Things to know before you begin operating an NMR

NMRs are expensive. They are delicate. Misusing or abusing them can cause thousands of dollars worth of damage.

Most damage is avoidable, some is not. If you understand how the instrument works, you will also develop some feeling for why things should be done a specific way. If, on the other hand, you do things your own way and disregard normal procedure, you run the risk of damaging the instrument so that you and everyone else will not be able to use it for an extended period of time.

Because of the danger posed by improper use of the instrument, those taking care of the NMRs often will revoke or severely curtail the access certain individuals have to NMR instrumentation. This is simply the reality of NMR operation in a multi-user environment. Please keep this in mind if and when an NMR caretaker has a word with you about proper operating procedure.

Liquid-state NMRs normally operate in the following manner:

A sample is made up in an NMR tube. The sample typically consists of a solute and a solvent. The solvent is usually deuterated, meaning that is has deuterons in place of its protons. A proper amount (0.6 to 0.7 mL when using a 5mm diameter NMR tube) of the sample solution (solute and solvent) is placed in an NMR tube.

Normal NMR tubes range in price from about a dollar per tube to more than $20 per tube. It is important to keep in mind that you get what you pay for. A cheap tube will often have a widely varying wall thickness, a varying outside diameter, and will have a prounounced bend or bow that will make it difficult to spin and shim. The more expensive the tube, the less likely it is that the tube can be blamed for poor results.

Using an expensive NMR tube does not guarantee good results, but using a cheap NMR tube will often give problems with spinning, shimming, and hence with the line shapes you obtain, not to mention the possibility that you may break your tube (if it is badly warped) and contaminate the NMR probe with your sample.

Improper cleaning of NMR tubes can also render an expensive tube useless. Do NOT leave NMR tubes in a drying oven for extended periods of time – this causes the tubes to warp and flow under the force of gravity, thus making them non-cylindrical. The best way to clean a tube is to rinse it with appropriate solvents and finish with a couple of rinses of HPLC-grade acetone. This final solvent rinse can be quickly expelled from the tube with either dry air, nitrogen, or argon blown through a drawn-out Pasteur pipet. If you want, you can also place the nearly-dry tube (don't start a fire!) flat in a glassware oven for ten minutes.

Placing the correct amount of solvent in the NMR tube is important for a number of reasons. The most important reason is that the standard shims you use as a starting point for shimming on your particular sample assume that the solution meniscus is located at a certain position above the detected region of the

sample. This means that with a normal amount of shimming you will obtain better signal-to-noise if you use 0.6 to 0.7 mL of solvent, even if this means diluting your sample.

In cases when the amount of the solute is limited, an extensive amount of shimming of the higher-order shims (z3, z4, z5, etc.) can compensate for the use of a smaller sample volume. That is, you have a choice: you can either spend more time shimming on a smaller volume of solution, or you can dilute your sample down to 0.7 mL and spend all the time that you would have had to spend on shimming just collecting data instead. Informed individuals often choose the latter, but in some cases – e.g., those working with small amounts of natural products – people actually do find it necessary to resort to non-standard shimming methods (pulsed field gradient shimming), special NMR tubes (e.g., Shigemi tubes), or even special NMR probes (e.g., Varian nanoprobes).

If the NMR tube slides up and down too easily in the spinner, then somebody has already contaminated the spinner (or it is old). If you notice that the tube slides up and down too easily, then you should either clean the spinner, use another spinner, or get an NMR-caretaker to help you clean or replace the spinner. If the tube slides down too far upon insertion into the magnet, bad things can happen (broken probe, broken sample, impossible to shim by hand).

Inserting a dirty tube into the NMR will cause two problems: one, it will deposit chemicals and/or dirt in the probe that will generate an unwanted background signal; and two, it will make sample spinning difficult.

The reliance of the lock circuitry of the NMR on observing the NMR signal from deuterons requires the use of isotopically enriched solvents.
This is why deuterated solvents are often referred to as NMR solvents. Deuteration of the solvent also serves another important purpose in that it allows one to observe the proton signals of the solute without a large proton signal from the solvent. The solute proton NMR signal would otherwise be overwhelmed by what would be a much more intense proton NMR signal from the solvent were it not for the replacement of the protons on the solvent molecules with deuterons.

Momentary changes in the magnetic field strength are also compensated for by the deuterium lock, as long as the changes do not occur too rapidly. This means that the momentary turning on or off of high-amperage electrical devices, e.g., laser power supplies, arc welders, etc., will normally not render an NMR completely unusable – although the effect of external perturbations are often apparent to the discerning eye. In general, the best NMR results are obtained when the rest of the world is asleep and not using electrical appliances and other devices.

The lock also serves another important function – it allows one to improve the homogeneity (evenness) of the magnetic field in conjunction with the shims.

Low quality NMR tubes have walls with a varying thickness, and the glass may itself have a heterogeneous composition. A perfect NMR tube will have an

invarying chemical composition, will be perfectly cylindrical, and will have a perfectly rounded bottom. Cheap tubes deviate farther from this ideal than do expensive ones, and hence cheap tubes introduce more variations in the magnetic field strength than do good ones.

Different NMR instruments and their probes will tolerate different amounts of abuse before they fail. The only way to know how much abuse is too much is to break them. This is not information you want to obtain.

If one understands the material and heeds the advice given in this document, then it is very unlikely that one will cause a great deal of avoidable damage to an NMR (with the exception of bringing a large ferromagnetic object near the magnet or when conducting a variable temperature experiment). To summarize, one should understand the importance of the following:

a good quality NMR tube
using a deuterated NMR solvent
using the proper amount of solution
cleaning and positioning the NMR tube in the spinner