Standard Operating Procedure

Read the EH&S Standard Operating Procedures Fact Sheet before filling out this form. Print out the completed form and keep a readily accessible hard copy in the lab (also keeping an electronic copy is highly recommended).

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SOP Title: Flame-sealing NMR tubes under vacuum

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Section 1 – Process

First obtain a medium-walled NMR tube and charge it with the desired solution. Attach the tube to a Cajon adapter, making sure all o-rings are in place, and tighten the joint. Make sure that the opening of the tube is above the bottom o-ring as the joint is tightened; otherwise the system will not be sealed. If you are setting up the experiment in a glovebox, close the Teflon stopcock at this point; if you are setting it up outside the box, attach the setup to your Schlenk line and flush the solution with nitrogen or argon for about 30 seconds before closing the stopcock. Once the stopcock is closed and the solution is under inert atmosphere, attach the setup to your line and put the arm of the Cajon under vacuum.

Once the Cajon arm is evacuated, immerse the NMR tube in liquid nitrogen up past the height of the solution for about 30 seconds. Now open the Cajon stopcock to put the frozen solution under vacuum for about 30 seconds, then close the stopcock and remove the liquid nitrogen to allow the tube and the solution within to thaw under static vacuum. Be sure your hood sash is closed and lowered as far as it can be as the tube thaws; you should see bubbles of inert gas (and air if you set the experiment up out of the glovebox) leave the solution under static vacuum. Once the solution is fully liquid, reimmerse the tube in liquid nitrogen for 30 seconds, open it to vacuum for 30 seconds, close the stopcock and allow the solution to thaw once again.

Immerse the tube in liquid nitrogen for another 30 seconds and then put it under vacuum for 30 seconds, but instead of closing the tube off to vacuum, now obtain a butane torch and use the tip of its flame to make three or four "dimples" in the walls of the tube just below the joint of the Cajon. Now take the body of the tube (above the level of liquid nitrogen) between your thumb and forefinger and begin to apply gentle torque as you sweep the middle of the flame back and forth across the "dimpled" area. While handling the torch, make sure that if you are wearing gloves, that they are fire-retardant. As the glass begins to melt, you will be able to twist the top of the tube into a swirled shape rather resembling an ice cream cone; after making several turns and ensuring that the tube is now sealed, pull the body of the tube away from the Cajon, using the flame to melt and sever the string of hot glass

connecting the two. Gently place the sealed tube in secondary containment (a sufficiently tall Erlenmeyer flask should do) and allow it to thaw with the hood sash closed and lowered. Once the entire tube has reached room temperature, check the seal by inverting the tube and allowing the solution to flow to the swirled top. If there is a leak in the seal, you will see bubbles of air flowing into solution. Otherwise, you have successfully sealed an NMR tube. Backfill the Cajon adapter with the inert gas you use on your line and remove it, then disconnect the top of the NMR tube from the joint once it has cooled sufficiently.

Note: NMR tubes containing D_2O (or H_2O) as solvent should not be sealed using this method, as these liquids expand upon freezing and will crack the NMR tube.

Section 2 – Hazardous Chemicals

The chemical hazards of this procedure vary considerably depending on which solvents and solutes are present in the NMR tube being sealed; however, most NMR solvents share the hazardous property of flammability. Care should thus be taken to avoid contact of flame with the solution or heating the tube too near the solution's edge.

Section 3 – Potential Hazards

Aside from the hazard of flammable solvents mentioned in Section 2, the greatest hazard in this procedure is the possibility that the NMR tube will implode or (more rarely) explode. Occasionally, tubes will crack when thawing, which is why it is especially important to close the hood sash as tubes are thawing on the Cajon, and why a newly sealed tube should be placed in secondary containment. This is not a common occurrence, but it does sometimes seem to occur with neither rhyme nor reason, so the possibility should always be kept in mind. In our group, we have noticed that this occurs more often in tubes containing dichloromethane solutions than in other solvents. Also, tubes containing H_2O or D_2O should not be subjected to freeze-pump-thaw, as they will expand when freezing and crack the tube. A similar warning applies to any solvent whose density in the solid phase is lower than its density as a liquid.

Care must also be taken to avoid the condensation of oxygen into the tube when it is immersed in liquid nitrogen. Liquid oxygen, when mixed with any oxidizable compound, can be a shock-sensitive explosive and is extremely hazardous. Therefore it is critical to ensure that the Cajon adapter is tightly sealed and equipped with o-rings in good condition. The threads that tighten the joint of the Cajon adapter are prone to misalignment, which can allow oxygen to condense in the NMR tube. If the threads are aligned properly, a gradual increase in resistance will be felt when the Cajon joint is tightened. If the resistance felt while tightening the joint is abrupt, then the screws are misaligned and the joint must be loosened and retightened. Additionally, the condition of the Cajon adapter o-ring should be visually inspected prior to use. Taking these precautions will minimize the chance of a leak from the atmosphere. Sealing tubes under active, as opposed to static, vacuum will also reduce the risk this happening. Good hood sash technique, as mentioned in the above paragraph, is also important to minimize this hazard.

Care should be taken to avoid burning one's fingers by accident when using the butane torch, especially when twisting the tube and flame-sealing it simultaneously. It is also important that gloves worn at this point be fire-retardant. Vessels of flammable solvent should be removed from the hood while this operation is being performed.

Finally, butane torches used for sealing NMR tubes (and flame-drying glassware, *etc.*) should be stored away from solvent vapors. When such torches are exposed to solvent vapor for extended periods of time, the tubing within can degrade and leak, leading to a situation where the torch's entire top portion may be set alight and spew fire dramatically (and dangerously) upon ignition.

Section 4 – Approvals Required

It is not necessary to obtain approval each time an experiment of this sort is performed; however, if you have not sealed an NMR tube before, you should ask a student or postdoctoral researcher with experience in flame-sealing tubes to demonstrate proper technique on a "dummy" tube (*e.g.* filled with acetone), and to supervise you the first (and perhaps second) time(s) you seal a tube. Flame-sealing should not be performed when you are the only one in lab.

Section 5 – Designated Area

Flame-sealing of NMR tubes should be performed on a Schlenk line in a hood. Due to the flammability and explosion hazards, this operation should not be performed on a benchtop Schlenk line. If the tube is to be charged with air- or moisture-sensitive materials, this setup should be performed in a glovebox.

Section 6 – Special Handling Procedures and Storage Requirements

No general special handling requirements or storage procedures apply to this technique, though certain materials may require special care (*e.g.* air or light sensitivity). Sealed tubes should be stored in secondary containment. Torches used in the sealing should be stored in a well-ventilated area away from solvent vapors.

Section 7 – Personal Protective Equipment

Thick goggles, fire-resistant gloves and a fire-resistant lab coat should be worn at all times during this procedure, and the hood sash should be closed and fully pulled down whenever possible. If the material in the NMR tube is particularly energetic, use of a blast shield may be advisable.

Section 8 – Engineering/Ventilation Controls

It is essential that the fume hood used be operating well with a sash that moves smoothly and does not stick. If the experiment is set up in a glove box, it should be conscientiously maintained at appropriately low water and oxygen levels.

Section 9 – Spill and Accident Procedures

If an NMR tube breaks in the hood or in secondary containment as it thaws, the necessary cleanup will depend on what material is in the tube. If there is pyrophoric material in the tube, an appropriate fire extinguisher should be kept within quick and easy reach.

If a tube implosion or explosion causes non-life-threatening injury, administer necessary first aid and obtain medical attention. If the injury is life-threatening, call 911 (642-3333 from a cellular phone). Any injury must be reported to EH&S.

Section 10 – Waste Disposal

When a sealed-tube NMR experiment is complete, the tube can be opened by scoring around the sealed top with a file and cracking it open. If the contents may be pyrophoric, this should be done in a glove box. The contents of the NMR tube should be disposed of in a manner appropriate to the chemicals they contain (including quenching of any potentially reactive material). Once the opened tube has been cleaned, it may be disposed of in a glass waste box or reused for a second sealing, depending on its length.

Section 11 - Decontamination

No hood contamination should occur if the sealing is done properly; if a spill occurs (see Section 9), proper decontamination procedures will depend on the chemicals in the tube.

Section 12 – Process Steps

Process Steps	Safety Measures
1. Obtain medium-walled NMR tube, charge with solution to be used in experiment.	
2. Attach to Cajon adapter	Make sure that the threads of the Cajon adapter are correctly aligned to ensure a good seal
3. Flush with nitrogen or argon (if experiment not set up in a glovebox)	
4. Seal Teflon stopcock on Cajon	
5. Put arm of Cajon under vacuum	
6. Freeze solution in liquid nitrogen, ~30 seconds	Ensure no leaks present to avoid condensing liquid oxygen
7. Check that solution is frozen	
8. Put solution under vacuum (~30 seconds) by opening stopcock on Cajon	
9. Close stopcock on Cajon	
10. Remove tube from liquid nitrogen, allow to thaw	Make sure hood is fully closed
11. Repeat steps 6-10	
12. Repeat steps 6-8	
13. Use torch to “dimple” NMR tube	Use caution with flame and solvent level, make sure you are wearing fire-retardant gloves
14. Apply torque to NMR tube while running flame over top	
15. Twist tube several times into swirl pattern	
16. Pull tube away from Cajon, melt string of glass connecting the two	
17. Let tube thaw in secondary containment	
18. Check seal by inverting tube	
19. Backfill Cajon arm with inert gas and disconnect remnants of top of tube	Don’t burn yourself with still-hot glass or metal

Training Documentation

Name (Printed)	Signature	Date