ARC-MMA&ISS User Guide during Phase 2A under CV-19 CRB-109 NMR Only

Updated July 15, 2020

The ARC MMA & ISS Centers hope to return to more regular, self service operations for our investigator cohorts, with options for training new users in the near future. This is an important and popular feature of the MMA & ISS that is highly anticipated. We know that most of you look forward to being trained by experts in the ARC as this enables you to design and run your own experiments on state of the art instrumentation.

However, many of the ARC-MMA-ISS labs continue to operate in **Full-Service mode only** during Phase 2a, although there will be more exceptions and options as we learn more about how to manage the CV-19 problem. Please discuss your specific needs with Lab Managers and Staff.

Additionally, we are moving to increased self-service NMR availability in the CRB-109 lab on both the ASC400 walkup NMR and the US400 NMR with SampleCase™. There will be announcements about that soon.

The 400 MHz NMRs in CHEM1 are still not *generally* available at this time for self-service operations. The 500 and 600 MHz NMRs are available for self-service, but *not* walkup NMR by appointment only through *Advanced NMR* service requests in the iLab.

To be very clear: Phase 2A protocols outlined below and at this time apply only to *NMR users seeking access to NMR resources in the CRB-109 lab only*.

Those CRB NMR resources are limited. You should continue to use the NMR resources in CHEM1 for BATCH, BUNCH NMR requests that will continue to be done by our Full Service program.

Samples needing more than ten minutes should not use the CRB NMRs *(without advice and consent from staff)*. Also, Project level and Special requests for NMR continue to be honored and managed in the CHEM1 building using the Advanced NMR request found on iLab.

CRB-109 General CV-19 Access Rules, Phase 2A (significant updates in purple):

- Pandemic PPE Must be worn at all times. Do not congregate in the hallway. Practice social distancing. Protective EyeWear is always required. Remove your gloves when you are not handling samples, before touching the keyboard, or non-lab building surfaces, door knobs.
- The CRB lab is open to all NMR operators. However, **our advice is** that investigators that are not resident in CRB please continue to use CHEM1 resources when they can. This is a CV-19 social distancing policy guidance.
- Time spent doing walkup NMR is considered part of your lab shift time as per guidelines.

(Note: if you have an approved, special NMR project in the CHEM1 lab – that is NOT considered part of your lab shift)

- 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. Staff continue to provide full service operations in CRB-109
- 1:1:1 ONE lab scientist may be on ONE console at a time. Only ONE lab scientist at a time may be on deck outside CRB109 waiting for either console.
- That is a total of two investigators, one at each NMR console, that may be in the lab at one time. The current occupancy in the lab is TWO. Plus, ONE investigator on deck. If you are in the hole then please remain in your lab area.

DO NOT CONGREGATE IN LOBBY!

- Only routine operations that can be complete in ten minutes on a sample may be done. Depending on user-feedback, these conditions may be relaxed at certain times of the day. For single samples please use the ASC400 walkup NMR, WUP, leaving the US400 with Sample Case for users with multiple samples to maximize efficiency in the lab.
- Please – do not hog the US400 samplechanger. Be aware of and considerate to your Shift Mates. Large sample volume needs that outstrip limited capacity, and severely limite others' use should continue to go to CHEM1 – just as you would do before the CV-19 pandemic.
- Slack Open Slots – US4 12 open – when you leave.
- 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 your 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.

PLEASE FOLLOW THESE STEPS for ACCESSING the ASC400 (WUP) and US400 (US4) NMR in CRB109 DURING YOUR WORKING SHIFT.

You Must also follow the Access Rules for CRB-109 during Phase 2A, highlighting the basic steps below.

DO NOT CONGREGATE IN THE LOBBY
1-1-1
W-W-W

STEP 1

PPE including face mask and safety glasses 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 NMR service through iLab "Request Service". You only need to do this once per month.

STEP 3

Use "Slack" #mma-crb109-general to virtually queue your walkup access.
!You Must Do this to Retrieve Samples, Too!

Please state in Slack whether Walkup (WUP), US400 (US4 #) with number, #, of samples, e.g. if eight samples then, "US4 8", or Retrieval (RET).

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.

When you are next in queue, go down and wait in the on-deck circle whether for Walkup (WUP), US400 (US4, #samples), or Retrieval (RET).

STEP 4

The NMR site is empty and so you may go in and do your routine NMR experiment. Practice good hygiene, social distancing in the CRB109 lab, and clean up after you are finished. *If using US4, SLACK number of Open Slots, e.g., "US4 10 Open"*

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. Just queue back up when you are ready.

ANALYTICAL RESOURCES CORE
COLORADO STATE UNIVERSITY

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

1. *"I have several samples I'd like to run, may I do this on the WUP…"*

   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. *"Everytime I get in to use the US400 (US4) there isn't enough room left for my samples.""*

   Bad Luck? Everyone – be sure to SLACK numbers of samples you submit in your Slack note: e.g., US4 6. This helps folks track availability of slots.

3. *Do I need to review the online notes about self-service access, submit my test as 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, WUP, 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, or WUP NMR.

   So, Maybe.

   Why not use the US400 SampleCase equipped NMR, US4 #, for this purpose?

5. *"Someones keep tying up the US400 with all their samples so why doesn't the ARC-MMA ban that activity!"*

   Ummm. Yea, might be bad form/etiquette? But we don't "ban" otherwise legitimate use of resources, and we aren't the etiquette police?! Suggestions: form an investigator user group and discuss this, apply gentle peer pressure, continue using the CHEM1 resources.

   We could turn on iLab calendar features to control access (!No, Please no!)

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, Shift Work. We are glad the US400 (US4 #) is now available to do more NMR.

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

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

8. *I am in CRB109. May I use the WUP instead if the US4 is tied up (and vice versa)?*

   Sure! Slack your intention, please, e.g., US4 # Complete check, WUP and go ahead and use the other NMR, obeying the new sample limits for that instrument, of course.

   .

CRB109 NMR Access Quiz One:

1. The phrase 1:1:1 refers to one person in the CRB109 lab, one person on deck, and one person in the lounge chairs. True False
2. You may run as many samples in CRB as you want because this is the most efficient and fast way to get your NMR data back. True False
3. The Slack Channel, #mma-crb109-general is used by investigators to communicate efficiently with colleagues their CRB NMR status and is not monitored by Staff. True False
4. CSU guidelines require that you wear the CV-19 appropriate PPE in CRB-109 even when you are alone. True False
5. The maximum occupancy of the CRB109 lab is two, plus one person retrieving their samples and one person on deck. True False
6. I can drop my samples off at the table in front of CRB109 and Staff will pick them up and deliver them back to me. True False
7. The Complete check mark should always be used on the Slack channel when I complete my NMR or sample retrieval and leave the lab. True False
8. The three functional positions for CRB109 are the WUP (ASC400 Walkup), US4 # (US400 SampleCase) and RET (Sample retrieval).

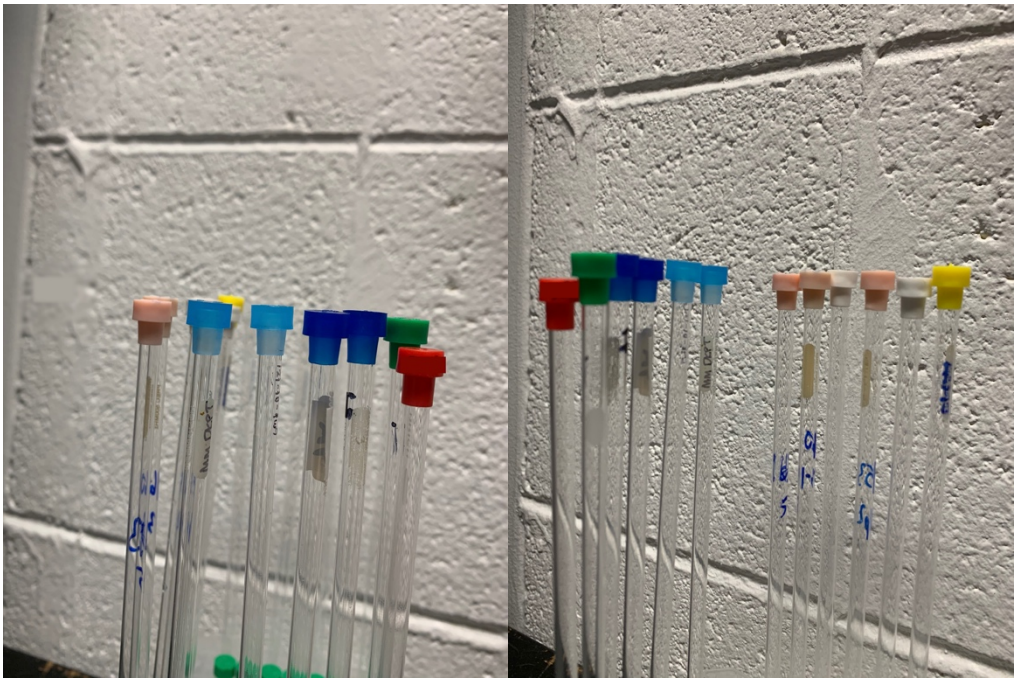
CRB109 NMR Access Quiz Two:

1. CSU guidelines require that you wear the CV-19 appropriate PPE in CRB-109 even when you are alone. True False
2. The maximum occupancy of the CRB109 lab is two, plus one person retrieving their samples and one person on deck outside. True False
3. I can drop my samples off at the table in front of CRB109 and Staff will pick them up and deliver them back to me. True False
4. The Complete check mark should always be used on the Slack channel when I complete my NMR (US4 or WUP) or sample retrieval (RET) and leave the lab. True False
5. The three functional positions for CRB109 are the WUP (ASC400 Walkup), US4 (US400 SampleCase) and RET (Sample retrieval).
6. The Slack code, “US4 6” means that it is my intention to put six samples on the US4 samplechanger.
7. It is a great thing to put my large number of samples on the US400.
8. One should Slack out the number of open slots on the US400, “US4 6 O”, when finished.

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 some groups 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