

VARIABLE-TEMPERATURE NMR on the Varian Inova-400, 500 and VXR-300 NMR Instruments

September 26, 2006

This guide is intended to supplement proper training and formal check-out by the NMR Facility Director, or the Director's Designee. When doing VT experiments, improper operation (or decision making) can have disastrous consequences for the instrument and other users.

First, Some things to think about:

- Not every instrument/probe configuration is compatible with the same temperature range. For example, the 4-Nucleus (n4n) probe and the triple-inverse (ntr) probe on the 500 have a very limited temperature range (-20° to $+50^{\circ}$ C.), and exceeding this can cause damage that is difficult and expensive to repair. Be sure you know what temperatures are permitted on the instrument and probe that you are using.
- When doing low-temperature NMR with liquid Nitrogen as the cooling medium, you must switch the instrument to use N_2 gas instead of air. Also, when going to high temperatures (greater than 60° C.) it is important to switch to N_2 to prevent the heating element in the probe from oxidizing.
- Important: N_2 gas is supplied by the liquid- N_2 dewar near the door. Don't assume that there will be nitrogen available all the time. Plan ahead, and let Dr. Shoemaker know at least two days in advance if you will need nitrogen gas for VT experiments.
- The Probe tuning, and shimming, will change when you change the temperature (especially for changes greater than $\pm 20^{\circ}$ C.). So you will need to know how to check and tune the probe. Also, re-shimming the field after a temperature change is usually required.
- When things go well, VT-experiments are very simple to perform. When things go wrong, it can get complicated. Remember, if you are heating (going to high-temperature), and the temperature control "runs away", the most important thing to do is to get the heater turned off to stop the heating. If you are cooling (especially w/ liquid N_2 in the heat exchanger), the most important, immediate thing to do is to get the heat exchanger out of the liquid nitrogen to stop the cooling. A little common sense goes a long way.
- Don't attempt to do VT experiments on your own (especially very high or low temperatures) until you have gained extensive experience under Dr. Shoemaker's supervision, and have been checked-out to work on your own.

The following pages contain a detailed description of running VT-NMR experiments.

I. Setup:

- A. Switch to nitrogen gas if necessary (if cooling with liquid N₂, or warming to any temperature above +60⁰ C.), using the liquid N₂ boil-off tank near the NMR lab door. Air is OK up to +60⁰ C.
 1. Make sure all 3 needle valves (black knobs on the regulator assembly) are closed.
 2. Open the main "Use" valve on the tank, on the same line as that connected to the regulator. The pressure (secondary gauge) should read between 60-80 PSI. Adjust the regulator as necessary.
 3. Open the needle-valve for the instrument you are using (Inova-500, Inova-400 or VXR-300).
 4. Near the magnet, after the air filters, locate the needle-valves labeled "Air" or "A" and "N" or "N₂". Close the *air* valve, and immediately open the *nitrogen* valve. To ensure that nitrogen is flowing, check the VT-gas and "cooling" gas flow-meters on or near the magnet let. Other ways to check are the sample spinning and listening to the regulator by the tank (you should hear the gas flowing). Double-check the pressure at the nitrogen tank, as it may have dropped when you started the gas flow. Use the regulator to keep it at ~80PSI.
- B. Carefully check the hose connections to the VT-dewar on the probe (latex tubing), and the black rubber "bootie" on the heat exchanger (attached to the magnet leg). Check the VT-gas flow-rate (should be just above 10-15 LPM) and *cooling gas* (about 15-20 LPM) flow rates. Adjust if necessary. Re-check the hose connections after adjusting because back-pressure can cause them to pop-off.
- C. Insert your sample into the magnet. Lock, shim, and setup for your acquisition as you normally would. Even take a quick spectrum if you wish, to be sure everything is working properly before changing the temperature (optional).
- D. Select your desired (target) temperature:
 1. Type **temp <Ret.>** to bring up the temperature control widget in VNMR. Slide the temperature selector by holding the Left Mouse Button (LMB) on the slider, or click the LMB to the left/right of the slider. Wait a moment after each change, as the computer needs to catch up. The green light (LED) next to the temperature readout should begin flashing, as the VT-controller attempts to reach the target temperature.
 2. If your target temperature is below ambient, then now is the time to add cryogenics to the heat exchanger. Place the styrofoam bucket around the stainless-steel coils, and slowly add your cooling medium. It is important to ensure that nitrogen gas is flowing through the system before adding cryogenics to the heat exchanger.
 - a) For temperatures between ambient and -30⁰ C., dry-ice/isopropanol works better, but it is a little messy. DON'T USE ACETONE in the Styrofoam bucket!
 - b) Liquid nitrogen works well; however, initially add only enough liquid to cover the bottom coil. Once your desired temperature is reached, and is holding steady, you can add more liquid if needed (for extended-time runs).

3. Watch the temperature readout (the red LED display) closely, to ensure that the controller is functioning properly. Over-shooting the target temperature is normal; however, the temperature should eventually settle-in on the target temperature.
4. What if something goes horribly wrong?...
 - a) If the temperature starts running-away (out of control), don't panic. It takes a few minutes for your sample to freeze or boil.
 - b) As described in the introduction, turn off the heater if the temperature is over heating.
 - (1) On the 500, open the left-hand console door, and the Temperature Controller is about 1/3 down from the top of the rack. There is a black toggle-switch labeled "*heater*". Turn that switch off.
 - (2) On the 400, the Temperature Controller is on the BACK of the console. There is a black toggle-switch labeled "*heater*". Turn that switch off.
 - (3) On the 300, just turn the power OFF to the temperature controller on the console (little red button).
 - c) If the temperature is dropping uncontrollably, remove the bucket with the cooling medium from the heat exchanger immediately. As the coils warm up naturally, the sample will stop cooling.
 - d) If you are worried about your sample, you may eject it after performing step (b) or (c) above, as appropriate.
 - e) After you deal with the immediate danger, try to fix what went wrong.
 - (1) With the Temperature Control panel (widget) open, *click* the "Turn Temperature Control Off" radio-button. On the 300, you might need to turn the VT-controller back on, and then immediately *click* the radio-button again. The temperature should gradually re-stabilize at ambient.
 - (2) Check the VT-connector at the probe (cable with black-mesh cover, connected to the probe via a DB-9 connector (looks like a PC COM-port connector). Don't remove it, but make sure that it is pushed on tightly. Wiggle it a little if you want, but do it gently.
 - (3) Re-check the gas flow-rates, and make sure all hose connections are secure.

- f) Once things seem to be ok, *click* on the [Reset VT] button, and the temperature display should momentarily display “PASS”, and then begin reading the temperature. On the 500, make sure to turn the heater back on (black toggle-switch), and make sure that the temperature is stable. Now try to set the temperature again.
- 5. Hopefully, you won't need any of the advice in step #(4), and everything is running smoothly. To run your experiment, simply check the probe-tuning and re-tune if necessary. Of course, you must have been trained to tune the probe to do this. That's a separate manual.
 - a) Be very careful not to touch the VT-heater/sensor cable when tuning the probe. This is the most common cause of losing temperature control.
- E. Wait long enough for your sample to come to thermal equilibrium at the new temperature. Wait at least 5 minutes.
- F. Re-shim on the sample, after waiting for temperature equilibration. This is very important because thermal gradients wreak havoc with shimming. If you shim before the sample equilibrates, you are just wasting your time, and you will have to re-shim later anyway.

II. Run your experiment normally.

- A. You can reduce the “Temp” window to an icon by *clicking* on the small arrow in the upper-left corner of the window. Remember to re-open the same window to change temperatures, don't type “temp” again because you will open multiple copies of the widget, and possible cause instrument instability.

III. Changing Temperatures:

- A. You can change to a new temperature by simply moving the slider in the Temperature Control window; however, there is one important thing to keep in mind if you are transitioning from cooling to heating (or from heating to cooling).
 - 1. If transitioning from cooling to heating, remove the cryogenic liquid from the heat exchanger as soon as your target temperature is above ambient.
 - 2. If transitioning from heating to cooling, don't immerse the heat-exchanger coils in liquid nitrogen until the target temperature is below ambient.
- B. Don't forget to wait for the sample to re-equilibrate at each temperature.

See the Next Page for instructions for Quitting after VT experiments.

IV. Finishing/Quitting after VT experiments:

- A. Remove your sample (*e to eject*), and press “i” to turn off the eject air. Note that no sample is in the magnet at this point, and the eject air is off.
- B. If you are heating, and no cryogen is being used with the heat exchanger, simply turn off the VT Control in the Temperature Control Window. The green LED will (should) turn off, and the sample should begin dropping to ambient.
- C. If cooling, remove the cryogenic liquid from the heat exchanger first, then wait a few minutes as things warm-up, then set the temperature to about 20-degrees.
- D. When the temperature is nearing ambient (20⁰ C.), you can insert the reference sample (ethylbenzene in CDCl₃). Make sure to turn on the eject air first!
 1. Type **e <Ret>** to turn on eject air, and insert the sample normally.
- E. After the temperature has stabilized at or near ambient, lock and shim on the reference sample.
- F. Setup for normal ¹H observe (Setup [H,CDCl₃]) and type **su <Ret>**. Check the probe tuning, especially if you changed it during your experiment. Make sure everything on the instrument is put back to its normal condition (i.e. the 300 should be tuned for ¹H and ¹¹B observe). Re-Tune all channels of the probe that you might have used at the high or low temperature.
- G. *Click* on the radio button to “Turn Temperature Control Off”, and watch the temperature. If it drops below the normal (ambient) temperature, the environment inside the probe hasn’t had time to warm-up (after low-temperature experiments). You might have to wait longer for things to warm-up in this case.
- H. When the temperature is stable with the Temperature Control set to “off”, then you can close the Temperature Control Window (Hold Right Mouse Button (RMB) on the bar at the top of the window, and *select* “Quit”).
- I. Close the N₂ Valve by the air filters, and immediately open the “Air” (or “A”) valve on (open it completely). Close the needle-valve on the N₂ dewar regulator, and close the large valve on the tank (on the “use” port) tightly.