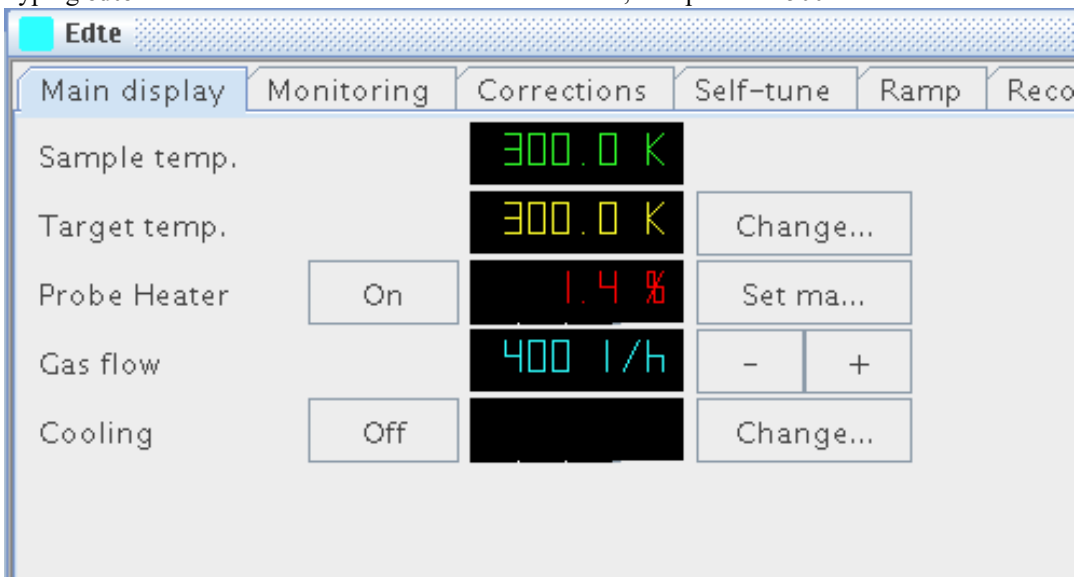
Variable Temperature

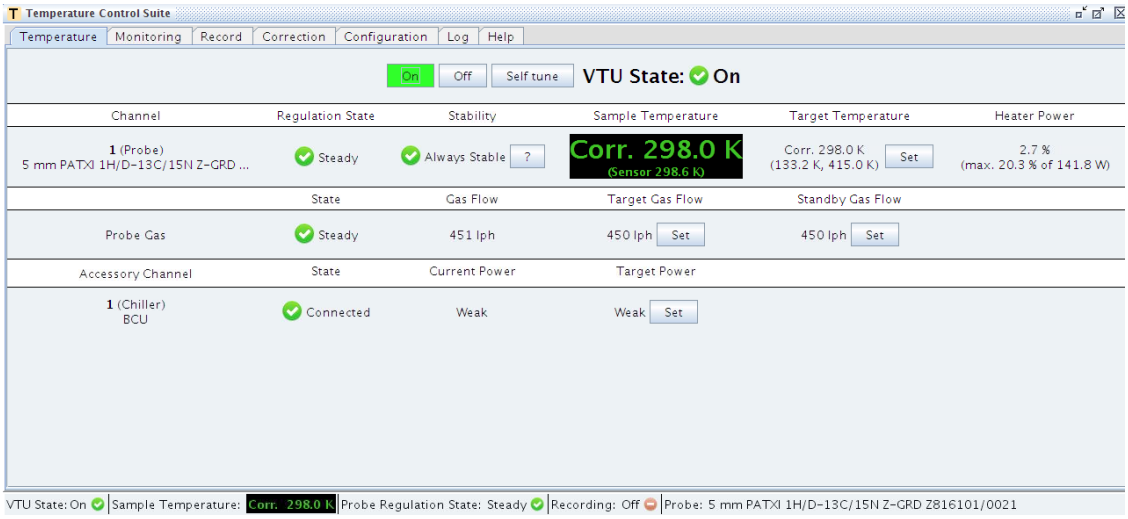
The variable temperature range is -150^{0}C (173K) to +150^{0}C (423K). <u>Do not exceed these ranges.</u> For temperatures above about 30^{0}C, the ceramic, or beige plastic spinner should be used. The blue plastic spinners will expand, deform and become stuck when heated above room temperature. Never use the blue spinners for high VT work. <u>The ceramic spinner should only be for VT work since it is fragile and will break if dropped (cost $1000)</u>. For low temperature work, it is best to use the ceramic or white spinner since they are heavier. Ask for assistance the first time you set up a VT experiment.

<u>Operating the Variable Temperature Controller</u>

There is a video that describes the operation of the VT controller for the 300wb. See below for details.
Typing **edte** starts the VT controller. Here is the interface, except on the 500 Ascend.



The 500 Ascend has a new VT interface and controller:



Low Temperature VT

This system works as follows: a heater within a liquid nitrogen dewar boils off cold gaseous nitrogen which then exits through an insulated hose that is attached to the probe by a ball-and-socket joint. This cold gas is then heated, by the sample heater, to the desired temperature. A sensor, located near the sample, sends a signal to the controller, which then increases or decreases the sample heater current so as to maintain the desired temperature. The following applies to all NMRs except the 500 Ascend. For the 500 Ascend, ask for a demo.

- Fill the liquid nitrogen dewar and insert the nitrogen boil-off assembly and hose into the dewar. Be sure an O-ring is in place. Clamp it using the metal compression fitting. A full dewar lasts at least 10 hours.
- Remove the green or black air hose from the probe and connect the nitrogen boil-off hose to the probe with the ball-socket joint. This ball and socket joint is very fragile and can easily be broken. To reduce the chances of breakage, be sure to not move the dewar after the hose is attached. That is, move the dewar into place and THEN attach the hose.
- Type **edte** to invoke the VT editor. Click on change next to target temperature and enter the desired temperature. There are two buttons within **edte**: **Heater** which enables the sample heater, and **Cooling** which enables the nitrogen boil-off heater. Turn these both on.
- You may need to adjust the cooling power which controls the current to the nitrogen boil-off heater. To do so, click on change next to the Cooling window. More current generates more cold gas. More gas allows a lower temperature to be reached but too much gas will lift the sample out of the probe. A value of 40% (300wb) or 55% (400SL) is the maximum usable value and allows a temperature of 180 K to be reached. You may also need to change (increase) the maximum sample heater current if the actual temperature remains below your set temperature. Do not set the max sample heater current above 50%.
- Once the target temperature has been reached, allow the temperature to stabilize for at least 10 minutes before taking an NMR spectrum. Although the controller may indicate the sample temperature is at the target value, the sample will lag behind the sensor because of its greater thermal mass.
- Once you are at the target temperature, the probe must be tuned and the sample shimmed. Both shimming and probe tunning depend on sample temperature.
- To shut down and return to room temperature, follow this procedure:
- Turn off both the sample heater and nitrogen boil-off heater. This is very important since the next step is to disconnect the gas source and the sample heater MUST BE OFF when no gas is flowing or it could burn out.
- Warm the ball-and-socket joint with the heat-gun. Often there is frost at the hose/probe connection and if the two are frozen together, forcing them apart can break the probe dewar (cost $600). Allow them to melt naturally, if necessary. Caution: the heat gun is slightly magnetic.
- Disconnect the nitrogen boil-off hose and reconnect the green or black air hose.
- Turn back on the sample heater and set the sample temperature to a value between the current temperature and room temperature. When this new target is reached, set the target temperature to 300 K, room temperature.
- Put away the liquid nitrogen assembly.
- **Allow enough time (at least 30 minutes) for the probe to warm to room temperature before the next person's time begins. Until the temperature is stabilized, the shim settings drift and a poor spectrum will result. Be courteous**!

High Temperature VT (above room temperature)

High temperature VT is much easier. Read the above procedure but the following is all that is necessary. One does not need liquid nitrogen for high temperature work.

- **The MAXIMUM Temperature is 150C.**
- Use the ceramic or beige plastic spinner. The blue plastic spinner expands, deforms and becomes stuck at high temperature. **Caution! The ceramic spinner will break if dropped and costs more than $1000.**
- Type **edte** to invoke the VT editor. Click on change next to target temperature and enter the desired temperature in Kelvin. Check the above limits on maximum sample temperature. Click on the **Heater** button which enables the sample heater. (it may already be on)
- When finished, simply enter a new target temperature of 300 K.
- Allow at least 30 minutes for the probe to cool before the next person's time.

Caution: Note the boiling point of your sample solvent and keep the temperature at least 10 K, below this value.

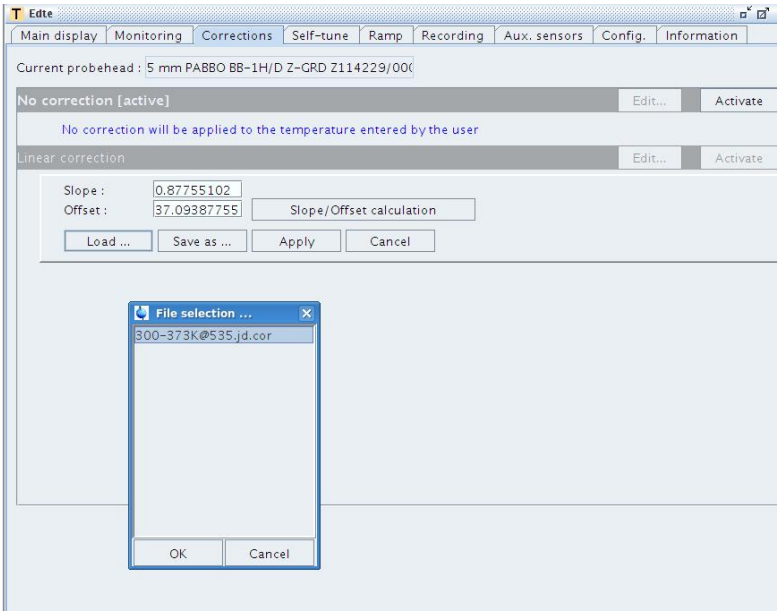
Near Room Temperature VT (slightly below)

For temperatures between 273 K and 300 K it is best to not use liquid nitrogen as the cooling gas. This is because the sample heater must be used at a very high current and provides poor temperature stability as well as increased risk of heater burn-out. It is better to use our ethanol bath with the electrical immersion cooler. In this set-up air passes through a coil of copper tubing that is immersed in cold ethanol. This acts as a heat exchanger and cools the air that then goes to the probe. Ask for a quick demonstration.

Temperature Accuracy

The indicated temperature on the controller contains a temperature-dependent error. For example, if the uncorrected temperature is 353K, the actually temperature is close to 359K. I have created two sets of correction factors, one for 300-373K and one for 180-300K. Whether or not the correction factors are enabled depends on the state the previous user left it. To enable them, start the temperature editor with edte. The following is for the 500 Ascend but the procedure is similar for the other NMRs. Select the Corrections tab, click Edit on the Linear Correction line, as shown below:

Then, click "load…" and select the file 300-373K@533.jd.cor or 200-293K@40%.jd.cor, as appropriate. Click apply and then click Activate on the linear correction line. The blue message "No correction with be applied…." under the grey No Correction remains but that is not important. Look ONLY at the grey lines for which mode is active. To disable, click Activate on the No Correction line.



The proper correction factor depends on air-flow rate and 535 l/hr is the calibrated rate. For low temperature using the LN2 evaporator, the flow is determined by the heater percentage and 40% is the calibrated rate.

To know the actual temperature it is necessary to use an NMR thermometer - the temperature dependent shifts of methanol or ethylene glycol. Over the range 250-320K the difference in shift between the methyl and hydroxyl resonances of 100% methanol, d in ppm, is given by

$$T(K) = 403.0 - 29.53\ d - 23.87\ d^2$$

Over the range 300-370K, the difference in shift between the methylene and hydroxyl resonances of 100% ethylene glycol, d in ppm, is given by

$$T(K) = 466.0 - 101.6\ d$$

both of these equations are taken from Cavanagh, Fairbrother, Palmer, and Skelton, "Protein Spectroscopy", Academic Press, New York, 1996. Bruker supplies a program, calctemp, that will calculate the temperature from a spectrum of methanol or several other common thermometer samples.

Videos

There is a training video on how to do variable temperature NMR, with emphasis on low temperature NMR. It can be viewed from NMR web site.