Air Free NMR Tubes

We use air free NMR tubes to analyze samples containing Grignard reagents, and nickel-, phosphorus-, and lithium-containing reagents, but should be used for any potentially air sensitive compound.

There are two types of air free NMR tubes in our lab:

Screw-capped NMR tubes and **J. Young tubes**

The department glassblower maintains that both types equally air-tight.

Screw-Capped NMR Tubes

These NMR tubes are useful because the cap can be changed to suit the experiment. A **bakelite cap** (pictured above) will give you the best seal but will not allow you to add reagents outside of the box. A **septum cap** may give a worse seal but allows you to inject reagents via syringe, which can be useful for kinetics experiments.

Screw cap NMR tubes should be loaded with a sample in the glovebox, sealed using either cap, then covered with electrical tape for a greater seal before taking them out of the glovebox. Removing tape too quickly can cause you to break the NMR tube, so be careful.

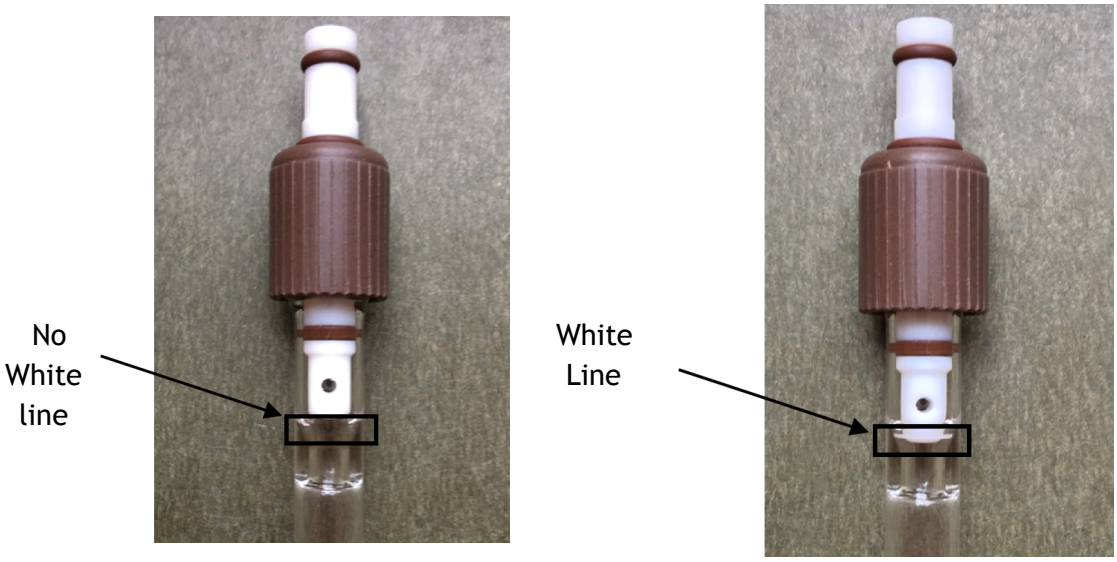
J. Young NMR Tubes

J. Young refers to the glassblower who invented the valve on the top of the tube. These NMR tubes are used to keep samples under nitrogen at normal pressure, but the valve that seals the tube can be connected to a Schlenk line using a Schleck-to-J. Young adapter to:

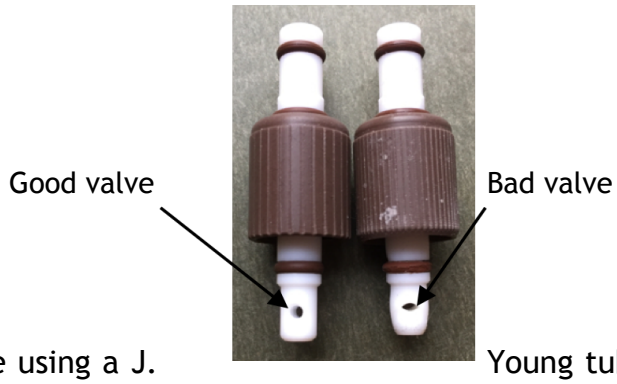
1. keep samples under vacuum or reduced pressure
2. freeze-pump-thaw solvents for NMR-scale studies

3. keep samples under an increased pressure atmosphere of nitrogen or other gases (i.e. H_2, ethylene, CO_2, etc.).

After loading the tube with your sample, the valve should be screwed on with two fingers only (*vide infra*). You will know that the tube is sealed when a small white line about 1mm thick appears at the point where the Teflon touches the glass of the tube:



We've had a problem with over-tightening the Teflon screw valves. You can tell if a Teflon valve has been over tightened by the shape of the hole at the bottom of the valve – if it's a circle, it's fine to use. If it's an oval, it's been crushed through over tightening at some point in the past, and may not seal the tube as well.



Note: if you are using a J. Young tube on the 700 MHz Ytterbium instrument for a 19F NMR study, poly(tetrafluoroethylene) in the cap can cause the baseline to be curved up in the -60 to -100ppm region.

Storing NMR Tubes

We store both types of NMR tubes in the gloveboxes. If there are none in your glovebox, check the ovens. To bring tubes into the glovebox:

1. Place the tube in an oven set to >130ºC overnight, and any caps or valves into a desiccator overnight
2. Quickly walk the tubes from the oven (and caps/valves from the dessicator) to a glovebox antechamber, and place them under vacuum in the antechamber for at least

five minutes. Refill the chamber with nitrogen, and repeat for at least two more cycles.
3. Bring the tubes into the glovebox, and place the tubes and caps into the place horizontally in the designated bin in the glovebox

Feel free to use as many as needed, but return them to the box as soon as possible keeping in mind that there are a limited number of air free NMR tubes in the lab.

Cleaning NMR Tubes

No seal is perfect, so air and moisture will get into the sample slowly. As such, Air-free NMR tubes should be cleaned as soon as the sample is no longer needed. Otherwise, elemental nickel could deposit onto the sides, grignard and organolithium reagents could eat at the glass, or phosphines and other organics could get absorbed by the cap and o-rings to contaminate future samples.

To clean an air-free NMR tube:

1. use an NMR tube cleaner with any solvent that can remove your sample, followed by water then acetone.
2. If there is still some residue, add at least 1.5mL of concentrated hydrochloric acid to the tube and let it sit overnight, then rinse the tube out with water in the NMR tube cleaner.
3. If this does not get rid of the residue, soak it in a stronger acid such as sulfuric acid overnight, and rinse with water in the NMR tube cleaner.
4. If this does not work, ask the glassblower for help. Other methods that clean glassware might end up destroying the tube.

Any NMR tube (including normal, non-sealable NMR tubes) should **never** be sonicated, heated with a torch, or placed high temp oven (>300ºC) as these can change the thickness of the glass and can ruin the NMR tube. Additionally, NMR tubes should never come in contact with strong bronsted bases, fluoride bases, or hydrofluoric acid. Borosilicate glass is slightly acidic and the silicon centers in the glass can be attacked by fluoride, so these reagents can eat away at the surface of the glass and destroy the tube or make the tube more fragile.

Broken NMR Tubes

As of October 2017, a J. Young tube costs about $50 for the glassblower to make. These are expensive and most labs have less than 10 of them because of this. To prevent breaking an NMR tube, you should avoid applying force to the NMR tube perpendicular to its length. During transport, you should carry your tubes in a 250mL Erlenmeyer flask that is cushioned with paper towel. If you've broken an NMR tube, save the threaded glass part (this is the most expensive part of the tube, about $45) clean it, and bring it to the glassblower so a new tube can be attatched.