NUCLEAR MAGNETIC RESONANCE RESEARCH RESOURCE

High Temperature NMR on the AV-300

Dr. Mike Lumsden
Coordinator, NMR-3
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IN AN EMERGENCY

If the power fails, the gas supply disappears, or you notice a burning smell, please stop all activities associated with your high temperature NMR experiments immediately! You should immediately turn the probe heater off, immediately remove your sample, and immediately contact a NMR-3 facility staff member.

SECTION A: OVERVIEW & HIGH TEMPERATURE RULES & RECOMMENDATIONS

Overview

The temperature control system works by introducing room temperature air into the probe via a ball-and-socket joint. A heater inside the probe heats the air to the desired temperature programmed into a temperature controller. The heated gas then flows upwards through the probe and bathes the NMR sample. A thermocouple situated ~ 1 mm below the sample detects the temperature and reports it to the controller. The temperature controller compares this reported temperature to the target temperature and adjusts the heater current accordingly to maintain the desired temperature.

Facility Rules Concerning High Temperature Experiments

- Spinning is not permitted with high temperature experiments.
- Consider the boiling point of your solvent relative to the temperatures you wish to probe. As a general rule, stay at least 10° below the boiling point.
- Variable temperature (VT) NMR experiments are by default only permitted during off-peak hours. You are required to book an extra ½ hour of "dead time" at the end to allow thermal equilibration of the probe with normal operating temperature (300 K).
- High temperature NMR experiments must be performed with the black, plastic cap in place over the bore of the magnet (where you put your sample into the magnet).
- Sealed samples are of particular concern when performing high temperature NMR experiments due to the risk of the tube breaking under increased pressure. If sealed samples are to be studied at high temperatures, you are required to use a new NMR tube. In addition, you must "test" the sealed tube in an oil/water bath for at least ½ hour at the highest temperature you expect to perform NMR experiments. As a rule of thumb, you can calculate the maximum pressure P_{max} = [NMR tube wall thickness (mm) / NMR tube O.D. (mm) X 2,000 psi]

Facility Hints & Recommendations Concerning High Temperature Experiments

- Whenever possible, it is highly recommended that you collect room temperature data before beginning your high temperature experiments (to ensure your sample is what you intended).
- After obtaining an initial room temperature spectrum, you should raise the temperature to the highest temperature you think you'll need. If you want to run spectra at several different temperatures, always start high and work your way back down towards room temperature.
- Although high gas flow rates are required to achieve the highest temperatures (and generally desired for tight temperature regulation), be aware that there exists the possibility of supplying too much gas flow such that the

sample can be partially lifted upwards out of the probe. If you observe a sudden drop in the lock level (or lose lock), your sample may have partially lifted out of the probe. Under such circumstances, you will have to reduce the gas flow.

- The o-rings in the white ceramic spinners tend to be tight so exercise extreme caution when inserting your NMR sample tube into it.
- At temperatures approaching the solvent boiling point, line shape distortions due to bubbling become a concern. These distortions cannot be removed through shimming.
- Since the cooling gas for high temperature work is room temperature compressed air (which is not easily preheated), large differences between the set temperature and cooling gas temperature can occur. Thus, much more regulation heater current will be required (compared to low temperature operation). Therefore, the usual approach for high temperature work is to fix the cooling gas flow rate at the maximum value and allow the regulation heater to single-handedly control the temperature.
- As a general rule for tight temperature regulation, the cooling gas should be 5-10 degrees colder than the set temperature. Since the AV-300 uses room temperature air for cooling, temperature regulation will be difficult in the range from ~295 to ~305 K. If you wish to perform temperature regulated NMR experiments in this range, make sure the flow rate is the maximum you can use without lifting the sample. A better solution entirely would be to pre-cool the compressed air using, for example, an ice bath. Please talk to facility staff if you wish to perform such experiments.

Temperature Limitations

- The AV-300 temperature controller and associated hardware are capable of producing temperatures from 200°C down to -150°C with a stability of +/- 0.1°C. However, the NMR probe limits the operational temperature range from 150°C to -150°C.
- Spinners: the plastic blue spinners that are used at room temperature on both the AV-300 and 500 have a limited operating temperature range of +/- 50°C (323 K – 223 K). Outside of this range, you must use the white ceramic spinner.
- The maximum shim system temperature is +80°C.
- The safe temperature range for the magnet flange / bore is 0 to +50°C.

SECTION B: THE SOFTWARE

A software program called "edte" is available to interface with the temperature controller. The main display tab of the edte program is shown in **Figure 1**. This is the area you will use to control the sample temperature as well as the heater. A brief description of each area in this display follows:

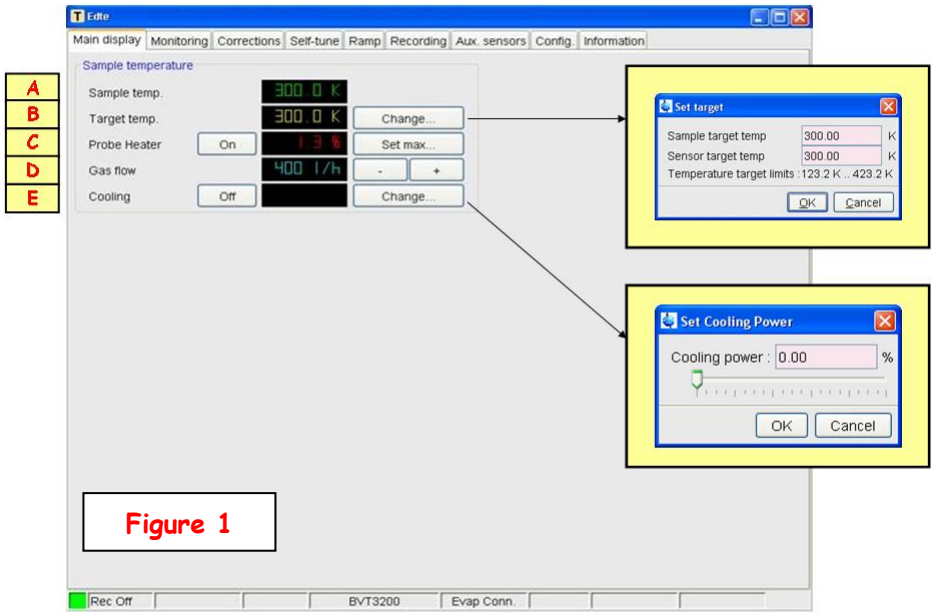

Figure 1

- **[A] Sample temp. Section:** this is the temperature of the sample in Kelvin as reported by the thermocouple.
- **[B] Target temp. Section:** the requested sample temperature. The operator can change the requested temperature by clicking on the Change… button and typing in a new value.
- **[C] Probe Heater Section:** (1) status of the probe heater (ON or OFF). Clicking this button toggles the heater on and off (2) display window which shows "—OFF--"if the heater is disabled or shows the heating power

being applied (% maximum power) if the heater is on (3) a button called "Set max…" limits the available heating power to some number below 100%.

- **[D] Gas flow Section:** flow rate in units of L/h. Adjusted using the "+" or "-" buttons beside the flow rate display. Increased flow rates are required here for higher sample temperatures.
- **[E] Cooling Section:** Shows (1) status of the N_2 heater (ON or OFF). Clicking toggles the N_2 heater on and off (2) the display window either shows "—OFF--" if the N_2 heater is turned off or it shows the power being applied (% maximum power) if the heater is on. A flashing "REFILL" or "EMPTY" warning is shown here if the liquid N_2 level in the dewar gets sufficiently low (3) a button called "Change…" which controls the nitrogen heater power and consequently the cooling capacity. Larger numbers are required here for lower temperatures.

SECTION C: Operating Procedures

Operating Procedures: Raising the Temperature

(1) Insert your sample into the magnet and then replace the black plastic cap over the bore of the magnet. Remember to use the ceramic spinner if you plan to go above 50°C.
(2) Lock and shim as normal and acquire a room temperature spectrum to ensure your sample is what you expect.
(3) Open the edte software by simply typing "edte" in the Topspin command line.
(4) Provided you are using the ceramic spinner, increase the air flow to 1200 l/h (for the blue plastic spinners, use 670 l/h). While increasing the air flow, monitor the lock level and ensure it remains stable. If a sudden drop in level occurs (meaning the sample has likely lifted), decrease the flow by one setting.
(5) Select the "Corrections" tab. You will see an interface like that in **Figure 2**. On the right hand side, there are two Activate buttons. Click the top one to turn off a correction to the set temperature.
(6) Click the "Ramp" tab to show an interface like that in **Figure 3**. First click the Activate button to enable temperature ramping. Then set the ramp rate to 2 degrees/minute and the ramp holdback to 1 degree.
(7) Return to the "Main display" tab and ensure the Probe heater is on (turn it on if it happens to be off). In the edte "Target temp" section, click on the Change… button. Enter the highest temperature you plan on studying (remember to stay 10 degrees below your solvent's boiling point).
(8) Optional: Click on the "Monitoring" tab in edte to monitor the temperature increase. In this window, the left y-axis is temperature and the right is heater power. At equilibrium, the heater power fluctuations (red line) should be less than 0.1%.
(9) Optional: When the desired temperature has been reached, perform a "self-tune" which is described in **Appendix 1**.
(10) Optional: If you require your real NMR sample temperature to be adjusted to this temperature, use the batman program and follow the procedure in **Appendix 2b**.
(11) Wait ~10 minutes for your sample to reach thermal equilibrium and re-shim and re-tune the probe. Acquire your NMR experiment(s).
(12) Optional: If you want to know your actual sample temperature, follow the calibration procedure in **Appendix 2a** (assuming you did not perform batman in step 10).

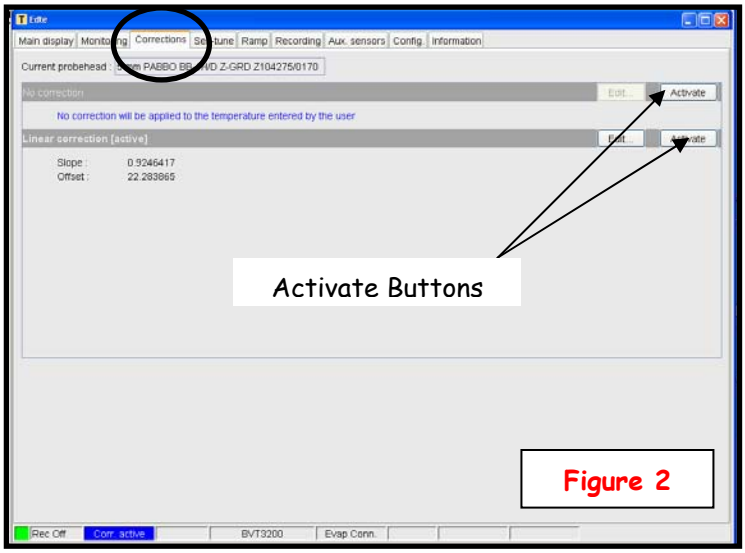

Figure 2

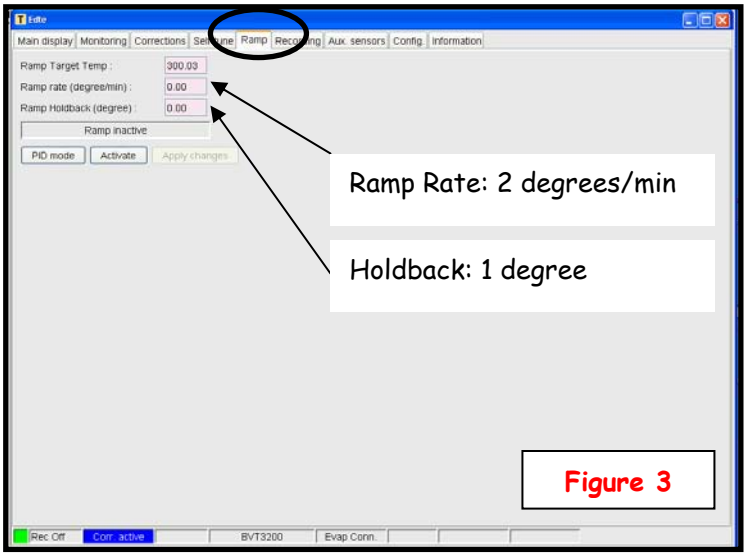

Figure 3

(13) Once finished at this initial, highest temperature, decrease the set temperature to the next desired temperature and repeat the sequence outlined in steps 9 through to 12.

Operating Procedures: Returning to Room Temperature after Finishing High Temperature VT

(1) When your NMR experiments are complete, adjust the target temperature to 300 K.
(2) Remove the black plastic cap from the bore of the magnet and eject your sample. Replace the cap.
(3) Adjust the air flow to 1200 l/h.
(4) You should now have at least another 1/2 hour of time signed out in FACES for the system to re-equilibrate thermally. You and only you are responsible to have the probe at room temperature before the next person uses the spectrometer! You can determine if equilibrium has been re-established by turning the air flow to 0 l/h and making sure the temperature does not rise.
    - If it does rise, increase the air flow back to 1200 l/h and manually turn the probe heater back on (it is automatically disabled when the air flow goes to zero).
    - If it does not rise, set the air flow to 400 l/h and manually turn the probe heater back on.
(5) Select the "Corrections" tab and click the bottom Activate button to turn a correction to the set temperature back on (see **Figure 2**).
(6) Click the "Ramp" tab and click "PID mode" to turn off the temperature ramp (see **Figure 3**).
(7) If you performed one or more self-tunes, you must read in the standard temperature control parameters for the day-to-day operating temperature of 300 K. In edte, click on the "Config." tab and at the bottom in the "Miscellaneous" section; click the "Load configuration …" button. A list of configuration files should now be present; select the file bbfo_300K_400lh.tcf and click Open to load the controller parameters. Note that if you did not self-tune, this step may be skipped.
(8) Before Finishing: check that the probe heater is on, the gas flow is 400 l/h, and the temperature is set to 300 K.

Appendix 1: Self-Tune

Self-tune is a procedure built into the edte software which tunes the temperature controller at a given temperature. In theory, once self-tune is performed, the controller will provide more stable temperature control (limited fluctuations) as well as a quicker response to any deviation from the desired temperature. You should consider performing a self-tune when you change the cooling gas flow rate (i.e. anytime you change the air flow for high temperature experiments) as well as whenever you change the target temperature by more than 10°. To perform a self-tune, perform the following steps in the edte software:

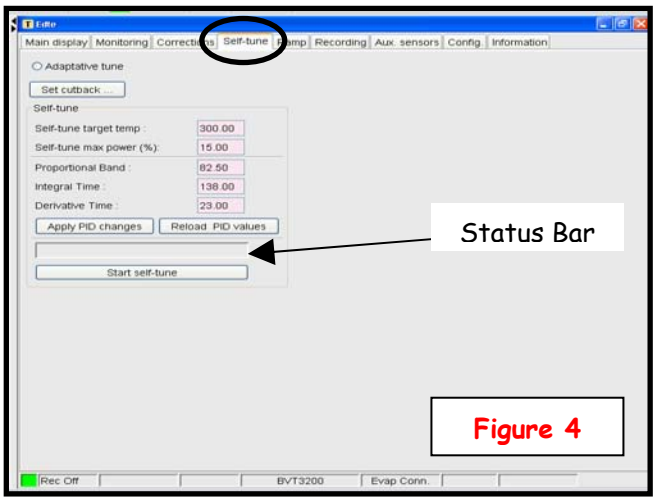

Figure 4

(1) Click on the "Self-tune" Tab in edte to open up the self-tune interface (shown in **Figure 4**).
(2) The "Self-tune target temp" and "Self-tune max power (%)" are by default set to appropriate values and shouldn't be changed.
(3) Start by clicking on the "Start self-tune" button. Once you do this, a message "Self-tune is running" will be displayed in the status bar and the start button changes to a "Stop self-tune" button which you can click to stop the tune early.
(4) The tune takes on the order of a few minutes to complete. You will know it's finished when the status bar message area is empty and the "Stop self-tune" button changes back to a "Start self-tune" button.

Appendix 2: Temperature Accuracy

Given that the temperature sensor is not located directly within the NMR sample; differences in temperature are expected between that reported by the sensor and the real NMR sample temperature. Experience has shown that these differences increase the further away you are from ambient temperature. For some experiments performed at elevated temperatures, this difference is of no practical consequence. However, if the actual temperature of your sample is important, you will need to perform temperature calibration experiments using the standard sample 80%

ethylene glycol in DMSO-d6 (valid over the range 300 – 380 K). For this sample, the temperature is related to the chemical shift difference between the aliphatic and OH proton resonances of ethylene glycol.

To calibrate, first consider creating a new dataset in your folder called "Temp Calibration" or something similar and performing the experiments there. Insert the temperature calibration standard into the magnet and lock, tune the probe, and shim. Always wait ~10 minutes for temperature equilibration. Then proceed according to which of the following two scenarios applies:

(a) Your NMR Experiment(s) Do Not Require Acquisition at any Specific Temperature BUT Knowing the Real Sample Temperature is Important…

- Load the standard proton NMR parameter set 1d_1H, set DS = 0, NS = 1, obtain a proton spectrum, and process using the default processing parameters.
- Type **"calctemp"** in the TopSpin command line and then enter "G" to specify the correct glycol sample. The sample temperature will be calculated and displayed.
- Consider repeating this experiment again in 2-3 minutes to ensure that the temperature has stabilized.

(b) Your NMR Experiment(s) Require Acquisition at a Specific Temperature

- Load the standard proton NMR parameter set 1d_1H, set DS = 0, NS = 1, obtain a proton spectrum, and process using the default processing parameters.
- Type **"batman"** in the TopSpin command line and enter the following:
    - Target temp in Kelvin
    - Stabilization time in seconds: default is 120 but recommend at least 300
    - Precision: accept the default of 0.5 degrees
    - (G)lycol or (M)ethanol: Type G
    - Glycol (P)ure or (B)ruker Glycol Sample: Type B
    - Hit Return to indicate the sample is in the magnet and ready for temperature calibration
- The program will adjust the edte target temperature to that requested. Once this temperature has been reached and is accurate to within the precision for at least 10 seconds, the program waits for an amount of time equal to the stabilization time. It then determines the sample temperature. If the sample temperature differs from that requested by more than the precision, another loop is performed using a recalculated target temperature in edte. This process continues until the sample temperature is equal to that requested (within the limits of the specified precision).