

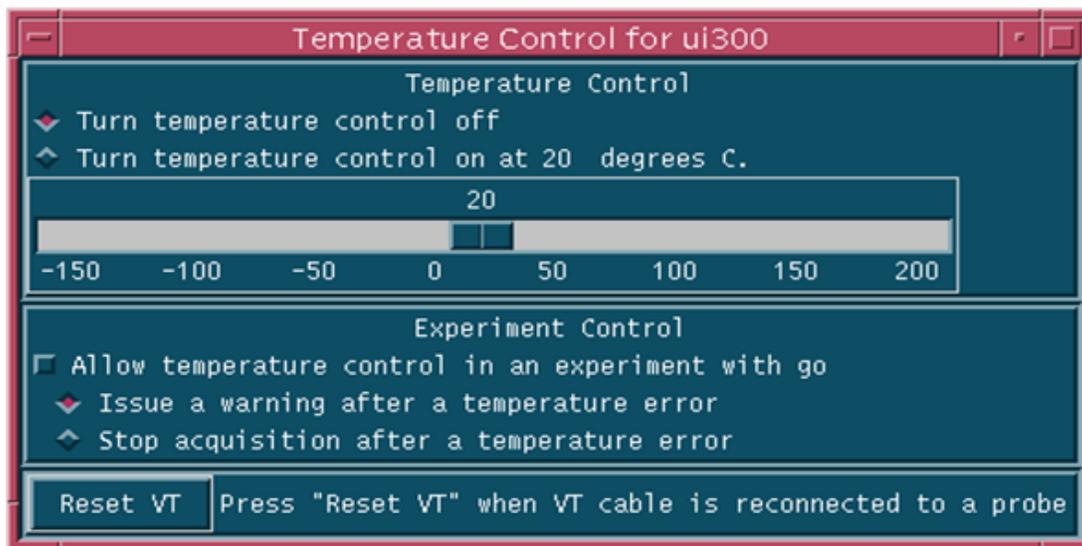
Variable Temperature Control Including Use of the FTS Unit

You need special training from NMR Lab staff to perform VT on any spectrometer. *Get trained before you proceed.* This approach to VT control allows both easy heating and cooling. Spectrometers not equipped with the FTS Unit typically need liquid nitrogen for cooling. The lowest probe temperature using the FTS device is -70 degrees C. Probe temperatures below -70 °C require the use of Liquid N₂ on a non-FTS unit.

Keep the temperature 10°C above the freezing point of your solvent, and 10°C below its boiling point!!

Equipped with FTS Unit: UI500NB, UI400, & VXR500 (FTS unit default off)

Not Equipped with FTS Unit: U400 & U500



Always Keep Checked: “Issue a warning after a temperature error”

Basic Operation

- 1) Temperature control on all spectrometers is done via the Temperature Control window shown above. If the window is not open and the icon is not present, type “**temp <rtn>**” to open it. Locate the window conveniently on the screen so you can monitor its settings. You may minimize it once a stable condition is achieved (click the small dot in the upper right corner of the window).
- 2) *Never* check “Allow temperature control in an experiment with go”. Leaving this *unchecked* deliberately disables temperature control with the commands “temp=## su” within individual experiment; this is the safest approach compared to other options. Instead, just check “Issue a warning after temperature error”.
- 3) To change the temperature:
 - a) Left click on either side of the slide bar. Clicking on the low side lowers the temperature and clicking on the high side raises it. A left mouse click changes the setting by 1°C per click and a right mouse click changes the setting by 0.1°C per click.

b) Temperature changes should be made in steps of 20 °C or less. Allow several minutes before the next temperature change. Otherwise, your sample tube can break, the probe can be damaged, and your advisor can be billed for costs!

- c) Click to the left or right of the bar to decrease or increase the setting – but do so very carefully! It is safest to just click, not slide, your way to the desired setting.
 - d) It can take 10-15 minutes to achieve a target temperature, so be sure to make a reservation long enough to achieve the initial temperature, and allow about 10 minutes to return the probe to room temperature.
- 4) When you are done, change the temperature to 20°C, then click “Turn temperature control off.” As mentioned above, change the temperature gradually. In addition, close the Temperature close window; no icon should remain. Press Set Point 1 on the FTS if you used the FTS. Confirm that the probe temperature returns to room temperature.

Temperature Determination and Calibration

The digital VT panel readout gives the probe temperature as measured by an uncalibrated thermocouple in the probe. Actual sample temperature is best determined with a neat solvent in a separate reference tube. After you determine the temperature of the reference sample, insert your sample of interest, and it will achieve the same temperature in a minute or two.

Reference tubes typically available in the NMR Lab contain neat methanol or neat ethylene glycol. Generally, you take a spectrum and the difference between two reference peaks is converted to temperature. When you do this, it is nice to have the x axis in Hz. Switch axis labels by typing axis = ‘h’ and switch back by typing axis = ‘p’. You can always reference one peak to zero Hz by typing rl(0h) and then measure directly the difference in Hz between two peaks.

To determine the temperature, insert, for instance, the methanol reference sample. Acquire a 1-scan spectrum, and shim only if necessary. Set the left cursor on the left (-OH) peak and the right cursor on the methyl peak. Type:

tempcal(‘m’)

and the software gives you the temperature. If you use neat ethylene glycol, again set the cursors, and type

tempcal(‘e’)

Alternatively, you can go to the SCS NMR web page and use the NMR Thermometer Spreadsheet at:

<http://scs.illinois.edu/nmr/handouts/>

This spreadsheet contains citations for the temperature formulas it employs. It also provides advice on what neat solvents to use for specific temperature ranges. See the appendix for a screen snap of this spreadsheet.

For 25°C, use methanol.

NOTE

- Minimize the temperature control window after you adjust it; this prevents accidental changes.
- If you type **vtype=2** and perform an acquisition (**ga**), it will not acquire until the set temperature is achieved.
- If you type **vtype=0** and perform an acquisition (**ga**), it will acquire immediately, regardless of temperature.
- You cannot type temp to get the temperature control window unless **vtype=2**. After that, you can change the vtype setting to zero if you wish.
- Typing **vtype?** will reveal if the current vtype setting is 0 or 2.

FTS Emergencies – Important!

It is possible that the VT control software malfunctions, the FTS malfunctions, or you malfunction. The alarm usually sounds when the temperature goes up too quickly. You should approach high temperatures in smaller steps as you click beside the slide bar to set the temperature.

If the temperature runs away or if the FTS alarm sounds, do this:

- **Immediately “eject” your sample – it could explode or leak!**
- **Remove the spinner and sample from the top of the magnet**
- **Turn off the black VT control box at the back of the NMR Console**
- **Turn off the FTS toggle switch on the front of the top unit**
- **In the VT control software “Turn temperature control off”**
- **Turn up the VT gas to 15 L/min to make temperature equilibration faster**
- **Wait until the VT panel readout reaches a temperature close to room temperature**
- **Adjust the VT gas back to 10 L/min**
- **Turn on the FTS toggle switch and hit SP1**
- **Turn on the black VT control box at the back of the NMR Console**
- **Resume normal operation: put a sample back in the magnet and type “insert”**

The FTS alarm can also sound because of a pinched gas delivery tube, the house nitrogen being down, or a VT electronics malfunction. Ask the staff should any of these seem to occur. If you turn off the VT control panel in the back of the console, the VT software will probably hang, and you should probably just tell the NMR staff this has happened.

FTS Normal Operation

1. FTS Set Points:
 - SP1 = 25°C
 - SP2 = 0°C
 - SP3 = -20°C
 - SP4 = -40°C
2. Default Settings:
 - SP1
 - RUN ON
 - VT temperature set to 20°C, but make all temperature changes *gradually*.
 - VT **Off** in the VT control window (you may have to hit the button more than once).
3. Temperature Ranges:
 - The temperature range of the FTS unit is about -80°C to +25°C. Heating is performed by the probe.
 - The VT range of the NMR probes is variable, and posted on the magnet. *Do not exceed those limits.*
4. Normal Operation:
 - Select a set point on the FTS - **usually at least 10°C lower than desired temp**
 - RUN light ON (FTS panel)
 - In VNMR, set temperature to desired value. ***Temperature changes should be made in steps of 20 °C or less. Allow several minutes before the next temperature change. Otherwise, your sample tube can break, the probe can be damaged, and your advisor can be billed for costs!***
 - When finished, return to default settings in 2, above, but again, make temperature changes *gradually*.

SPECIAL NOTE: To achieve the lowest possible temperature, turn RUN light OFF on the FTS panel (press Run once), and increase the VT air flow to about 15 L/min (normally set to 10 L/min). Remember to change the VT air flow rate back to 10 L/min when you are done.

5) To Finish:

- Set the VT window to 20°C, but make all temperature changes *gradually*.
- Set FTS Unit to defaults:
 - SP1 and RUN ON (these are default settings)
 - Don't skip SP buttons: if you are on SP4, use SP3, SP2, then SP1
 - Bottom unit (chiller) OFF
- Change to standard sample (NMR dummy tube or 1% CHCl₃/CDCl₃)
- Set VT gas flow rate to 10 L/min on meter
- Wait until a temperature within 5 degrees of room temperature is achieved on the red digital readout
- VT **Off** in the VT control window (you may have to hit the button more than once)
 - Close VT control window so that it disappears
- Type logoff and sign out of log book as usual

Sample and Standard Handling Strategy

Here is a sequence of operation to use for analyzing a shimmed sample at a calibrated temperature.

- Put an NMR tube of your solvent only into the magnet. Lock and shim.
- Change the temperature to the target temperature, and maintain lock and shim
 - This requires prior knowledge of the setting needed to achieve the desired temperature
- After thermal equilibration and shimming, remove your solvent blank, and insert your sample.
- Allow for thermal equilibration, shim, and take data as desired on your sample.

Helpful Information

- The boiling point of liquid nitrogen is -196°C .
- The boiling point of ethylene glycol is $+197^{\circ}\text{C}$.
- In Mnova, the package called "Reaction Monitoring" is very useful for dynamic studies of kinetics or thermodynamics because of the way it can display and analyze data with models.
 - The Arrayed Data section is especially helpful for display of a series of spectra

Liquid Nitrogen Use

The basic procedure is:

- Establish temperature control via the VT control window; set the initial temperature to 10°C .
- Position the bucket in place
- Pour liquid nitrogen into the bucket via the hole on top
- In 20-degree steps, proceed to your target temperature
- When done with NMR work, return to 20°C , but leave VT control window open and on
- Lower the liquid nitrogen bucket
- Wait for the cooling coil to warm up
- Turn off the VT control, and make sure you have a resultant temperature close to room temperature
- Close the VT control window and again, make sure the readout temperature is near room temperature

Appendix (see chart on next page)

An Excel spreadsheet is available as an alternative way to compute temperatures from reference spectra. A screen snap is shown below, and the spreadsheet is available on the NMR Lab web page under:

- Handouts and Tools
 - NMR Temperature Calculator

	A	B	C	D	E	F
1						
2	Spreadsheet from U Colorado, Boulder; Compliments of Rich Shoemaker					
3	Ethylene Glycol is useful for temperatures from ~300K to 380K					
4						
5	Temp. (Kelvin) <i>[Enter Value]</i>	Delta(ppm) [100% Ethylene Glycol]	Delta(ppm) [80% Ethylene Glycol in d6DMSO]			
6	350.0	1.1486	1.0218			
7						
8	Delta(ppm) [100% Ethylene Glycol] <i>[Enter Value]</i>	Temp.(Kelvin)		<p>Source: Bruker Instruments, Inc. VT-Calibration Manual</p> <p>80% Ethylene Glycol (DMSO-d6): $T = (4.218 - \Delta)/0.009132$</p> <p>100% Ethylene Glycol: $T = (4.637 - \Delta)/0.00967$</p> <p>($\Delta$ is the shift difference (ppm) between CH₂ & OH peaks)</p>		
9	1.4400	320.76				
10						
11	Delta(ppm) [80% Ethylene Glycol in d6-DMSO] <i>[Enter Value]</i>	Temp.(Kelvin)				
12	0.9	365.00				
13						
14						
15	Methanol is useful for temperatures from ~180K to 300K					
16						
17	Temp. (Kelvin) <i>[Enter Value]</i>	Delta(ppm) [100% Methanol]		<p>Source: Bruker Instruments, Inc. VT-Calibration Manual</p> <p>100% Methanol: $T = -23.832\Delta^2 - 29.46\Delta + 403.0$</p> <p>($\Delta$ is the shift difference (ppm) between CH₂ & OH peaks)</p>		
18	180.00	2.5027				
19						
20	Delta(ppm) [100% Methanol] <i>[Enter Value]</i>	Temp.(Kelvin)				
21	1.5050	304.68				
22						
23						
24	Temp. (Kelvin) <i>[Enter Value]</i>	Delta(ppm) [4% Methanol]		<p>Source: Bruker Instruments, Inc. VT-Calibration Manual</p> <p>4% Methanol in Methanol-d4: 180-300K, $T = (3.86 - \Delta)/0.00782$ (approximate)</p> <p>for more accurate values, use the following, depending on T: 180-230K, $T = (3.72 - \Delta)/0.007143$ 230-270K, $T = (3.92 - \Delta)/0.008$ 270-300K, $T = (4.109 - \Delta)/0.008708$</p> <p>($\Delta$ is the shift difference (ppm) between the CH₂ and OH peaks)</p>		
25	280.00	1.6704				
26						
27	Delta(ppm) [4% Methanol] <i>[Enter Value]</i>	Temp.(Kelvin)				
28	2.4524	180.00				
29						