ARC-MMA / CIF User Guide during Phase 1 under CV-19
CRB-109 NMR Only Addendum for Phase 1B

Updated June 22, 2020

The ARC-MMA / CIF continues to operate in **Full-Service mode only** during Phase 1, exceptions may apply, discuss needs with Lab Managers and Staff. Additionally, some limited self-service NMR will be available in the CRB-109 lab on the ASC400 walkup NMR only. The US400 sample changer is *NOT available* at this time for self-service operations.

To be very clear: Phase 1B protocols outlined below and at this time apply only to *single-serve, routine 1H, 19F and 31P walkup NMR users in the CRB-109 lab only*. All BATCH, BUNCH NMR requests will continue to be Full Service in the CHEM1 Lab Only. Samples needing more than ten minutes should not use the ASC400. Also, Project level and Special requests for NMR continue to be honored and managed in the CHEM1 building by special service request.

CRB-109 General CV-19 Access Rules, Phase 1B:

- PPE Must be worn at all times. Do not congregate in the hallway. Practice social distancing.
- At this time, the CRB walkup lab is for CRB resident investigators, only. Other investigators please continue to use CHEM1 resources. This is CV-19 social distancing policy guidance.
- Time spent doing walkup NMR is considered part of your lab shift time as per guidelines.
- Always use the *SLACK* #mma-crb109-general channel to virtually queue up, signal that you are done in the lab, communicate generally with colleagues. Staff do not follow this channel, so use the #mma-nmr-general channel for communications with Staff
- Observe the Slack provided Block Out Schedule (if any) including Staff set-aside times.
- 1:1:1 One lab scientist may be in the lab at a time. One lab scientist may be on deck. One sample may be run per visit (but see later note). !

  DO NOT CONGREGATE IN LOBBY!
- Only routine operations that can be complete in ten minutes may be done. Depending on user-feedback, these conditions may be relaxed at certain times of the day.
- Follow Staff instructions and If asked to leave when Staff are present then please do so immediately. ***Make way for and Avoid at all costs the AIRGAS Delivery person, Nate.***
- W:W:W Wash hands before using the keyboard and mouse. Wipe down the keyboard with provided sanitizer and paper towels gently when you leave (or use plastic wrap). Wash hands when you finish.

Later Note >" I have several samples I'd like to run…" That may be possible – but only if the Slack channel is clear and no one is on deck. Commonly Sensible. Otherwise, submit batch and bunches of samples to CHEM1, or Slack again and go back to your lab, wait for the next turn.

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PLEASE FOLLOW THESE STEPS for ACCESSING the ASC400 NMR in CRB109 DURING YOUR WORKING SHIFT.

You Must also follow the Access Rules for CRB-109 during Phase 1B, highlighting the basic steps below.

DO NOT CONGREGATE IN THE LOBBY

1-1-1
W-W-W

STEP 1

PPE Must be worn at all times. Do not congregate in the hallway. Practice social distancing.

STEP 2

If you haven't done this already then, Request walkup NMR service through iLab "Request Service". You only need to do this once per month. Excel fill-out forms will be available there and you should update these as you go, attach them back to the service request on iLab.

STEP 3

Use "Slack" #mma-crb109-general to virtually queue your walkup access.

Join here: https://join.slack.com/t/csu- arc/signup. For more info: Slack User Guide. Join other relevant lab and instrument Slack channels to stay informed about general lab or instrument specific updates. Communicate there with your name and reference your iLab Service ID, e.g., "CIF-MK-2336".

When you are next in queue, go down and wait in the on-deck circle.

STEP 4

The lab is empty and you may go in and do your routine NMR experiment. Practice good hygiene, clean up after you are finished.

STEP 5

Use the "Completed" check mark emoji on your queue position in Slack to acknowledge to the CRB109 community that you are finished, next batter is up. Also, use Completed check mark if you are delayed in the lab as a courtesy to others. Queue back up when you are ready.

FREQUENTLY ASKED QUESTIONS REGARDING STEPS TO ACCESSING THE ASC400 NMR in CRB109 DURING YOUR WORKING SHIFT.

1. *"I have several samples I'd like to run…"*

   That may be possible – but only if the Slack channel is clear and no one is on deck. Commonly Sensible. Else, Slack again and go back to your lab, wait for the next turn.

2. *"My lab elected me NMR-Pod captain and I'd like to setup lots of samples for my Pod on any NMR…"*

   Congratulations, who are you? and stay tuned.

3. *Do I need to review the online notes about self-service access, submit my acknowledgement, since I already know how to do this stuff safely?*

   Yes.

4. *"Would it be possible to arrange or schedule even for, e.g., 30 minutes slots on the ASC400 walkup to do a handful of samples?"*

   See 1. Above.

   The point of "WALKUP NMR" in this context is that as many investigators as possible get access quickly, in real-time, to the NMR to enable answers to their most basic questions about a reaction they are carrying out in their labs. That is the Highest Purpose / function / raison d'etre for the ASC400.

   So, Maybe.

   Are the various Labs, Principal Investigators, Students, Post-docs and other investigators willing to cooperatively provide for that Highest Purpose, accommodate those users, *Slack* out their schedules, amend them when pushed by their colleagues and other Pods?

   Show me your plan!

5. *"There are rumors that one member per group, or one member per pod will be enabled to use the NMRs for their group/pod members."*

   We heard the same rumors.

   Although appealing to some, this may be counterproductive overall. It satisfies *some* safety concerns but hurts the productivity of the investigator so assigned.

   If we *must* do this for safety, we will. Thankfully, the Head of Chemistry, Matt Shores, provided us with two GTAs that are helping us out in this regard this summer.

   The future is unknown. Live now.

6. *"I have an evening shift and it is rare that a GTA or student is around to do any NMR at all so wouldn't it be okay to let me do more NMR on the ASC400?"*

   That is unfortunate and one of the unfortunate consequences of CV-19, social distancing.

   This group of investigators may be able to make the case for access.

   Show me your plan!

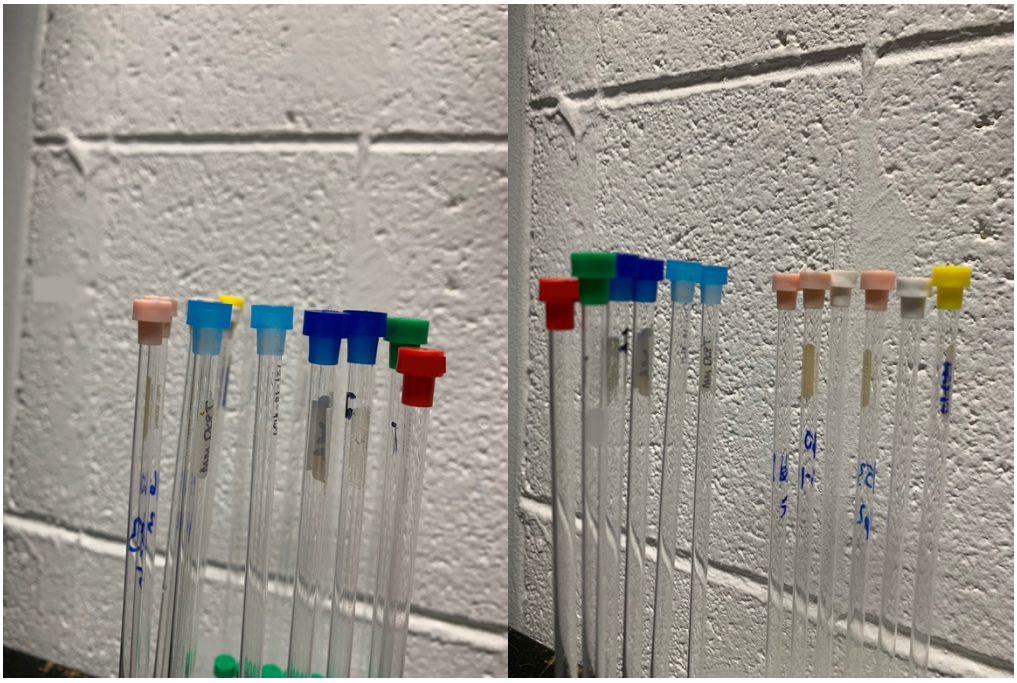
7. *There's a table now (soon) in front of CRB-109 for sample drop-off. Will Staff collect these samples to be run in CHEM1 lab?*

   No. Do not drop off samples destined for CHEM1 in CRB as they will not be collected.

NMR Tube Selection / Care and Feeding

One of the tubes in the pictures below should be inspected and rejected – discarded in the sharps waste and replaced by a new tube. Which one, what color is the cap? Why are you basing this on?

One of the tubes is apparently a bit different than the rest but intact? Which one? What do you think is going on here?



1 - visually inspect intact samples (caps on) by "stacking" them quickly, comparing with other tubes that are similar in size (7, 8, 9 inch). Further review tubes that are obvious "mis-fits" or your spidey sense tingles. You can also spot these after they go on the sample changer and one tube is obviously much shorter than others considering its group, manufacturer or style. 2 - some samples are "air-sensitive" meaning the sample will begin to degrade if the cap is removed so avoid doing that (unless criteria 1.). 3 - take a picture of the tube. 4 - open a private Slack channel with the submitter and attach the picture.

8:20

Fit and Polish - some tube manufacturers do not "polish" their tube tops where the cap fits. This is not a defect. You wouldn't know that anyway, because you didn't take the cap off, because the tube was a normal, regular height.

Cleaning and Drying It is widely thought that tubes baking in a drying oven can cause bending or other warping. See this article https://s3.wp.wsu.edu/uploads/sites/33/2013/10/NMR-Tube-Cleaning.pdf regarding how to clean tubes, suggesting that if they absolutely need to be baked to be cleaned, it should be only for 30 min, < 125C. Some say they should be laid flat, I believe they should stand vertically. Do not put caps in the oven as they will melt!

Historical Treatise on NMR Tubes, Glass, etc.

by Mike Olsen, Scientific Glass Blowing, Colorado State University

So, you're noticing there are patterns to glass failure? Don't feel bad - it took me decades to figure any of them out. It certainly did help having a couple of half-day seminars on glass fracture back in the 80s with Dr Josef Francel, the Mgr of New Product Development at Owens-Illinois (Kimble glass) who became a dear friend. I hate to say it, but you have to let the glass 'talk' to you, and an individual piece will tell you its story. There can be many issues involved in glass fracture, and you REALLY have to use your imagination to understand what REALLY happened to *that particular piece*, or what are now pieces...

So, an NMR tube has a history including its manufacture, storage and handling, usage, and cleaning. Then there are the applied forces from capping and spinning (and dropping), as well as any heating such as my attaching a valve to a tube. Then there's anything intrinsic to any potential meso-scale structure that glass might have at its surface or within its bulk, and how such structure might influence crack propagation. This last point is speculative, and where Roy and I left-off on a little bit of independent work we did about a year ago.

Now, to address your many questions, back in the early 80's I met Victor Plumbo, who with his brother invented the 'vacuum redraw process' used to fabricate precision ID tubing of many shapes and dimensions, including NMR tubes and multi-bore tubing. Using the Plumbo brother's technique of sucking a hot, slightly over-sized tube down onto a (I preferred W) mandrel coated with a release agent (typically colloidal graphite) I was making precision tapered ~1mm ID square-bored capillary segments for particle size spectrometry when working for https://www.pmeasuring.com/ in Boulder. Knowing I had done this, someone at Wilmad Glass later contacted me inquiring if I would be interested in fabricating NMR tubes for them at home in my spare time for $0.90/ea (they were about $10/ea retail at that time), and I declined.

NMR tubes are fabricated from a variety of glasses including fused quartz, but most typically of 'borosilicate' glass which is often described as 'Pyrex'. Borosilicate glass was invented in the late 19th century by Otto Schott in Jena Germany, and crafted into lenses by his good friend Carl Zeiss. That glass is now called 'Duran'. In the early 20th century the Corning Glass engineers (some would say reverse-) engineered several useful borosilicate glasses, so Corning's 'Pyrex' brand name includes several slightly different glasses (for example, the home cookware formula is different, and is now no longer even a borosilicate!), each identified by a 4-digit identifier. Standard lab Pyrex is 7740 (all my Pyrex is 7740), and the more expensive Pyrex NMR tubes are 7740. There are however cheap NMR tubes that are made from a chemically different 'Pyrex', and I'm not sure what it is, but the Chen group keeps buying them and asking me to attach 7740 J Young valves to them, and they won't stay attached due to a significant difference in the coefficient of expansion, resulting in bright stress 'fringes' when viewed in a polariscope. So, we've just touched on a first cause for NMR tube fracture: mis-matching of glass types when attaching a 7740 valve. I have attached a photo of two such tubes viewed in a polariscope, the right one showing colorful fringes at the base of the valve from a glass mis-match. But that's not really what you were asking about.

First, a word about annealing: my understanding is that NMR glass is so thin and low-mass that the redrawing process itself (where the closed-end of the evacuated tube is uppermost, and heat is applied with a multi-ported ring-burner, beginning at that closed end and proceeding downward) is intrinsically self-annealing, and after removal from the mandrel, the excess glass (which was attached to the vacuum source) is diamond saw-cut to length. Further, unless supported with a mandrel, any subsequent annealing (to 565 C for 15 min for 7740) will cause an NMR tube to sag or even noodle in the oven.

Dr Francel had a mantra that glass needs two things for a fracture to initiate and propagate: tension, and a surface defect. If you have one but not the other, it will not fracture. For example, putting a surface scratch under compression is OK. The saw-cut open end of an NMR tube is a gigantic surface defect

which will fracture if put under enough tension, like if the cap isn't put on right, or if cleaned with a pipe cleaner, or a q-tip is jammed in, etc. Then, there are NMR tubes that have been rattling around in a drawer, or tubes tinkling against each other and rolling around in a beaker. This is the history part I alluded to, as you get longitudinal scratching of the outside of the tube by scuffing in a drawer (the point of contact of a cylinder on a flat surface is a line the full length of the cylinder), and NMR tubes in a beaker will accumulate circumferential external scratches from contact with the beaker's rim. An NMR tube that fractures longitudinally was probably STORED differently than one that snaps in half.

Unless an NMR tube has been flame-worked, like attaching a valve (which I will briefly and crudely flame-anneal but will NOT oven anneal), there's really nothing that will show up in a polariscope. Close visual inspection of a tube at ~10X will indicate a tube that should be retired due to scratching, as scratches can't be repaired or polished. NMR tubes can easily be trimmed to eliminate jagged open ends, and I can also seal shut a broken bottom.

My final point regarding any potential meso-scale structure in the glass enabling or directing fracture is purely speculative, and based upon TEM images of quartz glass (containing 0.7 PPM of Na) showing a) a dramatically smooth surface on flame-polished and concoidally-fractured surfaces, and b) a very rough surface on ultrasonically 'crushed' samples, with the appearance of ~5 nm dia clusters arranged in twisted ropy columns. This last is something we have not seen previously discussed in the literature, and Prof Szamel also found intriguing. I can't imagine that anything post-manufacturing can affect internal glass structure, however what we observed over rather extensive regions all displayed a similar ropy axis of orientation that might presumably have different tensile strengths in different directions (presumably due to forces while still hot and plastic during manufacturing). Again, this anisotropy is tentative and speculative. I have attached a composite photo illustrating this: The red-boxed region in the lower-right image, is a very thin, conchoidally fractured surface (produced in a vortex mixer with isopropanol) which is enlarged as the upper-right image A. An FFT of A is the upper-left image, which exhibits a vague hexagonal pattern of bright spots. Two pairs of such spots were chosen (green boxes) and their inverse FFT produced the lower-left image labeled B (a sort-of dramatized topographic map). Combining images A and B enhances what I describe as a uniform ropy orientation. A third photo vaguely shows the ropy chains of 5 nm 'cotton balls' in a separate, ultrasonically produced fragment.

I<>n a similar vein, about 10 years ago I was wondering why some organic students would bring me lots of round-bottom flasks with star cracks, and other students from the same lab would not. The answer came to me with a thought experiment: Take two identical, empty 1 liter round bottom flasks. Hold them by their necks about an inch apart in front of you, and let them gently swing and tap each other - it's no big deal, but if you do it hard enough they might scuff. Now, fill each with a kilogram of water and repeat the experiment, and you'll probably wash the floor! Now, take those same flasks, plus several others of assorted sizes, submerge them in a tub of Nochromix, jiggle them around every day for a week or so, then drain, rinse and wash them in a tub with Alconox, similarly jiggling them around against each other in the suds. Just because they're submerged in liquid, doesn't mean they don't have exactly the same mass and velocity as when you held them in front of you in the open air. Thus, I propose that star-cracks originate from a sloppy dish washing technique. And, of those who bring me many flasks to repair, I have noticed that there are not just one or two, but sometimes seven or eight barely noticable star-cracks in some individual flasks - that was the give-away that it was an individual's technique of something that was causing them.

Keep the fire in your eyes!

- Michael