

11. Variable Temperature Measurements

by *cg fry*: created 11/11/94 – updated 4/27/2001

I. Variable Temperature on Phoenix (Bruker AC-250)

A. Initial Equipment Checks

- **Note that the actual sample temperature can be 20 K or more different from the VT set point!**
 - See the calibration curve on the board in the spectrometer room to gain an appreciation for how divergent set points and actual sample temperatures can be.
 - **NEVER** go closer than 5°C—actual temperature—to a solvent's boiling point.
 - Never go closer than 25°C—set point—to a solvent's boiling point without performing a temperature calibration *immediately prior to* the measurement in question.
 - Do not exceed the range of temperatures for the Nalorac DB250-5B probe:

$$-150^{\circ}\text{C} \leq \text{TE} \leq +120^{\circ}\text{C}$$

- It is the user's responsibility to ensure that VT experiments are performed safely!
- Use the ceramic spin collar for experiments $35^{\circ}\text{C} \leq \text{TE} \leq 0^{\circ}\text{C}$.
 - Be careful with this spinner, which costs ~\$500!
- Use N₂ gas for all VT experiments.
 - Switch the wall gas from air to N₂.
- Use the LN2 tank usually stored next to the magnet for $\text{TE} \leq 305\text{K}$ (do not use dry ice/ethanol/acetone baths; the LN2 tank works and costs as little or less).
 - After filling the tank, make certain the o-ring and ring-clamp are securely tightened.
 - hook the black hose in place of the green hose onto the probe
 - make sure the wall gas is switched from air to N₂

(you must perform the following checks to insure equipment will not be damaged)

- make sure heater and thermocouple (TC) are inserted correctly into probe
- *after* checking above, turn on Controller
- turn on heating tape variac (in corner next to magnet) if running $\leq 210\text{K}$, or $\leq 250\text{K}$ for $>1\text{h}$
- turn on the LN2 heater (**not** the control heater);
 - changes in LN2 heater setting (table below) optimize the heater inside the LN2 tank to maximize the hold time for the tank; use the following as initial settings:

LN2 heater setting	Temps. available	~ hold time
20	$\geq 220\text{ K}$	$> 12\text{ h?}$
40	$\geq 190\text{ K}$	$> 9\text{ h?}$
60	$\geq 150\text{ K}$	$> 6\text{ h?}$

(please give lab director feedback how settings and holdtimes work)

B. Changing set-point

(perform only from AC-console; the arrows on the controller will change the setpoint, but then the setpoint for your experiment will not match the stored TE)

- Enter **TE** <ret> type in new temperature in Kelvin, then <ret>
- Enter **PASC TESET** <ret>
- SP on controller should flash then change
- wait until temp falls below set point, then turn on main heater

C. Taking data

- Wait ≥ 10 minutes for the temperature to equilibrate (longer with larger temp excursions).
- For quantitative data, you must retune the probe at each temperature. Probe tuning may change for 30 or more minutes following a temperature change.
- For X-nucleus work, the decoupler must be retuned (including non-quantitative data) after any change in temp $> 20^\circ$.
- Plan your experiments so a minimum of 30 min is included at the end to allow the magnet and probe to re-equilibrate to ambient temperatures for the next user. *It is your responsibility to stop experiments early enough so you do not interfere with the next users scheduled time.*

D. Finishing up

- turn off heater
- turn off LN2 heater
- replace LN2 hose with green hose with wall N2; *do not force* the connector—if you do and it is frozen, you will snap off the ball-joint connector
- wait until temp ≥ 250 K
- turn off VT controller power
- switch back to air from N2
- turn off Variac controlled heating tape

E. Self-tune (if control is erratic)

- turn heater off and wait for temperature to stabilize
(if the sample might freeze, leave heater on throughout; self-tune will not be quite as good)
- hold down  button until **Pr** comes up on display
- press  until **St** is on display
- press **s** and **t** buttons simultaneously
- turn on main heater
- SP will blink for about 1 minute, then A-T will blink until the self-tune is finished
- temperature control should now work well

II. ¹H NMR Chemical Shift Thermometers

A. Low Temperature: *methanol* (with 0.03% concentrated HCl)

temperature range: 175–330K (–100 to 55°C)

$$T_{meas}[K] = 403.0 - 29.46(\Delta\delta_M) - 23.83(\Delta\delta_M)^2$$

where $\Delta\delta_M$ is the chemical shift difference (in ppm) between the methyl and hydroxyl peaks. Refer to A.L. Van Geet, *Anal. Chem.*, **42**, 679, 1970.

B. High Temperature: *ethylene glycol* (neat)

temperature range: 310–440K (35 to 165°C)

$$T_{meas}[K] = 465.8 - 102.24(\Delta\delta_{EG})$$

where $\Delta\delta_{EG}$ is the chemical shift difference (in ppm) between the methylene and hydroxyl peaks. Refer to M.L. Kaplan, F.A. Bovey and H.N. Cheng, *Anal. Chem.*, **47**, 1703, 1975.

III. Automated VT Runs

There are two sets of .AU routines:

Phoenix
VTAC.AU
VTXAC.AU

- Neither of these routines will provide quantitative data, since the probe will detune with changes in temperature (if you need quantitative data, you will have to retune the probe between each change in temperature). In addition, do not attempt to run VTXAC.AU over a range of temp >20°C, due to probe detuning. Tune the probe at the mid-point temperature for all experiments using these sequences.
- Setup and shim as normal
- Enter:

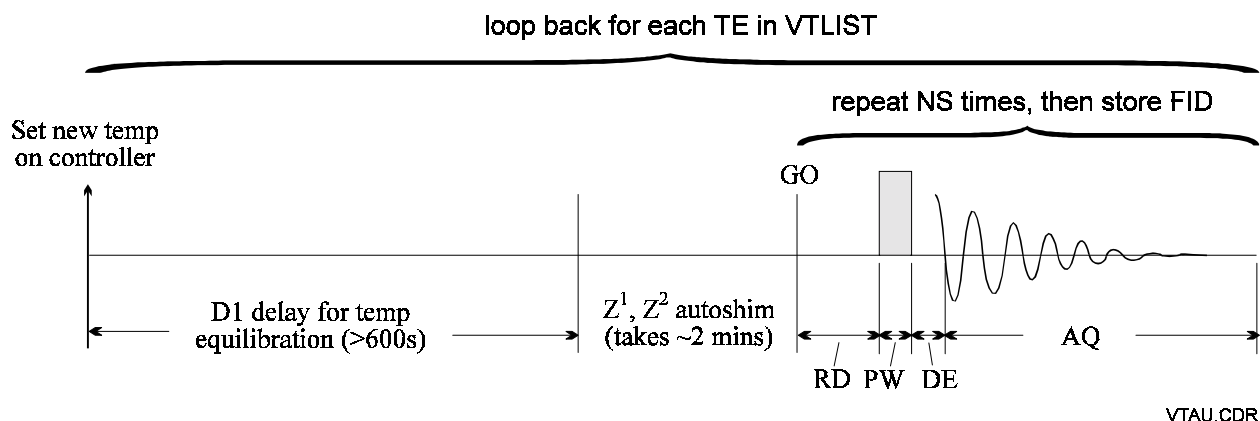
AS VTAC.AU	for VT ¹ H or coupled X-nucleus on Phoenix (AC-250)
AS VTXAC.AU	for VT X-nucleus with ¹ H decoupling on Phoenix (AC-250)
- The only parameters to change are:

D1 = **(enter in seconds)** wait time following temp change to come to equilibration (usually > 600 secs)

VD normally use default **VDLIST.001** (i.e. just type return)
enter list of temperatures in K
end by typing **EN**

NE = # of temperatures in VDLIST

for VTX: **D5** = **5M** (enter as shown, or 0.005 since we want 5 milliseconds)
- If you are running unlocked, see me about other routines that will not try to autoshim.



IV. Example Automation Routine Listing

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VTXAC.AU
; Measure X w 1H-decoupled spectra at temps specified in VT list
; Autoshim between temps

; C.G. FRY - 25 OCT 94

1  ZE
2  TE                      ;read in 1st temp from VT list
3  PASC TESET              ;set temp in B-VT 2000 unit
4  D1 CPD                  ;hold time for VT stabilization (>5 min)
   TU4                     ;autoshim Z1 and Z2 (takes about 2 mins)
5  ZE
6  GO=6 CPD                ;uses RD and PW from normal job file
7  WR #1                   ;1st temp .001, then increments by 1
8  IF #1
9  IN=2                    ;loop back NE times for other temps
10 D5 D0                   ;D5=5M to turn decoupler off
11 EXIT

;read in normal job file, e.g. CDCL3.1DJ
;enter AS VTAC.AU
;type in VT list, use EN<ret> to end list
;make D1 long enough for good temp stabilization
;NE must = # temps in VT list
;D5=5M (type in M following the 5, to set to milliseconds)

;enter filename WITHOUT extension

```