Variable Temperature (VT) NMR using TopSpin and (sometimes) IconNMR

I. Introduction

Changing temperatures on an NMR spectrometer involves working correctly through a variety of compromises and safety-related issues. The primary compromise in high-resolution NMR is accepting large systematic, but reproducible errors (if procedures are correctly followed) in the measured temperature in order to preserve high-quality shims. In particular, the thermocouple cannot be placed close to the sample without seriously impacting resolution. **It is therefore common with NMR probes that temperatures can be up to 20°C off**; the error increases as the temp diverges away from ambient. These errors can be corrected, however, as described below. Another reality in working on standard liquids NMR probes is that temperature gradients will be present across the sample: working at −100°C, a typical gradient would be 0.5°C/cm. Keeping the sample length short — e.g., using 450 µl, or Shigemi tubes — will reduce the total temperature gradient and assist in minimizing convection currents. [Don't use < 450 µl, as that won't shim properly. Don't use > 600 µl as that greatly increases temperature gradients by extending the solvent column beyond the temp-control region of the probe.]

Safety is a critical issue in working with VT. The most important factors are the following:

1. Sealed samples to be run at elevated temperature must be checked at temperature prior to introduction to the spectrometer. An exploding sample can destroy the NMR coil: this has happened once in our labs, and cost $8000 to repair in 2008 (would cost > $20K now). A similar explosion in a cryoprobe could cost considerably more than that.
2. The shim stack temperature, T_{ss}, should always be within the range $-30°C \le T_{ss} \le 70°C$. Turn the shim stack gas flow on — flow meter hanging on the back side of the magnet on Persephone (this is done automatically on eos, nyx and phoebe) — when working away from ambient temps.
3. ***Change temperatures slowly when using cryoprobes,*** i.e., the Prodigy probe on nyx, and for any VT work on callisto.

Varible temperature work can be done in concert with IconNMR in the UW Chemistry facility, but only under the following conditions:

a) The researcher must have been through Chem 636 or similar training. There are few recourses for graduate students; plan on taking Chem 636 if NMR VT is to be a part of your research project. We will work with postdocs and visiting faculty to get you sufficiently trained.

b) Temperatures between -30 to +70°C are changed only via manual topspin use. Initial temp calibrations should be done in topspin at that time. MeOH or glycerol spectra can be obtained in Icon, but the setting of temperatures accurately for the needed experiments must be done in topspin prior to starting Icon.

c) Icon runs of multiple samples can then be done at a single set temperature.

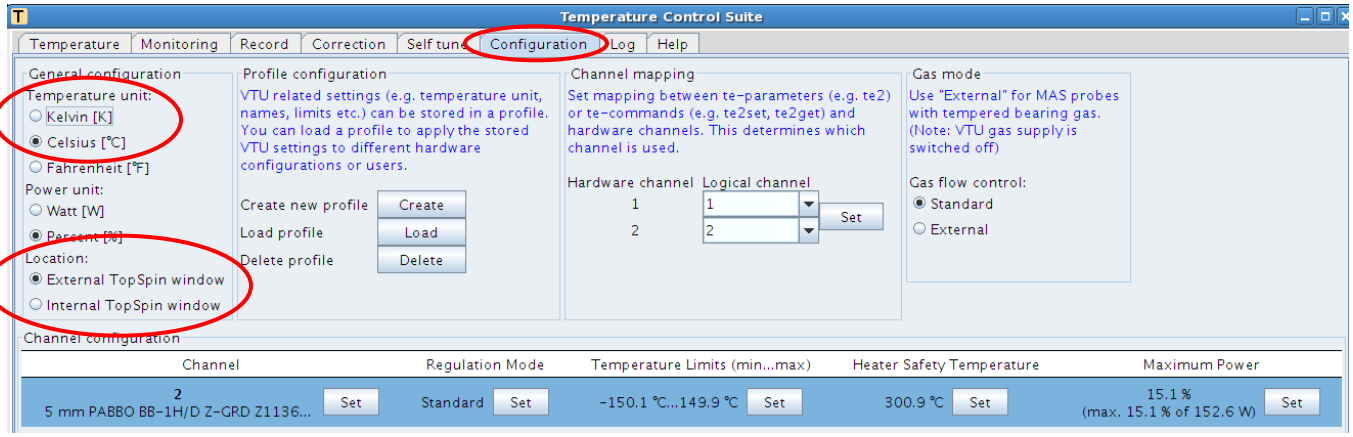
See section V below for more details about setting up shimming for these experiments in Icon.

Temperature ranges accessible within the Chemistry NMR Facility:

Spectrometer	**Probe**	**VT range (°C)**	**comments**
eos (400)	bbfo+ (SmartProbe)	-130 to +130	
persephone (500)	bbfo+	-130 to +130	
persephone (500)	solid-state probes		see Cathy for details
nyx (500)	bbfo+	-130 to +130	
nyx (500)	prodigy LN_2 cryoprobe	-30 to +70	
phoebe (600)	HCN-F LHe cryoprobe	-30 to +70	
artemis (400)	bbfo+		not for VT use
callisto (500)	DCH LHe cryoprobe		not for VT use
setup in Topspin, samples run in IconNMR:			
all spectrometers	all probes	-30 to +70	other temps done only in Topspin

Running VT experiments on persephone, nyx, eos:

1st time: When doing VT for the first time running, you may want to change some configuration settings. Type **edte** in topspin, and click on the Configuration tab:



a) You can toggle the temperature between Kelvin and Celsius.

b) Typically, switching the screen so it can be "External" to TopSpin is best. That way the Temp screen can be kept open continuously in the right-hand monitor.

II. Summary of VT setup: Perform the following steps (with more details provided below):

a) select the Correction protocol appropriate for probe and desired temperature (these won't exist on most spectrometers except at ambient temperatures; uncheck Corrections if a protocol doesn't exist)

b) set the **Target Gas Flow** and **BCU Target Power** as specified in the Correction protocol; if the protocol doesn't exist, use the following:

temp T (°C)	Target Gas Flow	BCU Target Power	comment
T < -100	1000	strong	LN_2 dewar required
-100 < T < -55	700	medium	LN_2 dewar required
-55 < T < -30	700	strong	use BCU only (LN_2 required on persephone)
-30 < T < 0	600	medium	use BCU only (LN_2 required on persephone)
0 < T +40	500	low	use BCU only
+40 < T < 130	500	off	use probe heater only

c) **turn off the VTU before modifying gas connections**

d) turn on the gas to the VT shim stack on persephone, using the manual flow valve on the back of the magnet (nyx, eos and phoebe do this automatically)

e) **temp changes will be limited to ≤ 3°C / min;** this is critical for cryoprobes to insure vacuum insulation is not broken by differential expansions; but is also enforce for all probes, as the magnets (shims) and probes (electronic tuning) cannot stabilize faster than that rate

f) wait at temp for ≥ 5 min for magnet+probe to come to equilibrium

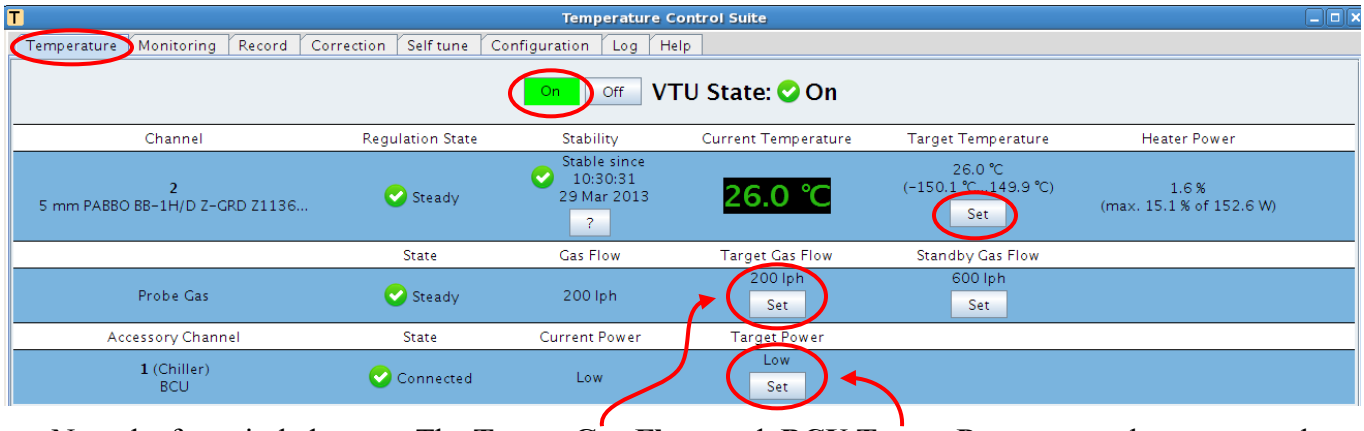
g) perform a Self Tune if temps are oscillating or taking too long to reach final temps

h) perform temp calibrations using MeOH or ethylene glycol samples (within allowable VT ranges) if accuracy is important; **calctemp** (or **calctc**) is a useful TopSpin au for calibrations

Temperatures can be > 20°C off; make certain your samples will neither boil (explode!) or freeze in the spectrometer.

III. Detailed procedure:

1. To review the current temperature control in TopSpin use the **edte** screen (type in TopSpin, or double-click the temp box in the status area at the bottom of the TopSpin screen).



Note the four circled areas. The **Target Gas Flow** and **BCU Target Power** must be set correctly.

2. Select the proper conditions to run at the temperature needed:

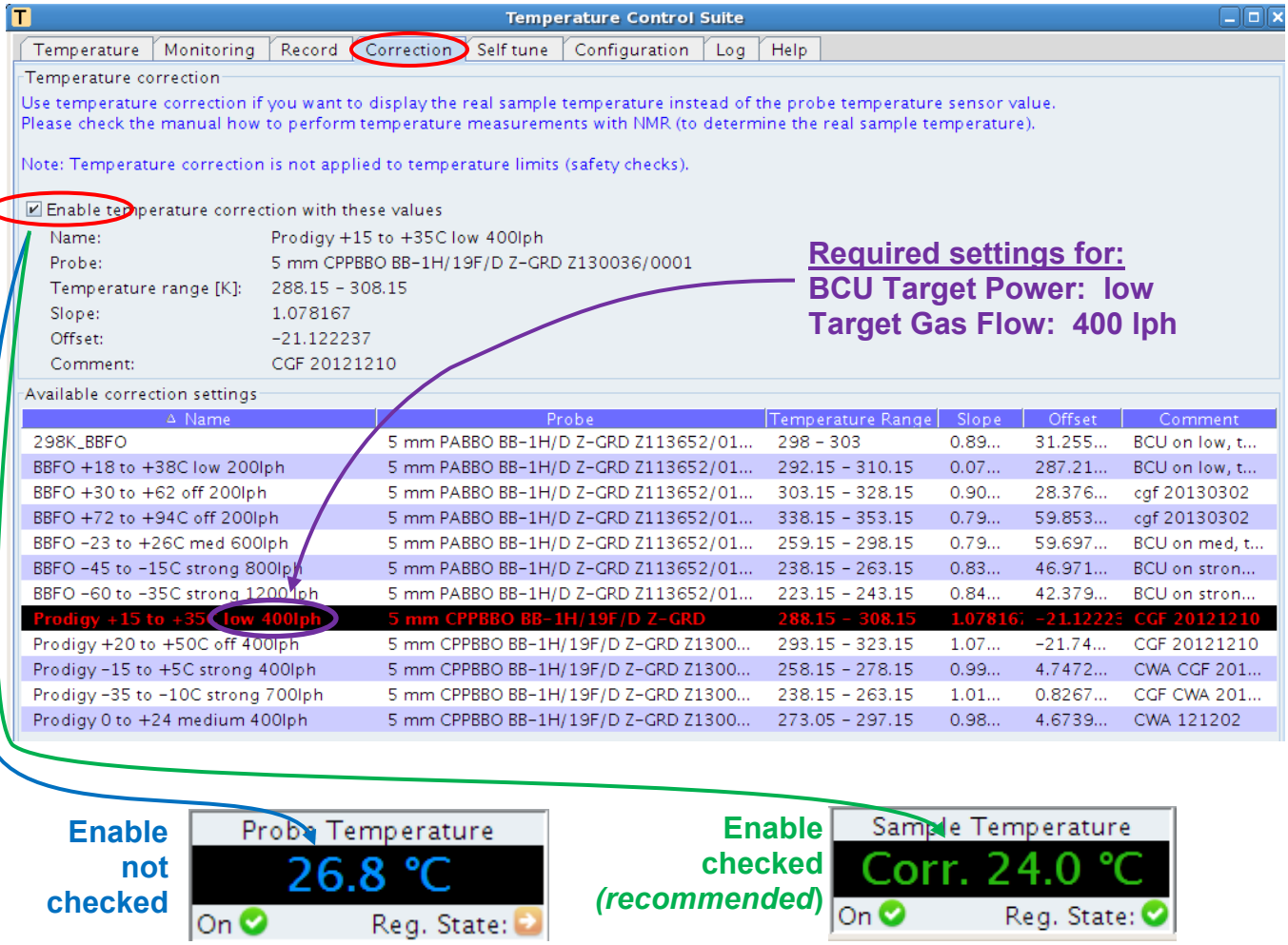
   → choose the appropriate **Correction** protocol (see below)

   The setting highlighted below for the Prodigy probe will enable sample temperatures to be set between 15 to 35°C, but only if the target gas flow is set to 400 lph, and the BCU is set to Low.

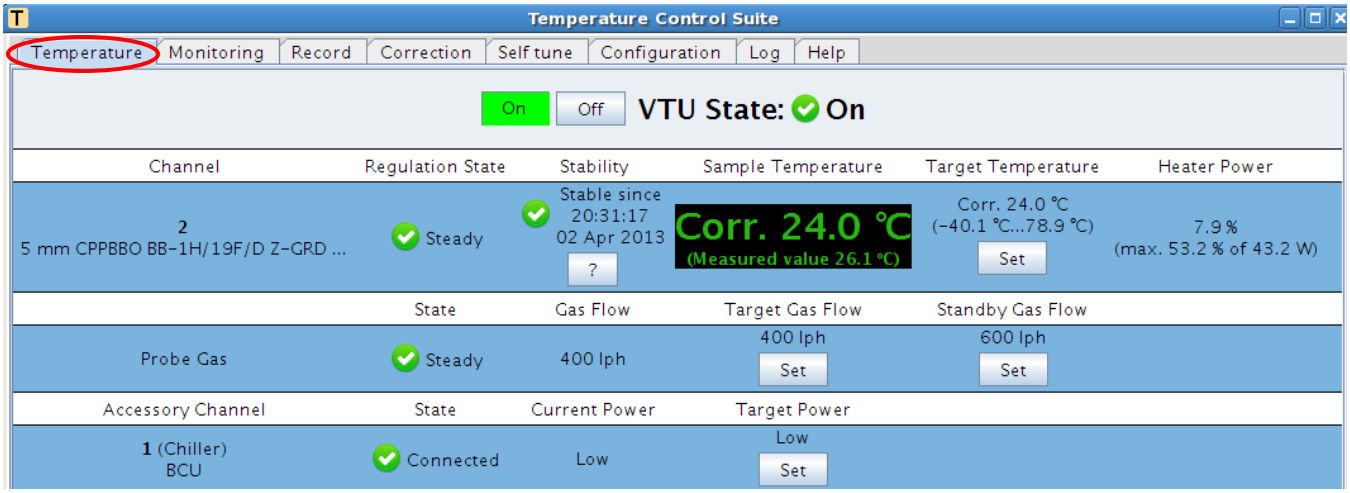
   a) *Recommended:* Check the "**Enable temperature correction with these values**". The displayed temperature will show **Corr.** before it in the TopSpin status bar as shown below on the right. The displayed temperature should be accurate with a few degrees; more accuracy requires calibration as discussed below.

   b) VT can be run without Enabling the correction (unchecked, with the status showing as on the left). Still use the **Correction** settings for setting the Target Gas Flow and BCU Power (or see the table in the Summary above).

      It is critical to understand, however, that without corrections, the sample temperature and thermocouple temperature may differ by > 20°C. Samples may freeze or boil if care is not observed; expensive damage to the probe may then occur, and groups will be held responsible for paying for resulting repairs.

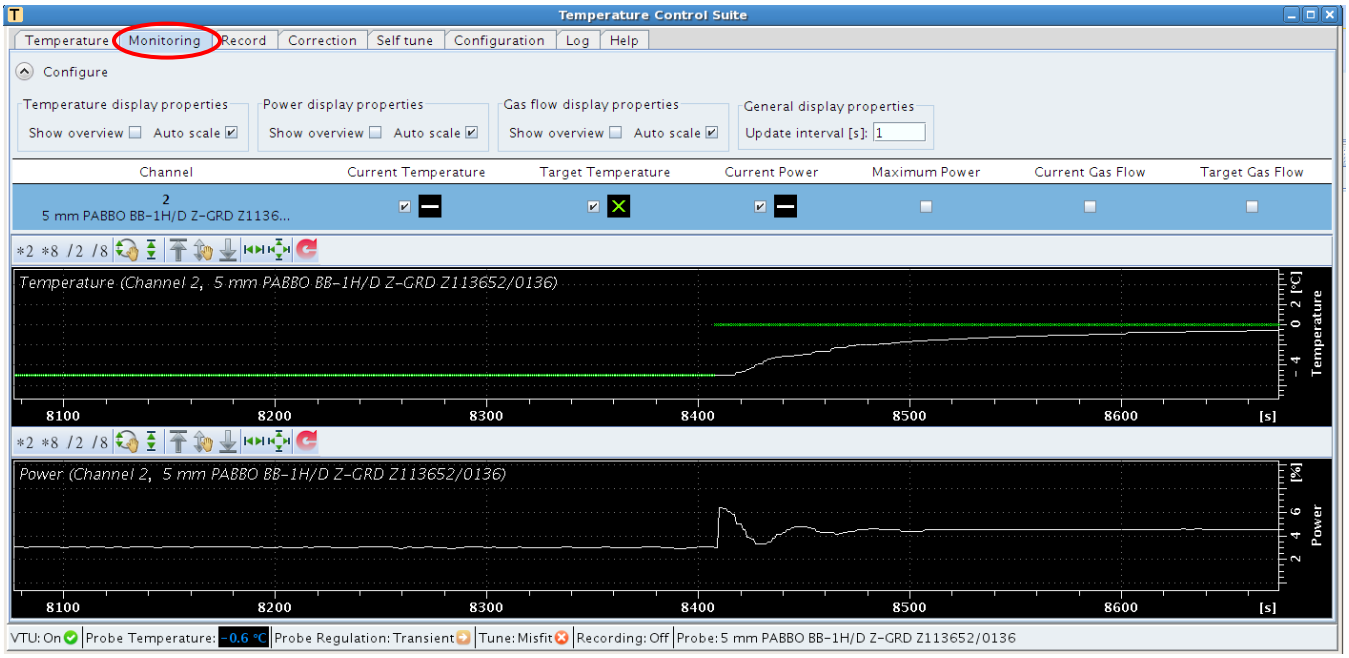


c) The Temperature tab shows the corrections in detail (when corrections are enabled), as shown below. The "Measured" temperature is that at the thermocouple; the corrected temperature is that computed by the Correction protocol, which should be close to your sample temperature. Once again, the Measured and Corrected temperatures may differ by > 20°!



3. The temperature and various other experimental conditions can be monitored using the MONITOR tab. In the figure below, the three most important — "Current Temperature", "Target Temperature"

and "Current Power" — are checked and displayed. The Update interval can be slowed down to monitor a longer period of time. Use the RECORD tab to save the temperature status in long runs.



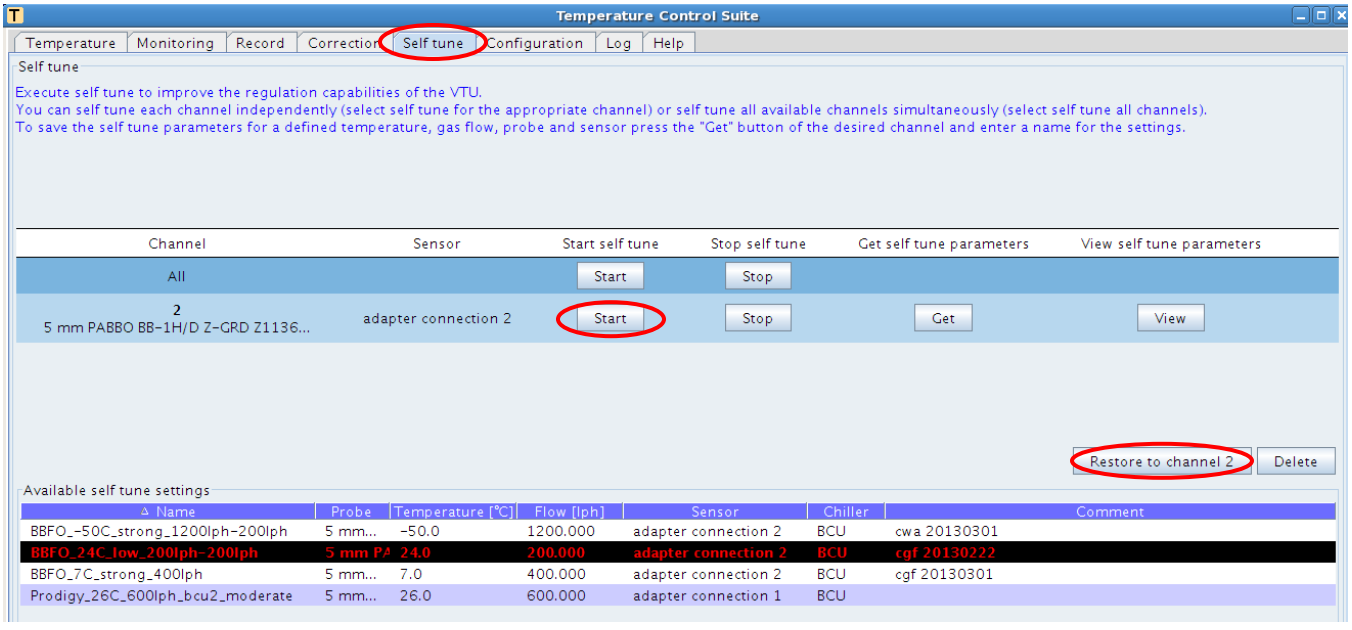
4. If the temperature oscillates, or takes too long to reach the requested value, perform a Self-Tune:

   a) wait for the temp to get close to requested

   b) click on Start

   The procedure is automatic and will take ~5 mins.

   The Get button is a very bad misnomer: information is "gotten" from the VT controller, but then is (when Get is pushed) STORED to disk. To retrieve a saved Self-Tune, use the **Restore to channel 2** button.



IV. Temperature calibrations:

These can be easily performed using:

a) 4% MeOH in CD_3OD for 180 to 300K. Lock and shim as normal.

b) Neat ethylene glycol for 300 to 380K. Here run unlocked and do not shim (the sample's too short to shim). See the on-line notes for running no-D samples at:

http://www.chem.wisc.edu/~cic/nmr/Guides/Ba3vug/AV3_noD-NMR.pdf

c) Use the command: **calctemp**↵ (answer in K) or **caltc**↵ (answer in °C)

If that command does not work (some problem with peak identification; annoying), copy the Excel spreadsheet at /home/nmrsu/Desktop/NMR-TempCal.xls to your Desktop (e.g., /home/fry/Desktop). Enter the chemical shift difference between the two peaks in ppm in the proper cell, and the temperature will be computed.

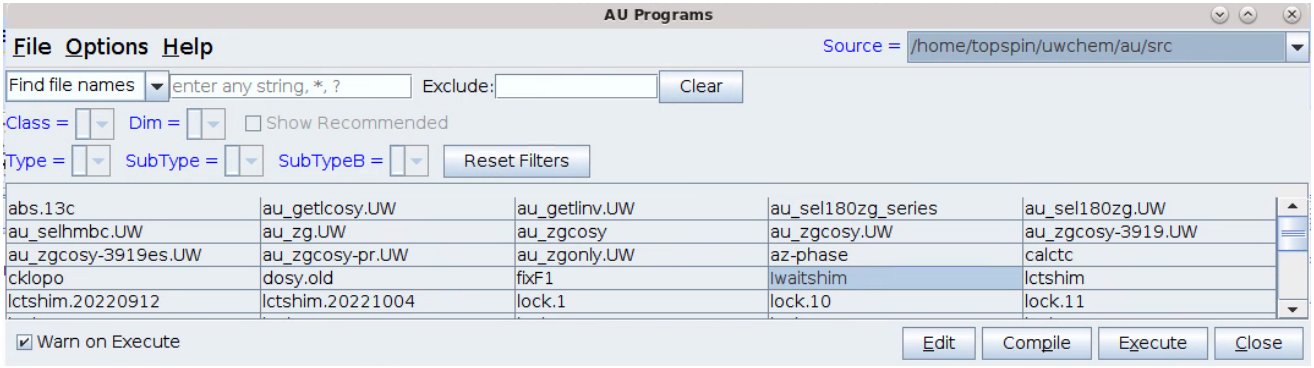
V. Using IconNMR to acquire data at a single temperature:

a) If at any point in this procedure you're uncertain what to do, find nmr staff for help.

b) Follow the instructions above to set the spectrometer to the desired temperature in Topspin.

c) Setup the automation routine that will perform shimming of the sample, starting with the facility template: **Iwaitshim**

i. At the topspin command line, enter: **edau**↵ The following dialog will open:



ii. Select **Iwaitshim** and click **Edit** at the bottom right. The dialog below will open.

iii. **File → Save As** and choose a filename, e.g., **Iwaitshim.cgf** . Put this into /home/topspin/uwchem/au/src (see upper right above).

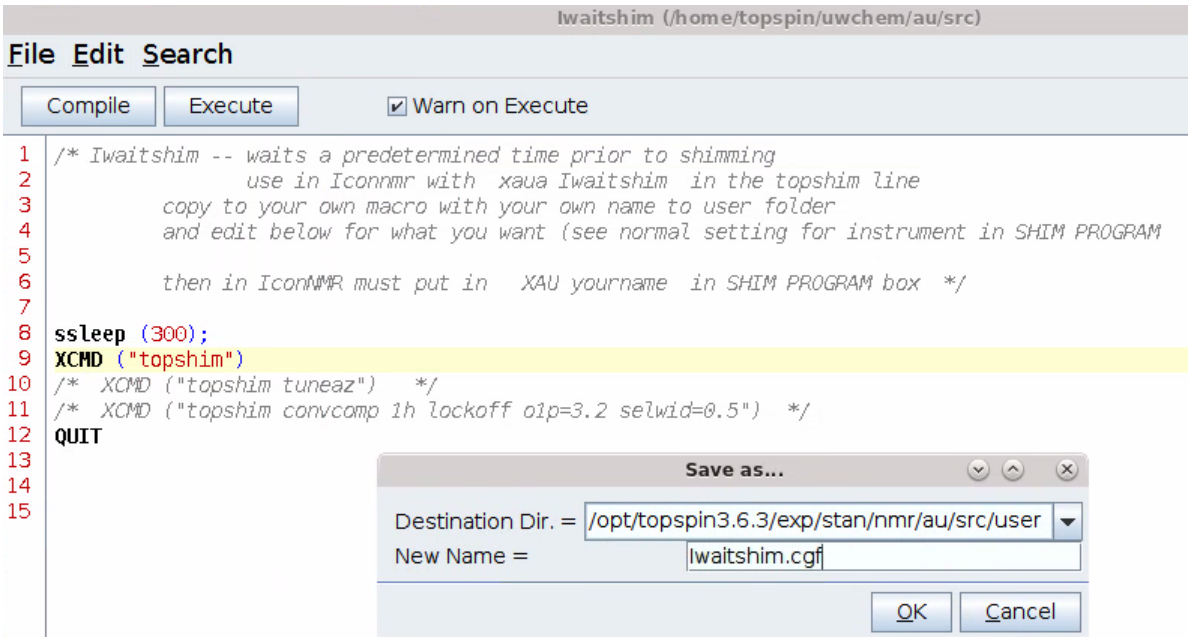
iv. The **ssleep (300);** command will wait 5 minutes before continuing to the next line

v. Choose the topshim line needed by adding and removing the commenting syntax:

/* .... */

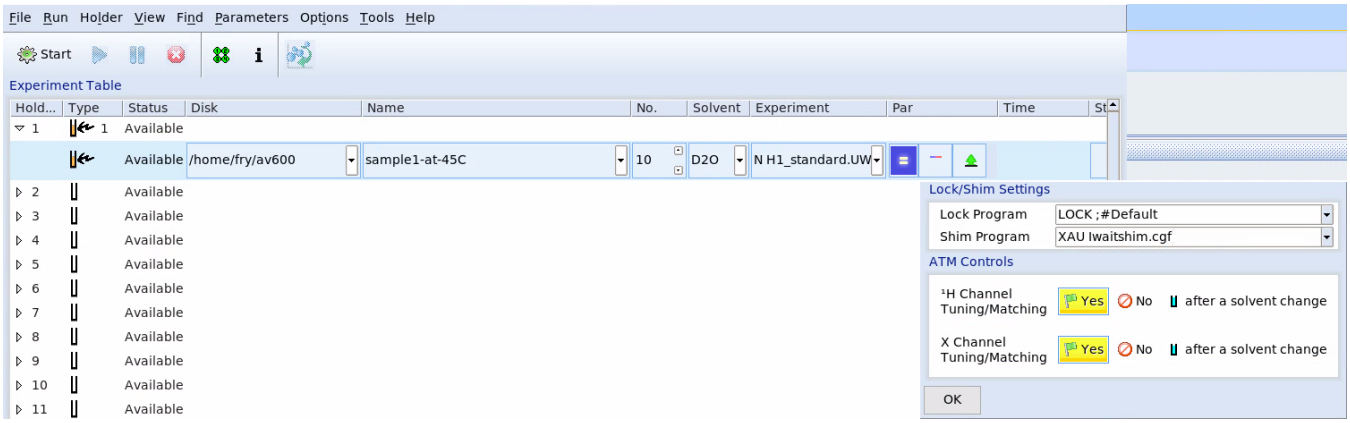
and change line 11 as needed (the o1p value) if performing noD shimming.

Include **convcomp** if using a cryoprobe (phoebe and nyx-with-prodigy probe).



c) Open Icon as normal (command line enter **icon**↵), and setup the samples.

In the Shim Program line, enter: **XAU Iwaitshim.cgf** (but using your filename).



Do the same for all the other samples. Each sample, as it is put in the magnet, will have a delay as set in the automation routine (300 sec in the example above) before shimming will be done.

VI. Exiting VT operation properly:

a) It is not uncommon that the Target Gas Flow has to be turned up to eject a sample; not sure why, but they often get "stuck" during VT runs. Turning the flow up to 1200 lph usually does the trick. Immediately reduce the Target Gas Flow back to normal setting (400 lph for BBFO+; 500 lph for Prodigy and TCI on phoebe).

b) Return to ambient 24°C. Adjust the Target Gas Flow and BCU power as appropriate: change them slowly toward the final values to prevent sudden changes of temperatures. For example, if you've been running with 1000 lph gas flow through the LN_2 dewar for −120°C operation, raise the temp to −80°C and the gas flow to 800 lph; wait a few minutes, then −50°C and 600 lph, etc.

c) Removing the LN_2 dewar:

   i) turn the Target Gas Flow slowly toward 400-500 lph (see discussion above), leave the BCU set to off, and raise the temp in increments to +10°C. Wait a few minutes once there.

   ii) ***Turn the VTU Off before disconnecting the gas connections to remove the LN_2 dewar.*** Once the dewar is removed, and the gas connection is reconnected probe-to-BCU, turn the VTU back on.

   iii) Set Target Gas Flow to 400 lph and BCU to low, go to 24°C and wait 10 min.

   iv) Enable Corrections with the ambient temp correction protocol. Restore the corresponding Self Tune. Everything should be stable at 24°C.

d) Turn the Shim Stack gas almost off on persephone (prefer to let it flow a small amount of gas at all times). nyx, eos and phoebe will self-regulate the shim stack gas.