Variable Temperature Control Using a Cold Bath

The temperature limits for the U400 are probe dependent. For the QUAD probe, the limits are -60_C to +100_C, and for the VARIAN probe, they are -100_C to +150_C. The internal probe temperature is set using the parameter ***temp*** and changed using the command ***su***. A two-hour training/checkout is required before any user is allowed to use the VT system on the U400. The training/checkout procedure will include a couple of VT calibrations and a VT experiment on a sample, preferably your own.

p NOTES & PRECAUTIONS:

1. Follow the VT operating procedures thoroughly to avoid damage to the instrument.
2. Use a good quality NMR tube. If required, seal the sample under vacuum and seal it properly. A poor quality NMR tube or an improperly sealed sample is much more likely to break inside the probe at low or high temperatures.
3. Select an appropriate solvent for the experiment. For low temperature experiments, the freezing point and solubility of the solvent should be considered. For high temperature experiments, the boiling point of the solvent and its vapor pressure at studied temperatures should be considered. For high temperature experiments, the chemical properties of your sample at higher temperatures are also of paramount importance. Any sample that may react at elevated temperatures and expand in volume should never be placed in the probe at that temperature. ***Whenever possible, you should test your sample by putting it in an oil bath at _10_C higher than the highest temperature of your NMR experiment.*** If this can not be done, and you are not one hundred percent sure of the chemical behavior of your sample at high temperatures, do NOT put it inside the probe. The NMR spectrometer is not a testing ground for chemical reactions and explosives!
4. L-N2 is recommended as the cooling media for low temperature experiments. If for whatever reasons you need to use a dry ice/solvent or salt/ice cooling bath, be careful not to spill its contents and make sure that the dry ice or ice is crushed to small enough pieces so that they will not interfere with the raising of the dewar. *DO NOT FORCE THE DEWAR UP ONTO THE COIL*!
5. The VT air flow rate is normally set at 10 LPM, with N_2 gas flowing through the exchange coil at all times. If your experiment requires a temperature that is lower than -15_C, you may need to increase the flow rate accordingly, but no higher than 15 LPM, in order to reach the desired temperature in a reasonable length of time.
6. When starting a low temperature experiment, make sure that you enter a temperature lower than the current room temperature using the parameter **temp** (*e.g.*, **temp=0**) and do a setup using the command **su** before raising the dewar up onto the coil.
7. *ALWAYS CHECK THE PARAMETER* **temp** *IN THE* dg *PARAMETER GROUP BEFORE TYPING* **su**, **ga**, *OR* **go**. It is very easy to forget, but whenever you select a set of standard parameters using the Setup menus, or call up a data file from your directory, or do an **wft** or **ft** on the data you have called up, or join another experiment, the setting for the **temp** parameter will very likely be different from that of your current VT experiment.

8. When finished with a low temperature experiment, warm up the probe to 0_C, then lower the dewar off the coil very slowly to prevent or lessen the sudden pressure surge in the VT lines and the probe.
9. It is your responsibility to leave the system at room temperature and with the VT off.
10. Remember to turn the power supply to the solenoid on and off exactly as instructed.
11. If knowledge of the exact probe temperature is required, you can either calculate it from the calibration curves posted or calibrate it yourself. Be aware that a temperature calibration is dependent upon the flow rates for the VT, spinner, and body air. If any of these is changed, the calibrated temperatures for the same set temperature might be different.

~~~~~~

Low Temperature Operating Procedure

1. Set up the experiment as you would normally, *i.e.*, insert your sample (if your sample is not stable at room temperature, you should wait until the desired temperature is reached for the insertion), retrieve a standard shim file, select an appropriate set of standard parameters and make any necessary changes, lock on the sample, and shim roughly on Z1C and Z2C.
2. Enter the desired temperature using the **temp** parameter and start the temperature control with the **su** command.
3. a) Open the top cover of the VT cabinet and *turn on the power supply to the solenoid* on the front right-hand side of the VT cabinet.
   b) Put the dewar inside the holder and fill it with L-N2 to about 2/3 full, then place the dewar inside the VT cabinet — *make sure the handle is turned to the right-hand side of the cabinet door*, or you will not be able to raise the dewar.
   c) Raise the dewar slowly by pulling the cable on the opposite side of cabinet door. You can refill the dewar through the top of the VT cabinet, but you will need to be ***EXTREMELY CAREFUL NOT TO SPILL L-N2 ONTO THE POWER SUPPLY***. A cover for this power supply is being installed to prevent that from happening. Check the L-N_2 level in the dewar periodically and refill it when necessary to maintain a sufficient amount of L-N_2 to cover at least the full length of the coil.
4. The temperature should start to drop and the VT status light on the VT console should be flashing until the set temperature (±0.5_C) is reached.
   NOTE: You may need to increase the VT air flow rate to _15 LPM if you are going below -15_C.
5. Once the desired temperature is reached, any sample which cannot be handled at ambient temperature can be transferred into the probe.
6. Re-optimize the lock phase as well as the shims at the new temperature.
7. An equilibration time of 10 to 15 minute is needed for the sample to reach the set temperature after the VT status light becomes steady.
8. Check and make sure that the parameter **temp** is set to the desired temperature and start the acquisition as usual.

* * * * * * *
~~~~~~

9. When finished with the low temperature experiment, enter **temp=0** followed by an **su**. When the temperature reaches 0_C, lower the L-N_2 dewar off the coil very slowly to prevent or lessen the sudden pressure surge in the VT lines and the probe due to rapid temperature change of the coil. *NOTE: when the power to the solenoid is on and the dewar is lowered, the VT air bypasses the exchange coil and goes directly to the probe, thus providing a mechanism to cut off the cooling source immediately in case of an emergency such as a low-temperature runaway.*

10. After the dewar has been lowered off the coil, *turn the power supply off*, then set **temp=20** and do an **su**. Wait for 30 minutes before turning the VT off by entering **temp='n'** and **su**. *NOTE: You should remove the L-N_2 dewar from the VT cabinet so that the exchange coil can warm up to and stay at room temperature after VT has been turned off. Also note that setting **temp>20** during the 30-minute warmup period will NOT speed up the process, as only the probe will be warmed, not the exchange coil.*

11. After turning the VT off, monitor the temperature for another 5 minutes to make sure that it does not fall below 10_C, then logoff the instrument as usual.

~~~~~~

High Temperature Operating Procedure

1. Set up the experiment as you would normally, *i.e.*, insert your sample, retrieve a standard shim file, select an appropriate set of standard parameters and make any necessary changes, lock on the sample, and shim roughly on Z1C and Z2C.

2. Enter the desired temperature using the **temp** parameter and start the temperature control with the **su** command.

3. The temperature should rise fairly quickly and the VT status light on the VT console should be flashing until the set temperature is reached.

4. Re-optimize the lock phase as well as the shims at the new temperature.

5. An equilibration time of 10 to 15 minute is needed for the sample to reach the set temperature after the VT status light becomes steady.

6. Check and make sure that the parameter **temp** is set to the desired temperature and start the acquisition as usual.

* * * * * * *

9. When finished with the high temperature experiment, enter **temp= 'n'** followed by an **su** to turn off the VT. The temperature should come down rather rapidly to room temperature. Once room temperature is reached, logoff the instrument as usual by following the logoff procedure.

~~~~~~

Error Conditions:

Sometimes when you type **su** or **ga**, an error message such as *"VT does not acknowledge command"* will appear. If this happens, turn off the VT unit by pressing the red "POWER" button next to the "STATUS" light on the VT console under the laser printer. Wait 10 seconds, then turn the VT unit back on by pressing the "POWER" button again. Try **su** or **ga** again — everything should be working now. Please note the problem in the log book.

Emergency Procedures for VT Runaway:

High Temperature Runaway — Eject the sample with **e** <rtn>, turn off the power of the VT unit by pressing the red button on the VT console, and remove the sample from the top of the magnet. Try to regain control of the temperature by setting **temp=20**, turning the VT power back on, and doing an **su**. If the temperature does not start to come down, turn off the VT power and call for help.

Low Temperature Runaway — Lower the L-N_2 dewar from the exchange coil and eject the sample if there is a danger of freezing. Try to regain control of the temperature with the **temp** and **su** commands.

Low Temperature Calibration

— A neat sample of Methanol (CH_3OH) is used for low temperature calibration.
— Because there is no deuterium in the sample, the experiment will have to be run unlocked and shimming will have to be done using the FID.
— A typical low temperature calibration curve should at least have the following data points: 0, -20, -40, and -60_C. If time allowed, calibration at -10, -30, and -50_C should also be included.

* * * * * * *

1. Insert the sample and turn the lock off in the VNMR ACQUISITION window.
2. Load the standard shim file QUAD and select the standard parameters for 1H in D2O.
3. Set **pw=1**, **gain=1**, **nt=1**, **at=1**, and **lb=1**.
4. If you are doing a single-point calibration, set **temp=**desired temperature followed by an **su**. If you are doing the whole calibration curve, set **temp=0** for the first calibration point followed by an **su**. Then, raise the L-N_2 dewar with enough L-N_2 to cover the coil Remember to check the L-N_2 level in the dewar periodically and refill it when necessary.
5. Once the desired temperature is reached (indicated by a steady VT status light), set up an fid-autoshimming by entering **method='fz123'** and start it with the command **shim**. It will take 3 to 5 minutes to finish.
6. When shimming is complete, take a scan with **ga** and reference the right peak to 0 ppm. Then place the two cursors at 4 and -2 ppm respectively and type **movesw** to reset the spectral window.
7. Start the acquisition with **ga** and reference the right peak in the spectrum to 0 ppm. Then place the first cursor at the center of the left peak and the second cusor at the center of the right peak and type **tempcal('m')** (m for methanol), which will calculate the difference in Hz between the two peaks as well as the calibrated temperature.
   NOTE: An equilibration time of at least 15 minutes is required for the sample to reach the set temperature after the VT status light becomes steady. Whether or not the sample has reached the equilibrium temperature can be checked by taking two or more acquisitions at a 3-minute interval and measure the difference in Hz between the two lines and the calibrated temperature (see step 7 below). If the difference between two acquisitions is smaller than 0.5 Hz or 0.1_C, it can be assumed that equilibrium has been reached.
8. If you are doing the whole calibration curve, repeat step 4 to 7 for the rest of the calibration points.

~~~~~~
~~~~~~

High Temperature Calibration

— A neat sample of Ethylene Glycol ($HOCH_2CH_2OH$) is used for high temperature calibration.
— A typical high temperature calibration curve should at least have the following data points: 20, 40, 60, 80, and 100_C. If time allowed, calibration at 50, 70, and 90_C should also be included.

* * * * * * *

The procedure for high temperature calibration is essentially the same as that for low temperature calibration described above, except that

a) in step 4, if you are doing the whole calibration curve, set **temp=20** (instead of temp=0) for the first calibration point, and of course, you will not need to do anything with the VT cabinet by the magnet;
b) in step 7, type **tempcal('e')** (e for ethylene glycol) to calculate the real temperature instead of tempcal('m').