

## Temperature Control and VT Experiments on Varian Spectrometers

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**Calibration of Sample Temperature:** See section 3.5.3 in Claridge, and/or use the thermocouple probe available from the facility.

### I. VT Guidelines

**Be careful with the equipment! It is always the user's responsibility to ensure that VT experiments are performed safely.** Even relatively minor probe repairs can cost more than \$1500; a catastrophic tube break in the probe would likely cost > \$5000 to repair.

**Researchers should check the stability of their samples prior to performing VT experiments.** This requirement is particularly important for high-temperature experiments. If the sample is sealed, it (or a sacrificial sample) should be checked in a water or oil bath outside the NMR (i.e., in the researcher's lab) to insure the integrity of the sample and tube. Samples should never be run in the NMR if the pressure is estimated to rise above 5 atmospheres. Thick-wall NMR tubes can be purchased to improve the integrity of samples that might go above 1 atmosphere.

The potential exists during VT experiments of damaging or even destroying a magnet, with the associated repair costs running between ~ \$10,000 for a best-case scenario to ~ \$100,000 or more for a disastrous case.

**A. Probes** – There are five potential areas of trouble with the probe:

1. **Do not use a set-point outside the recommended range** for the probe you are using:

**bbext:**  $-150^{\circ}\text{C} \leq \text{temp} \leq +120^{\circ}\text{C}$

**bbswgo:**  $-100^{\circ}\text{C} \leq \text{temp} \leq +100^{\circ}\text{C}$

**hcx:**  $-100^{\circ}\text{C} \leq \text{temp} \leq +80^{\circ}\text{C}$

**hpx (500 & 600):**  $-150^{\circ}\text{C} \leq \text{temp} \leq +100^{\circ}\text{C}$

**hcn5 & hcn3:**  $0^{\circ}\text{C} \leq \text{temp} \leq +50^{\circ}\text{C}$

Older probes (ask Charlie) can go to higher temps.

2. **Always use N<sub>2</sub> gas** when performing VT experiments:  $\text{temp} \leq \text{ambient}$  or  $\text{temp} \geq 40^{\circ}\text{C}$ .

Using air, when hot, will degrade the probe components. Using air, when cold, will introduce moisture through the VT lines.

3. **Always turn off the heater current when the VT gas is stopped or interrupted** (e.g., during the switch from air to N<sub>2</sub> gas. To turn the heater current off:

on the UNITY: push the red button on the VT controller to turn the power off

on the INOVA: click the HEATER CURRENT switch—on the back right-hand side of the console—to off

4. **Make sure the probe body gas is kept at a good flow rate** for the temperatures you are working at; failure to do so will cause the tuning capacitors to freeze. ***Do not force the capacitors during tuning; if they appear to be frozen, warm the probe*** (or try increasing the probe body air, and wait 5 mins or so before trying again). The probe body flow should be increased until it is audible in the lab when working  $-80^{\circ}\text{C} \geq \text{temp}$  or  $+80^{\circ}\text{C} \leq \text{temp}$ . Ask where the probe body gas flow control is located on each spectrometer if you do not know.
5. **Do not freeze or boil your sample.**

*It is important to understand that the actual sample temperature can be 20 K or more from the VT set point!* Sample tubes can break and cause much damage in the process:

- a) **NEVER** go closer than  $\leq 5^{\circ}\text{C}$ —**actual temperature**—to a solvent's boiling point.
- b) Never go closer than  $\leq 15^{\circ}\text{C}$ —set-point temperature—to a solvent's boiling point without performing a temperature calibration *immediately prior* to the measurement(s) in question.
- c) Do not go closer than  $\geq 5^{\circ}\text{C}$ —actual temperature—to a solvent's melting point.
- d) The actual sample temperature (as opposed to the set-point temperature) depends upon the gas flow rate through the system. The relationship is not always what one might expect (e.g., a greater flow rate does not always lead to a more extreme actual temperature), so use the same flow rate used during temperature calibrations [and make a notation in your notebook as to the flow rate in every experiment].

## **B. Magnet** – The concern with the magnet is two-fold:

1. **The RT shim stack** (the barrel the sample floats through during insert and eject) must never be presented with temperatures  $> 70^{\circ}\text{C}$ . Staying within the recommended temperature ranges—shown above in section I.A.1—will prevent such trouble by keeping the outside of the probe body (which is in contact with the RT shim stack) below  $70^{\circ}\text{C}$ . It is important that good RT shim stack air is kept flowing during VT experiments. Ask where the RT shim stack gas flow is located on each spectrometer if you do not know.
2. **The vacuum** in each magnet is contained in a large dewared section joined by ~8" diameter o-rings at the top and bottom of the magnet. It is imperative that the o-ring not be presented to temperatures varying much outside ambient temperatures. If the o-ring fails, the magnet will likely quench (lose superconductivity), with significant time and

expense being required to get it back to field. The following steps are used to protect the magnet o-ring:

a) When working

*always* for experiments below  $-80^{\circ}\text{C}$   
for experiments lasting  $> 1$  hr below  $-40^{\circ}\text{C}$   
for overnight experiments below  $0^{\circ}\text{C}$

**turn on the Variac next to the magnet.** This will warm the heating tape wrapped on the magnet top and bottom. 35 is the typical setting for the Variac, but the rule-of-thumb is to have the Variac set high enough to only *warm* the heating tape; **the heating tape should never be hot to the touch!**

b) Use the top bore cap (usually kept in the U500 room) with the attached tube that leads the cold gas away from the top of the magnet for all temps as discussed in the previous paragraph.

## C. Sign-up Considerations

**Users must allow sufficient time for temperature equilibration of the probe and magnet following their VT experiments**—unless it is prearranged that the next user also wants to perform VT at or near the same temperature. This means allowing a **minimum of 30 minutes** for equilibration from VT measurements. *This time is required before a stable shim (line shape) can be obtained by the next user.* Greater temperature extremes require longer equilibration times (~45 mins to recover from  $-120^{\circ}\text{C}$ , if that temperature was held for  $> 1$  h). It is the responsibility of the user performing VT experiments to ensure that the research of others is not impacted by their experiments.

## II. VT Checklist

### A. Checklist for High-Temperature Experiments

**Researchers should check the integrity of their sample(s) prior to performing high-temperature experiments. See the warning and suggestions at the beginning of this document.**

1. All the newer Varian probes have an upper temperature limit of  $120^{\circ}\text{C}$  or less (see section I.A.1 above). If you need to go higher in temperature, see the facility staff about using one of our older probes.
2. Turn off the heater current (see section I.A.3)! Then switch the wall gas supply to  $\text{N}_2$  if you will be running  $\geq 30^{\circ}\text{C}$ ; this will prevent oxidation of the probe components. [Currently, both INOVA spectrometers run continuously on  $\text{N}_2$  gas.]

3. After switching the gas flow, turn the heater current back on, and:
  - UNITY: type **A** on the VT controller terminal, **T28.0** to change the set-point.
  - INOVA: type **temp** in VNMR, click on RESET at the bottom of the temp panel, and then move the temp in the panel by dragging the cursor to a *different* temp (not back to the same temp!). Change to the temp desired in step 7 below.
4. Adjust the probe body gas flow appropriately (see section I.A.4).
5. Insert your sample, and check the boiling point temp for your solvent system. Never go closer than 15°C for the set-point temp, **temp**, if you are unsure of the calibrations. *Never* closer than 5°C below the actual temp of the boiling point for a sealed tube.
6. Set the flow of the VT gas, and document this flow rate in your notebook.
7. Set the set-point temperature using the menu buttons MAIN MENU → UWMACROS → SETTEMP, or use the **temp** panel. Do *not* change the temperature parameter **temp** directly.
8. Allow at least 5 mins ( $\leq 10^\circ$  change) for the temperature to stabilize. For large temperature changes ( $60^\circ$  or more), it may take  $> 30$  min for the sample temperature and magnet/shims to stabilize.
9. You must tune the probe after all temp changes  $\geq 10^\circ\text{C}$ .
10. Shim and acquire data “normally.”
11. Change **temp** back to ambient (26°C) using the SETTEMP button (on the UNITY, remember that the actual setting is made on the controller terminal), and allow at least 15 min for cooling.
12. Turn off the heater current prior to switching the wall gas back to AIR (U500 only). Turn down the electronics gas flow. Once all is reset, set temp control to +26°C (see section II.A.2).

## B. Checklist for Low-Temperature Experiments

1. Check that the probe you will be using has a low-temperature limit sufficient for your needs (see section I.A.1). Note that the **hcn5** and **hcn3** probes on the INOVA-600 cannot go below 0°C (due to the triple-axis PFG in these probes, there is no VT dewaring in these probes).
2. Turn off the heater current (see section I.A.3)! Then switch the wall gas supply to N<sub>2</sub> (U500 only). If a dewared-LN<sub>2</sub> tank is required, check if it needs filling (charge to your group if so; the assumption is that charges for fills will even out over time). Use safety glasses and gloves when handling any LN<sub>2</sub> equipment (when the tank is full, LN<sub>2</sub> *will* splatter out—sometimes violently—when inserting the transfer line), and never shut (even partially) the door to the refill room while in the room!

3. After switching the gas flow, and hooking up the VT gas, turn the heater current back on:  
UNITY: type **A↵** on the VT controller terminal, **T28.0↵** to change the set-point.  
INOVA: type **temp↵** in VNMR, click on RESET at the bottom of the temp panel, and then move the temp in the panel by dragging the cursor to a *different* temp (not back to the same temp!). Change to the temp desired in step 7 below.
4. Adjust the probe body gas flow appropriately (see section I.A.4).
5. Insert your sample, and check the melting point temp for your solvent system. Never go closer than 15°C to this for the set-point temp, **temp**, if you are unsure of the calibrations. **Never** closer than 5°C actual temp above the melting point.
6. Set the VT gas flow, and document this flow rate in your notebook. It should coincide with the flow rate used for your temperature calibration.
7. Set the set-point temperature using the buttons MAIN MENU → UWMACROS → SETTEMP in VNMR (on the UNITY, remember that the actual setting is made on the VT controller terminal), or the **temp** panel. Do *not* change the **temp** parameter directly.
8. Allow at least 5 mins ( $\leq 10^\circ$  change) for the temperature to stabilize. For large temperature changes ( $100^\circ$  or more), it may take  $> 30$  min for the sample temperature and magnet/shims to stabilize.
9. If you are running  $\leq 0^\circ\text{C}$  overnight, or  $> 1\text{h} \leq -40^\circ\text{C}$ , or all experiments  $\leq -80^\circ\text{C}$ , turn on the heating tape via the Variac on the floor. This will prevent the magnet bore from getting so cold that the magnet o-ring seals freeze. ***Forgetting this step might damage the magnet!! The heating tape should never be warm to the touch;*** a typical setting is 35 (see section I.B.2).
10. You must tune the probe after the temperature equilibrates.
11. Shim and acquire data “normally.”
12. When finished, increase the temp in stages of  $\sim 20^\circ\text{C}$ . Wait  $\sim 3$  min before going higher. Once you are at ambient temps, wait at least 15 min for warming.
13. Turn off the Variac controller.
14. ***Turn off the heater current*** when equilibration is sufficient to not condense humidity in the probe/VT system. Failure to turn off the heater current at this step ***will*** damage the probe!!
15. Turn down the probe body gas flow.
16. Reconnect the normal AIR system (U500 only). Leave the transfer dewar hanging on the wall with a slow flow of  $\text{N}_2$  running through it; after another 30 mins or so this gas flow can be turned off.
17. Turn the heater current back on (section I.A.3) and set the controller temp to  $+26^\circ\text{C}$  (section II.B.3).