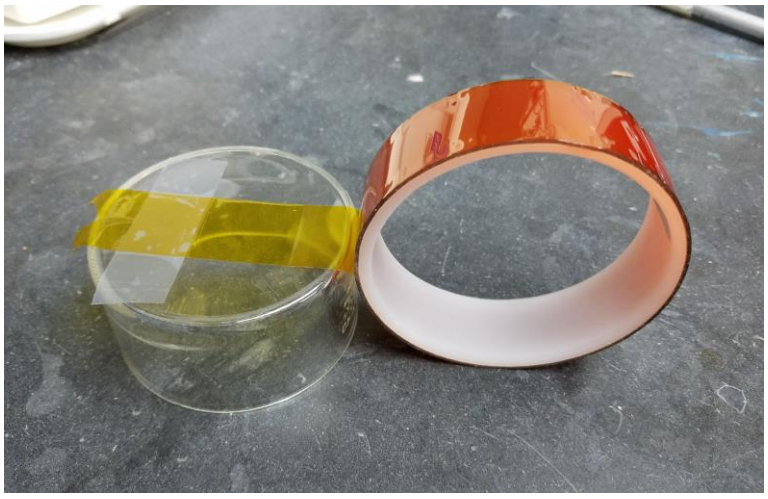
1. Appropriate PPE
2. Aluminum sample cell
3. Scotch tape
4. Kapton tape
5. Exacto knife
6. One or more metal spatulas
7. Mortar and pestle (preferably agate)
8. Balance with at least milligram accuracy (0.1 mg accuracy is better)
9. Flat working surface such as a glass petri dish



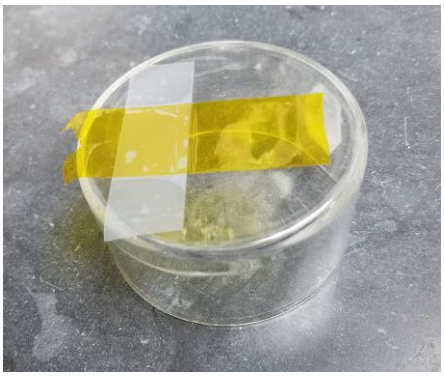
Step-by-step instructions for preparing sample in these cells are as follows:

1. Find a smooth, clean surface on which to work. Petri dishes and other flat, glass surfaces work well for this.
2. Pull a few cm of Kapton tape off the roll and stick a piece of scotch tape to it, sticky side to sticky side.

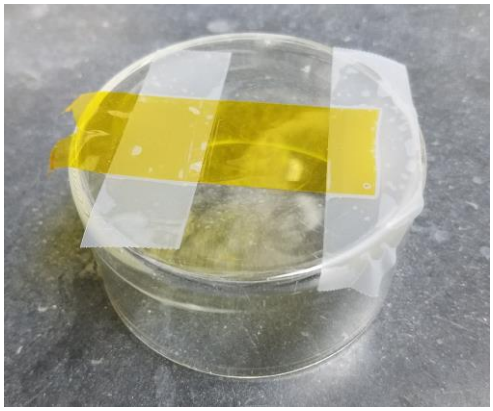
3. Stick the scotch tape to the petri dish (the stick side of the Kapton should be facing up) and then unroll several cm of Kapton.



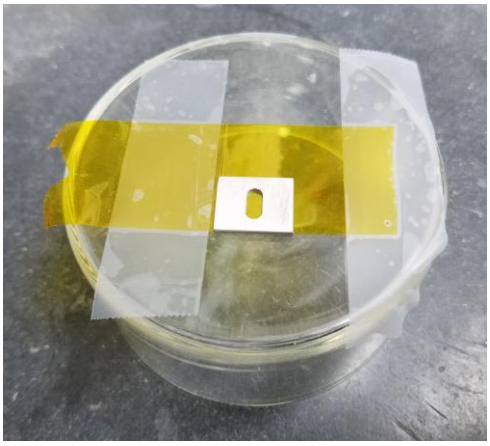
4. Cut this piece of Kapton off the roll so that you're left with the Kapton, sticky side up, on the petri dish with one end held in place with scotch tape.



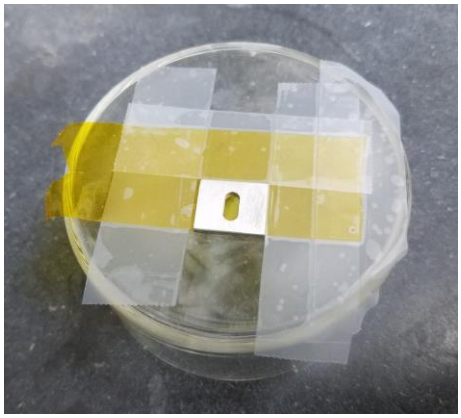
5. Use another piece of scotch tape to stick the other end of the Kapton to the petri dish. Make sure the Kapton is flat without any creases or ripples. You can reposition the Kapton as needed to remove wrinkles.



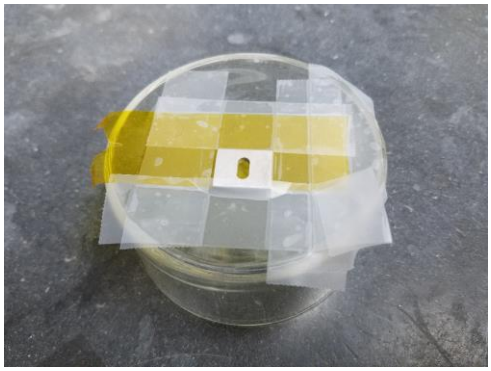
6. Place the sample cell on the Kapton tape. It's easiest to place this in one of the corners, but really anywhere will do so long as the entire cell in on the sticky part of the Kapton.

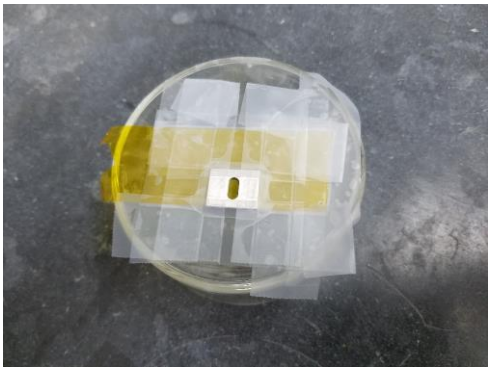


7. To make life easier later on, use scotch tape to cover up the remaining exposed sticky side of the Kapton. When you're done, the only Kapton adhesive you want accessible is the space within the sample cell window.



8. With that done, you next want to cover as much of the sample cell as possible with scotch tape. We do this so we don't contaminate the sides of the cell during sample prep. To begin, get a piece of scotch tape maybe 3" long and fold a ≈0.5" tab at one end (i.e. stick the tape to itself, sticky side to sticky side). Next, place this piece of tape on the sample cell as close to the hole **but not covering the hole** as you can. Your cell should look like the first photo below. Repeat this process for the remaining three sides of the sample cell. It doesn't matter which side you start / end with, just make a mental note of the order.

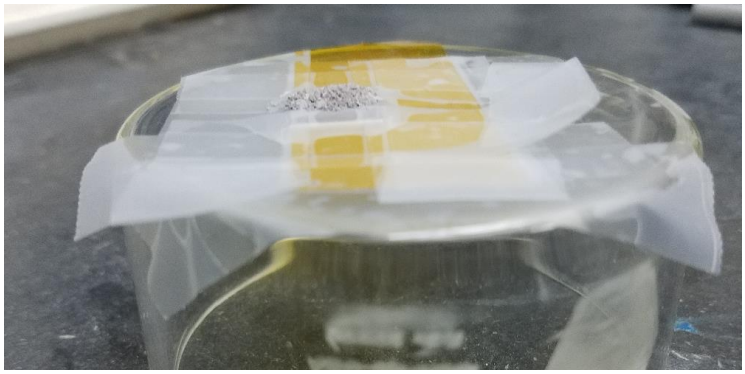




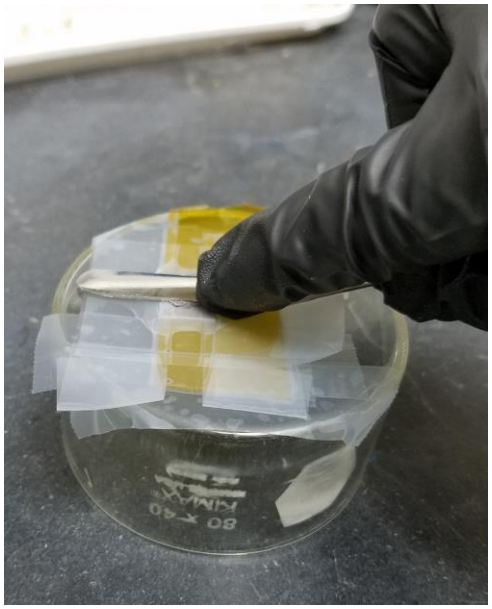
9. At this point the sample cell is prepared, so you can set it aside while you get your sample powder ready using the mortar and pestle.
10. For a mortar and pestle, despite its expense, agate is a far superior material to any other. Ceramic will also work, but these are less effective at grinding and their rough surface will lead to significant sample loss. Avoid materials such as wood and metal.
11. Weigh out the needed amount of sample (and BN if required) that you calculated in Appendix 1 and add those to the mortar.

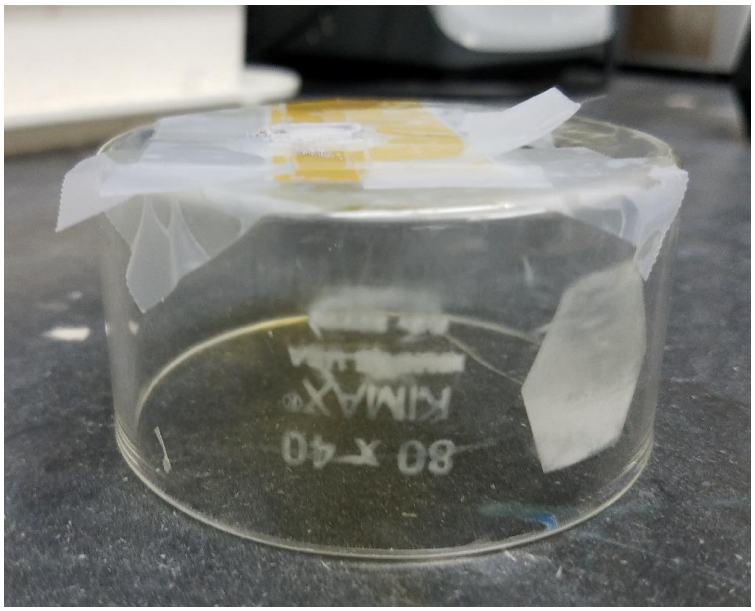
12. Grind the two together. When you think you're done, grind some more. The goal is to get a uniform, very finely ground powder where your sample is evenly mixed with the BN (this is easiest to see with colored samples). Particle size is particularly important for XAS / EXAFS experiments because the individual particles must be smaller than the attenuation length of the material, which in extreme cases can be only a few microns. There's no such thing as overgrinding, so err on the side of spending more time grinding.
13. Once the sample and BN are ground together, gather the material into the bottom of the mortar.

14. Using a spatula, scoop the powder into the hole in the sample cell. It will likely take several scoops, but in the end you want a nice, heaping mound of sample in the hole.

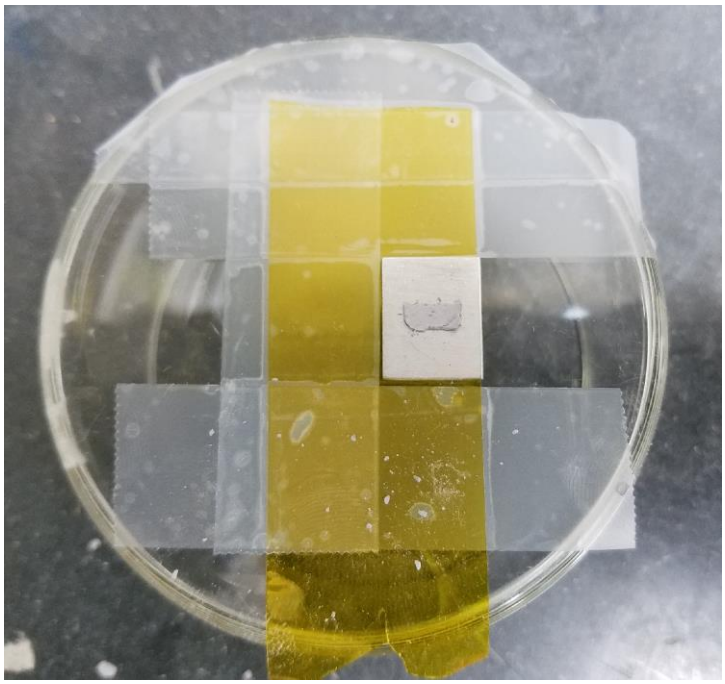


15. Using the flat side of a spatula, compress the mound into the hole, applying steady, even pressure to the spatula. You want to achieve a flat surface that's parallel to the face of the sample cell.



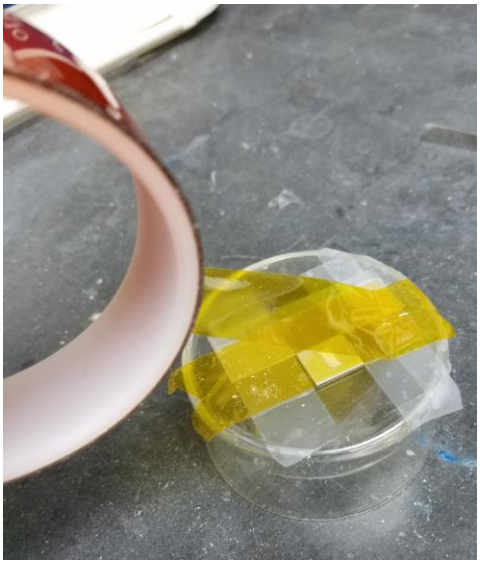


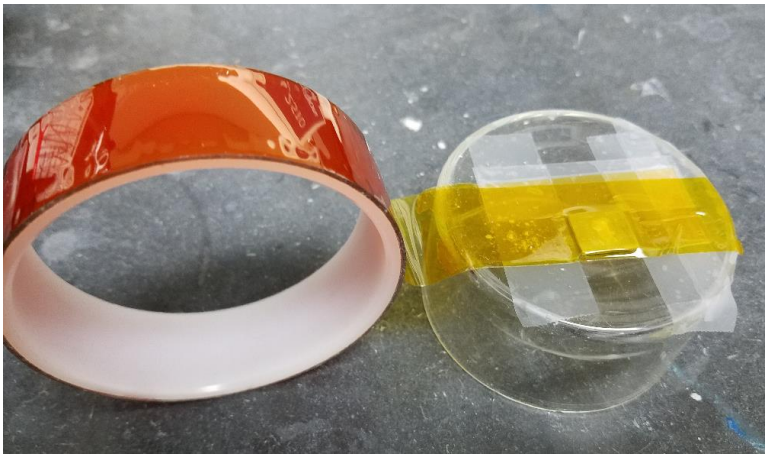
16. With the cell packed, remove the scotch tape pieces covering the face of the cell (the ones with the tabs), being sure to work in reverse order that you applied the tape (i.e. last piece on is the first piece off). Removing this tape will hopefully leave you with a nice, clean face on the cell.



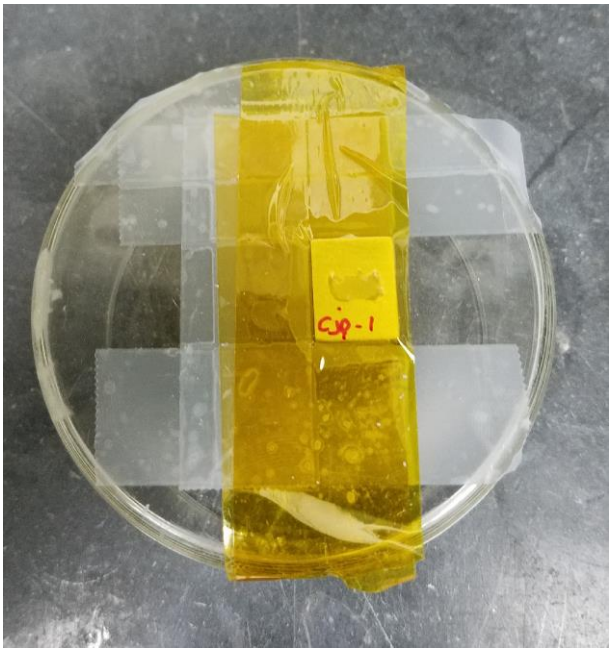
17. Now that the entire upper face of the cell is exposed, it's time to apply the final piece of Kapton to seal the powder into the cell. This is the step where it's easiest for something to go wrong, so

it pays to be careful and go slowly to try and avoid problems. The easiest way I have found to do this is to unroll a few inches of Kapton and stick the end to the petri dish a few cm away from the sample cell (left photo below). With the tape pulled somewhat tight, lay it flat onto the face of the sample cell, using your finger to apply even pressure as you do so. If all goes well, you'll end up with something that looks like the right photo below. The most common problem is for the top layer of Kapton to crease, which will create an unusable sample. If this happens, remove the Kapton and, if the surface of the sample wasn't disturbed too badly, try again.

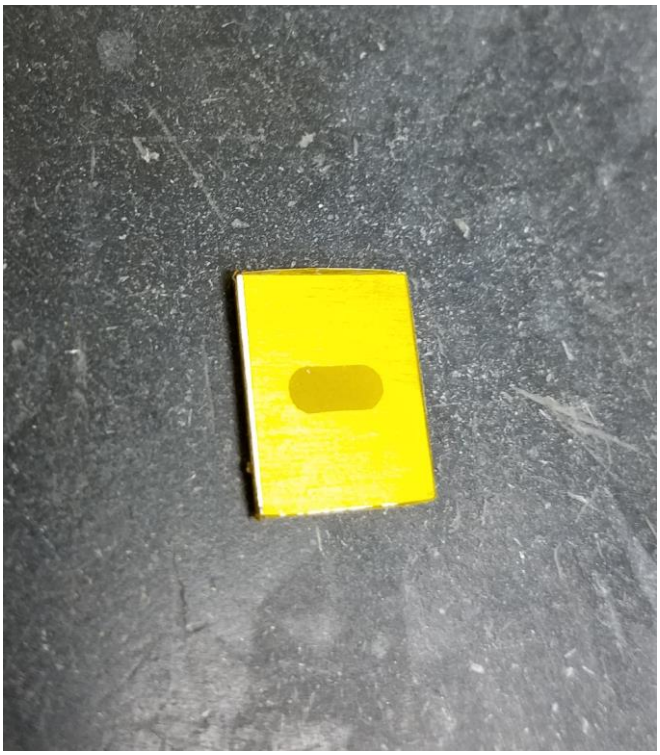




18. Cut the Kapton off the roll and the sample cell should be all sealed up. At this stage—before you cut it off the petri dish—it's a good idea to label the cell while it's still held in place. A fine tip sharpie works best, and be sure not to get ink over the window to the sample.



19. Once labeled, use the exacto knife to cut the tape holding the cell to the petri dish. When you're done, you should have a sealed sample that looks like this.



20. Lastly, use the Exacto knife to cut a few mm of the Kapton tape off the bottom of both sides of the sample cell, making sure not to cut the label off or get too close to the sample windows. This will ensure that the cell fits easily into our mounts, even at reduce temperatures.