High Temperature NMR

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Special Note:

This guide is intended to supplement proper training and formal check out by the NMR facility manager. Improper operation or decision-making when doing variable temperature experiments can have disastrous consequences for the instrument and other users.

How the NMR regulates the temperature:

Bruker uses a feedback loop to regulate the temperature. Figure 1 highlights key components of this system. The temperature is measured by a thermocouple sitting below the sample. The entire probe is heated using an electrical heater located at the bottom of the probe. This heat is then transfer using air flow.

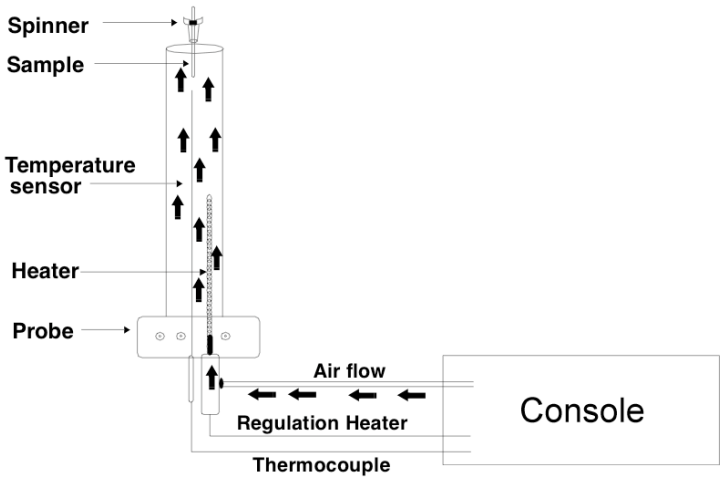

Figure 1. The key components of the temperature regulation system for Bruker NMRs. Note that this diagram is not to scale.

DOs and DO NOTs:

DO	DO NOT
Reserve at least 2 hours of time to elevate the temperature to 90° C, record a 1H 1D and cool the probe back to room temperature.	Get in a hurry
Use the white ceramic spinners for temperatures above 50° C	Use the blue plastic spinners for temperatures above 50° C

Increase the temperature in 10° C steps and allow it to equilibrate	Increase the temperature too rapidly.
Increase the gas flow up	Increase the maximum heater power to more than 10%
Know the boiling point of your solvent (see Appendix 1 for boiling points of common solvents)	Approach the boiling point of your solvent
Keep temperature below 90° C	Go above 90° C (see Justin if you need higher temperatures. Above 90° C we switch to N2 gas instead of air to prevent oxidation of the heating element)
Know that your compound is stable at the temperature you sample	Explode a sample in the probe. You will be held financially accountable for any damage to the probe.

How to set up high temperature NMR experiments:

#-1) Make sure you've gone over this procedure with Justin or Sarah before you begin.

#0) Use less solvent. You want a short sample (~25 mm or ~ 350 μL). This will make it harder to shim, but easier to maintain temperature across the sample. If you need help shimming Justin or Sarah will be happy to help.

#1) Insert your sample into the spinner and use the depth gauge to set the sample depth. Use the white ceramic spinner for temperatures above 50° C. The spinners are ***usually*** located in the second cabinet from the right on the south wall in Malott B042 and the top drawer on the right in SBC. The blue plastic spinners will warp at higher temperatures. The ceramic spinners have a "tighter" fit to the o-rings, so be careful inserting your tube.

#2) Log into the workstation. Follow the normal steps to set up your dataset, load acquisition parameters and lock.

#3) Type edte at the command line to open the temperature control window. Figure 2 shows the main display tab of this window.

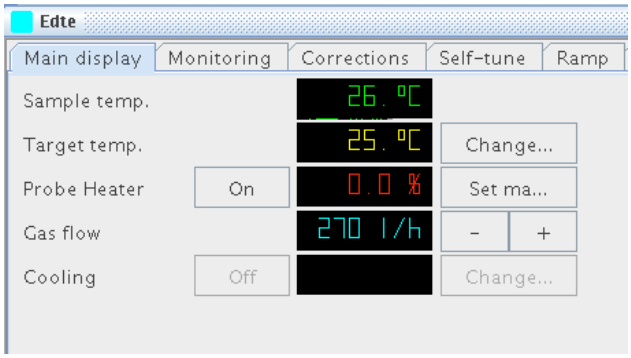

Figure 2. The main display tab of the edte window.

In this tab we monitor the current sample temperature, the target temperature, the output of the probe heater and the gas flow.

#4) In order to accelerate the response of the temperature regulation system, we increase the gas flow. If going to high temperatures, you can increase to 670 l/h (Fig. 3), although it is OK to use less. Click the + button once and see if that is enough to get to the desired temperature in a reasonable time.

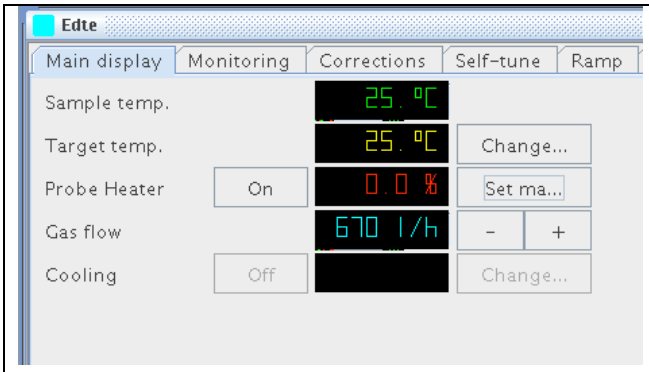

Figure 3. Increasing the gas flow.

#5) Click the change button to the right of the target temperature. Enter 35° C. Click on the monitoring tab to observe the sample temperature (green), the target temperature (yellow) and the heater output (red) as a function of time (Fig. 4). It will take ~ 5 minutes for the system to equilibrate (Fig. 5).

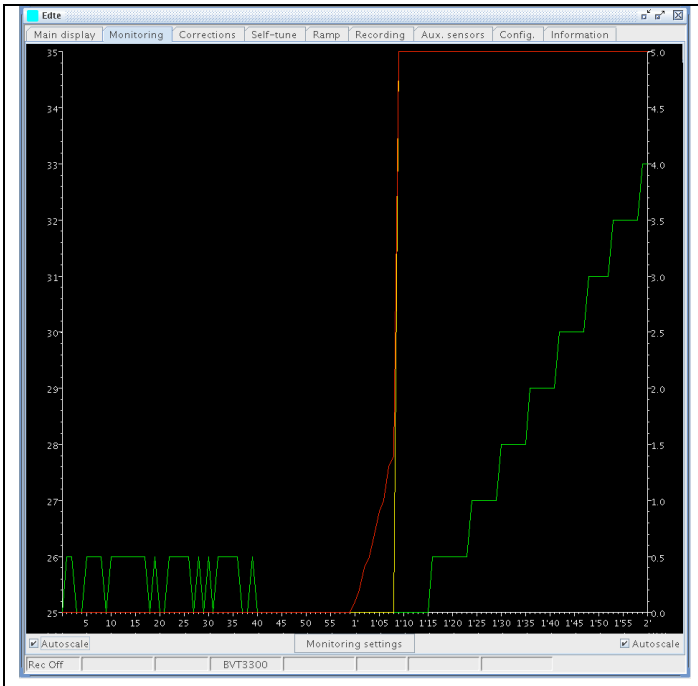

Figure 4. Monitoring the response to an increase in temperature.

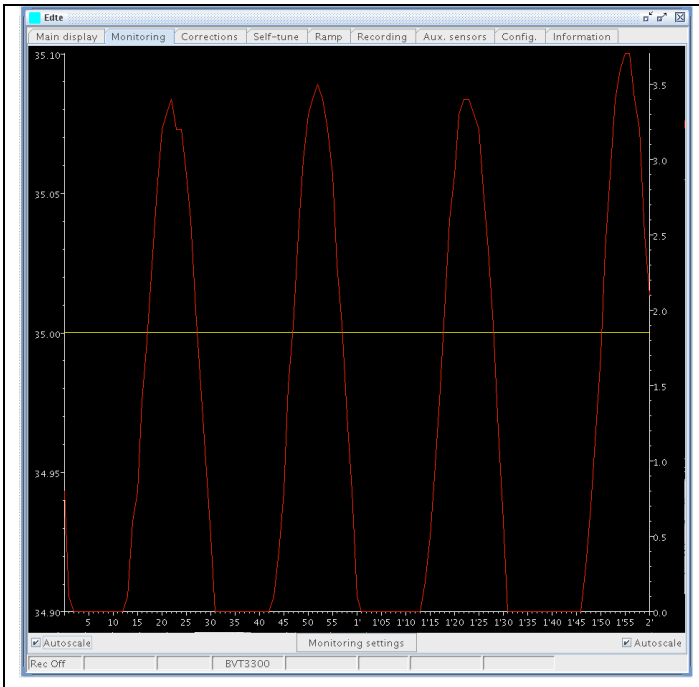

Figure 5. The temperature has reached equilibrium.

#6) After the system equilibrates, you can continue to increase the temperature in 10° C steps until you reach your target temperature. The reason we increase temperature so deliberately is that rapid temperature changes could damage the quartz inserts inside the probe. These inserts insulate and protect the coil, but they also isolate the gas flow from the thermocouple.

If the heater power (red line in monitoring tab) is at the maximum for more than 2 minutes and the temperature is not increasing, then you can increase the maximum output of the heater. Click the set max. button next to the Probe Heater percentage in the main tab (Fig. 6). Increase the maximum power by 1-2%. Go back to the monitoring tab and check if the temperature increases. Under no circumstances should you ever set the maximum power higher than 10%

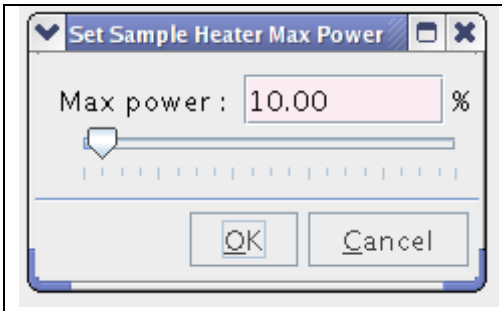

Figure 6. Set Sample Heater Max Power window. Under no circumstances should this be set above 10%.

#7) When you reach your target temperature and the sample has equilibrated you should shim. It is very important to wait for the temperature to equilibrate because thermal gradients will wreak havoc with shimming. Hence, it is a waste of time to shim before the sample equilibrates, because you'll just have to reshim once it equilibrates. Also, if you have been trained to tune the probe you can tune it at this step.

#8) Record a spectrum as you normally would.

#9) The final step is to cool the probe back to room temperature. First, reset the heat power to 5% and reduce the gas flow back to 270 l/h. Reduce the temperature by 10° C and monitor the temperature in the monitoring window (Fig. 7). Note that you don't need to let it fully equilibrate at each step. Give it ~1 minute before lowering the temperature another 10° C. Then final step (from 35° to 25° C) will take >5 minutes. Once the temperature reaches 30° C you can turn the probe heater off by clicking the button to the left of the heater percentage in the main tab.

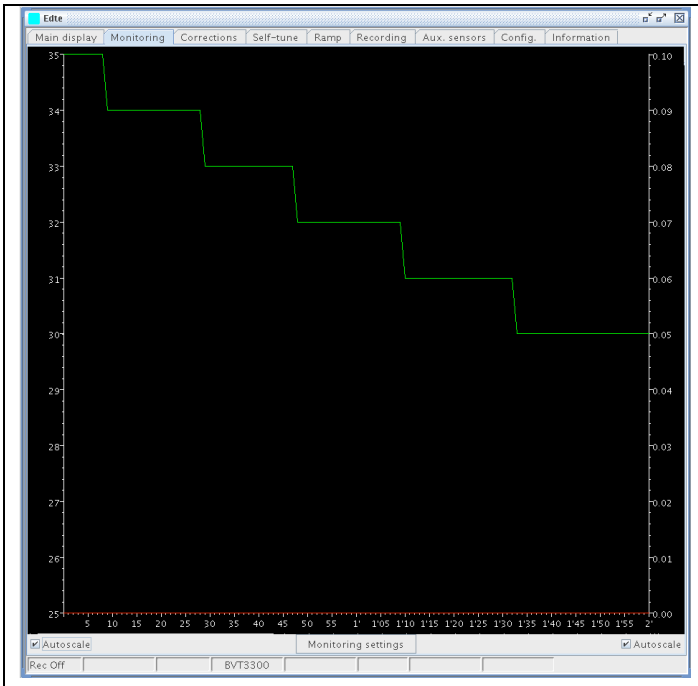

Figure 7. Monitoring cool down to room temperature.

What could go wrong:

If the temperature starts to increase out of control it is important not to panic. It will take several minutes for your sample to boil. Turn off the heater. Once the heater is off, then eject your sample. Please let Justin or Sarah know about any problems or issues.

Appendix 1. Boiling points of common NMR solvents:

solvent	boiling point (° C)
acetic acid-d4	118
acetone-d6	56.5
acetonitrile-d3	81.6
benzene-d6	80.1
chloroform-d	61-62
cyclohexane-d12	80.7
deuterium oxide	101.42
N,N-dimethyl-formamide-d7	153
dimethyl sulfoxide-d6	189
1,4-dioxane-d8	101.1
ethanol-d6	78.5
methanol-d4	64.7
methylene chloride-d2	39.75
pyridine-d5	115-116
1,1,2,2-tetrachloroethane-d2	147
tetrahydrofuran-d8	66
toluene-d8	110.6
trifluoroacetic acid-d	72.4
trifluoroethanol-d3	75