Guide for Variable Temperature experiments

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This guide is intended to illustrate the principles of temperature control in NMR, the risks associated with VT experiments, and necessary changes to operating procedures in order to get good data, operate safely and minimise disruption to other users. You should not carry out VT experiments unless you have been shown in person the important things to remember, this guide is for your reference and for documentation of things we expect you to do.

At the moment VT experiments are allowed only on Glengrant and Auchentoshan; although theoretically possible on Arran this is not currently allowed but the possibility can be discussed. On Arran the VT must always be operative - if you see an error message about the VT being switched off contact the NMR team immediately! In particular if there is no VT gas flow at all the sample space will cool rapidly, and will quickly reach the freezing point of water which can lead to tube breakage for water samples; if you see the temperature dropping rapidly an Arran you should eject your sample and contact us.

As with all aspects of hands-on NMR, please do contact the NMR team in case of any questions. This is particularly important given the potential problems caused by incorrect operation.

Booking time for variable temperature work

You should note that getting to your desired temperature, and in particular returning the spectrometer to a state where it can be used straight away by the next user will take a considerable time, and you must account for this in your bookings. **For long term experiments far from room temperature you should allow an hour after your experiments have finished, so you must finish your experiments one hour before the end of your booking**. Although reducing the sample temperature from e.g. 100°C to 25°C would in principle take of the order of 20 minutes, the rest of the probe and also the shim system will be at elevated temperature and as they have a large thermal mass and are not actively temperature controlled these take a long time to recover. If the shim temperature is not stable, this will affect lineshape stability for subsequent measurements, so it's necessary to allow time for the shims to return close to room temperature.

Figure 1: Figures in the margin show the relevant menu entries or sections of the TopSpin display

edte

Figure 2: As well as double clicking the temperature in the status bar you can type edte to open the temperature display

General notes on safety

Variable temperature experiments carry additional risks compared to operation at room temperature; boiling or freezing of the sample is possible, and potentially catastrophic damage to the hardware can occur. High temperature experiments have the risk of melting the shim system, and very low temperature experiments could in principle cause loss of the magnet vacuum, which would result in loss of the magnet (and the resulting cost of re-energisation, along with long delays). For experiments far from room temperature the system should not be left unattended, and in particular arrangements must be made to return the system to normal operating conditions as soon as the experiments are finished. If you have need to run extended experiments far from ambient temperature this should be discussed with the NMR team first.

We always require Wilmad 528pp or equivalent specification tubes, and this is particularly critical for variable temperature work. Economy tubes can be damaged during variable temperature experiments, which will have serious consequences.

Obviously you must only operate within the liquid range of your chosen solvent, and in general you should never set the temperature higher than 10 degrees below the boiling point, or lower than 5 degrees above the melting point.

The blue spinner turbines are absolutely only suitable for experiments between 0 and 80°C, but in general we recommend using the Kel-F spinners for experiments in the range +15 to +120°C, in case you do need to change the temperature to outside the 0-80 range. For temperatures below 15°C, we recommend using the ceramic spinners on Glengrant with a flow rate of 1000l/hr and strong chiller power as we have calibrated the deviations from reported temperature under these conditions in the range -50 - +15°C. Be extra careful when inserting tubes into ceramic spinners, as they may be a bit tighter than the others and so risk of sample breakage is increased.

Principles of temperature control in NMR

The temperature at which NMR experiments are carried out is important for a number of reasons:

- Temperature dependence of chemical shifts
- Rates of chemical/conformational exchange
- Rates of reaction in kinetic experiments

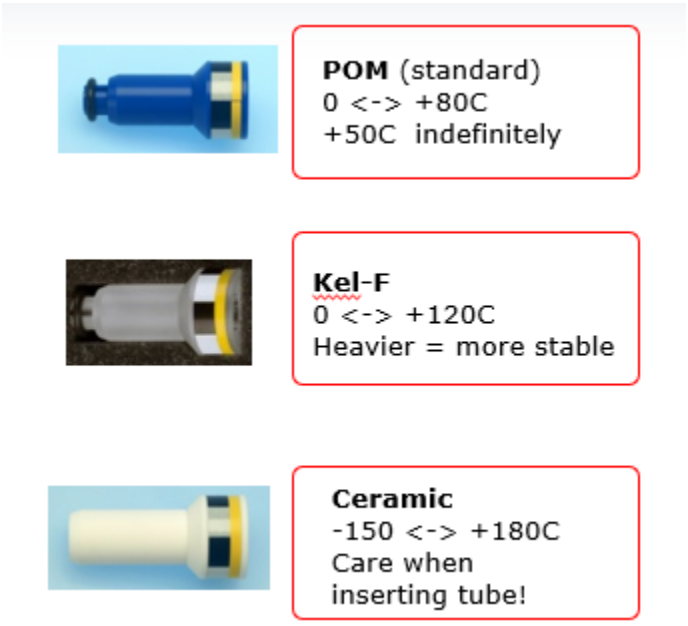

Figure 3: NMR spinner types and their allowed temperature ranges. In practive we recommend the ceramic spinners for all low temperature work as we have calibrated the temperature under high flow conditions which are only suitable for the ceramic spinners.

- Solubility
- Influence of temperature on diffusion/convection
- Sample stability

For standard NMR experiments in typical solvents, the exact sample temperature is not critical, more that the temperature remains as constant as possible and fairly uniform across the sample. There is a kind of de facto standard operating temperature of 25°C / 298K which is where all our spectrometers usually operate; this temperature is calibrated and checked periodically. The reproducibility of this calibration is of the order of +/-0.1K, and the stability over the timescale of normal experiments is substantially better than that.

In order to control the temperature of the NMR sample, we control the temperature of a stream of nitrogen gas passing over the sample; the gas passes over a heater and there is a temperature sensor close to the sample which reports the approximate sample temperature. On modern spectrometers the flow of the VT gas is measured and regulated using a mass flow meter, which helps to improve the reproducibility of the difference between the reported and actual sample temperature.

In the room temperature probes used on Auchentoshan and Glengrant (and also on the open access systems), the sample undergoes bidirectional flow as illustrated in figure 4. This has the effect of minimising vertical temperature gradients along the sample, which in turn helps to reduce convection; however it should be noted that

convection is likely to be present in most solvents other than water because there still exist horizontal temperature gradients in the probe. Because the probe itself is only capable of heating the incoming gas, the lowest achievable temperature in the probe is limited by the temperature of that gas. In order to perform experiments at less than 25°C, two approaches can be used: a chiller unit which cools the normal nitrogen gas stream, which on Glengrant can allow probe temperatures down to about -50°C and on Auchentoshan perhaps 0°C; or a nitrogen evaporator which consists of a heater element in a dewar of liquid nitrogen, which replaces the normal gas stream and allows temperatures down to about -100°C. Operation of the nitrogen evaporator is not discussed here, experiments at such low temperatures will be carried out by the NMR service if needed.

In the cryoprobe on Arran there is no space for such bidirectional flow, and there is simple one directional flow over the sample. As a result, the VT gas loses heat into the cold space of the cryoprobe, and the temperature of the sample becomes higher at the bottom than the top. This drives measureable convection in all low viscosity solvents (see the slides about manual use of Arran for more details).

Because the sensor is not exactly at the position of the sample (if it is too close it would affect the NMR lineshape), and partly because of imperfect calibration of the sensor, the reported temperature is not necessarily exactly the temperature inside the sample. We can calibrate the exact temperature, however, by acquiring spectra of a sample with two signals whose chemical shift difference obeys a known function of temperature. The commonly used samples are methanol (using the residual proton signals of nominally 99.8% deuterated methanol), over a range from 175-338K (essentially its entire liquid range), and ethylene gylcol (for temperatures 300-380K; this calibration is less precise). The calibration of the relationship between these spectra and the temperature is carried out by measuring the exact sample temperature under specific conditions using a sensor placed inside the liquid sample, then removing the sensor and measuring the NMR spectrum. This is repeated over a range of set temperatures and a mathematical relationship between the shift difference and temperature is derived. The highest quality data has been obtained for methanol, see [1]

A linear relationship between the measured and actual temperatures, is set in the VT unit for each spectrometer - this means that for temperatures close to room temperature, the displayed temperatures will be rather accurate. For very high temperatures there are deviations from the reported temperature, and for low temperature experiments using increased chiller power there are certainly significant deviations. Details of measured deviations are documented in

table 3.

Temperature regulation

In order to regulate the temperature very precisely, a proportional-integral-derivative controller is used. This looks at the current difference between the measured and set temperatures, the integral of the difference over some time period, and the derivative of the difference over some time period, and changes the power of the heater in the probe accordingly. This is able to produce much better control than simply a proportional controller looking at only the current difference - the outcome of such a controller can only be either stable but at the wrong temperature, or oscillating around the correct temperature. See the Wikipedia article for more details. [2]

On all systems the regulation parameters are set well for experiments around room temperature. In principle when changing to very different temperatures the optimum parameters could be changed in order to achieve the fastest transition to the new temperature (critically damped oscillation, where the temperature should overshoot once and then stabilise). However for safety purposes on all the systems here the temperature regulation is set to be slope limited, with a maximum slope of 5K/min. This means that even if you set a large temperature change, the temperature will be ramped up or down slowly avoiding the risk of thermal shock to any parts of the system. This does mean that temperature changes take a fairly long time, but by the time the measured temperature has stablilised the temperature inside the sample should also be quite close to the final value.

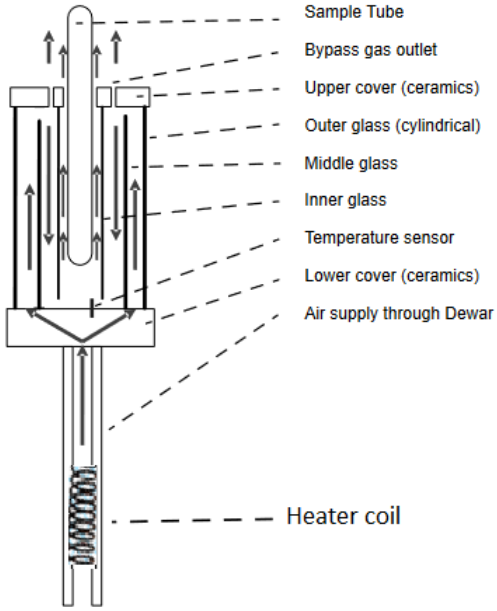

Figure 4: VT gas flow in the "extended turn flow" design of Bruker probes

Precooling of the input gas

To permit low temperature measurements, Auchentoshan and Glengrant are equipped with inline chiller units which cool the air before it reaches the probe. The unit on Auchentoshan is quite old and operates in a fixed mode providing gas at a temperature that will in principle allow operation close to 0°C. The unit on Glengrant is more powerful, and has 3 remotely settable chilling levels. By default the chiller is set to low chilling mode; this allows temperatures slightly below room temperature. For temperatures below about 15°C this has to be changed, and it takes some time for the temperature of the output gas to change. The setting of this chiller affects the temperature calibration - for the default low chiller setting the displayed temperatures will be correct to within about +/-0.1°C, for deviations at other settings see 3.

Safety features

In order to prevent excessive heating or cooling of the shim system and probe body, extra ambient gas is provided to these parts of the system. The probe gas ("flush gas") is controlled automatically, but the shim cooling gas has to be turned on manually. This is done by opening the needle valve situated below the sample changer, by turning it anticlockwise until the sound of the flow stops getting louder. Failure to do this for very high temperature experiments risks damage to the shim system, for very low temperature risks condensation on the base of the shim system which could lead to corrosion.

The major risks to the spectrometer, are that if the shim system reaches 353K (80°C) the epoxy holding the shim coils in place could melt; if the magnet flange reaches 273K (0°C) the O-rings sealing the vacuum space could shrink resulting in loss of vacuum (and then the magnet!). The shim coil temperature is reported in the acquisition status bar, see figure 5. If the shim temperature gets close to these limits, a warning message will appear on screen and for high temperature experiments you should immediately check the shim cooling gas is active, and if it is on with significantly audible flow then you must reduce the probe temperature immediately to avoid risk of damage to the system.

As an additional local measure we have implemented a routine that runs on TopSpin startup, which sets the VT unit to 298K, and the gas flow to whatever the current default for the installed probe is. The current reported temperature is also checked and if this deviates substantially from room temperature a warning message will be displayed, followed by another message when the temperature returns to normal. You should not rely on this to reset temperature after you have finished; you should take care at the temperature is reset significantly before the end of your booked time.

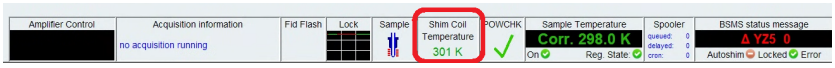

Figure 5: Acquisition status bar, with the shim coil temperature highlighted

Getting started

Firstly, make sure you have the correct spinner type: the blue spinners are rated only from 0-80°C so if there is any chance you will work outside this range you must use the Kel-F (translucent white) spinners, or for the lowest temperatures the ceramic (hard white) one, as this will be stable under the higher gas flow rates required

to achieve the lowest temperatures. The ceramic spinners tend to be very tight - take great care when inserting the sample and hold the tube very close to the spinner in order to minimise the risk of bending and breaking the tube. Make sure the tube is exactly aligned with the spinner, and you can rotate the tube back and forth while steadily pushing the tube in; ise minimal force and take as much time as needed. If you are struggling, come and see the NMR team - never force the sample, as there is a real risk of breakage (it's the only way I have ever broken an NMR tube...)

At some point we had the SampleXpress Lite sample changer on Glengrant and this may happen again in future, so here for reference are details of how to work with this. The sample changer only works with the blue spinners, so you need to remove the carousel and turn the changer off in order to work with the other types. To do this:

- Use the **`sx ej`** command to remove any sample that may be in the magnet
- Remove all samples from the carousel (taking note of positions)
- Store the samples in the rack by the spinner box
- Turn off the changer by pressing the button on the front until the lights turn off
- Lift up the carousel and remove it
- Place the carousel on top of the console to the left of the desk
- You can now use the **`ej`** and **`ij`** commands to insert samples

It is usually worth at least getting your sample in and checked at room temperature, so you can check the sample is OK before spending time changing the temperature. Make a new dataset and lock/shim/atma as normal and acquire a spectrum and if all looks as expected you can proceed with next steps. If you need to insert a sample at a fixed temperature, you should get the system stabilised on a dummy sample and then you can exchange samples once the system is stable at the desired temperature.

Before setting the temperature, think about the following points:

- What range of temperatures do I need to use?
- Is the solvent compatible with the required temperature range?
- Have I used the appropriate spinner?
- Is the shim cooling gas turned on?
-

To set the temperature you can open the temperature control window with the **edte** command, or double-click the sample temperature indicator in the acquisition status bar. The temperature control window on Glengrant looks like figure 6; on Auchentoshan the same except that there is no chiller control option.

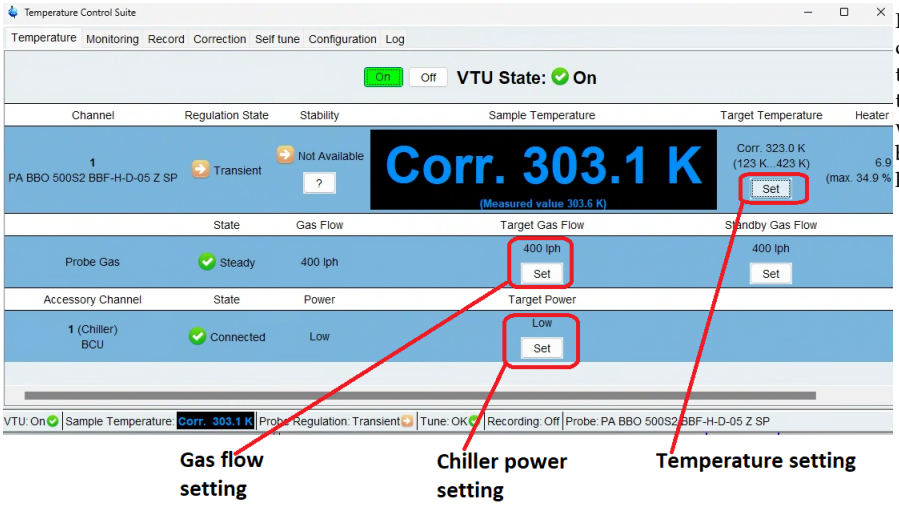

Figure 6: EDTE temperature control display. "Corr" indicates some correction function has been applied to the temperature; the colour will be green when the set temperature is reached, blue when lower than set, red when higher.

The (calibrated) temperature is set under the target temperature, and if necessary the target gas flow rate can be set - for temperatures below 15°C on Glengrant this should be set to **1000 l/hr**. On Glengrant the chiller power can also be set; this should be low for experiments around room temperature or above, and maximum for temperatures below 15°C. The practical lower limit on Glengrant is around -50°C (223K). If you just want to get the sample cooler and don't care about the exact calibration, you can keep the flow rate as normal and just set the chiller power to medium (down to 0°C) or strong.

For high temperature experiments, you can just set the required temperature; you should turn the chiller power to "off" above 80°C.

For low temperature experiments, you will probably need to change the chiller power as well as the gas flow and temperature; these should be done separately to avoid the system cooling down too rapidly:

- Change the chiller power as indicated in table 1 or table 2
- Wait for the temperature
- Set the gas flow as indicated in table 1 or table 2
- Change the chiller power as indicated in table 1 or table 2

- Wait for the

Once the target temperature is set, the display of the measured temperature will change - it will be blue if the measured temperature is less than the set temperature, and red if higher. The stability indicator in the temperature control window, and the "reg. state" indicator in the sample temperature widget in the status bar, will indicate whether the temperature has stabilised. You should wait for the temperature to stabilise before proceeding.

Steps to repeat at the final sample temperature

Once the sample temperature has stabilised, you may need to repeat some parts of the setup process for optimal results. You should lock the sample if you have not already done so, and then retune the probe with **`atma`**, as temperature changes of the tuning components can occur, affecting the resonance frequency of the probe circuit. Most importantly you should (re)shim the sample, as changes to the temperature of the shim system will change the effect of the shim coils and change the lineshape. If you are planning to run long experiments, you may want to do things like acquiring preliminary 1D spectra, relaxation measurements, etc, and then repeat the shimming before starting your long experiments to get the best starting lineshape.

For shimming the sample at temperatures away from room temperature you must consider that convection is guaranteed to be present in the sample for solvents other than water/D_2O, so you should always use the "convcomp" option as part of your topshim command (the **`tshim`** macro includes this). It may be worth adjusting the offaxis shims as well, so the "tunea" option can be used, and "plotall" to allow inspection of the data in case of problems so e.g. **`topshim tunea convcomp plotall`**. The macro **`tshim`** does this automatically so you can always use that.

If you are planning long measurements at a single temperature, note that the shim system will take a rather long time to equilibrate itself. As a result the optimum shim settings may change during your experiment, particularly if you shim the sample very soon after the temperature has been reached. In order to mitigate the effect of this, the "autoshim" tool can be used. To turn this on, you can type **`autoshim on`**, or right click on the BSMS status widget in the status bar and select "toggle autoshim mode".

The autoshim function operates completely unlike topshim - it uses only the height of the lock signal to assess the shim quality. It is not efficient for initial shimming but will run continuously during experiments and maintain a good shim state. After a fixed interval

(e.g. 10s here), one set shim function will be changed by a set number of units, and the effect on the lock signal noted. If the lock level goes up this represents an improvement in the field homogeneity, and next time this shim function is changed it will be changed in the same direction. If the lock level goes down, that shim will be changed in the opposite direction next time. All the set shims are cycled through repeatedly, so generally Z, Z2, X, Y and then back to Z. Note that even during gradient experiments, where the lock signal is periodically dephased by the gradient pulses, the autoshim routine can still work reliably.

Convection

At temperatures significantly different from room temperature, it is almost guaranteed that in organic solvents convection will be present - modern probe designs help to reduce this effect but it is never eliminated completely. Apart from the impact on shimming, for most 1D and 2D experiments convection has minimal impact; however for diffusion experiments it is usually disastrous. For DOSY/diffusion measurements away from room temperature you must use the convection compensated experiments (pulse program dstebpgp3s or dstebpgp3s.ptg). In low viscosity samples some 2D experiments can lose signal due to convection; if 2D experiments look like they are failing unexpectedly check with us.

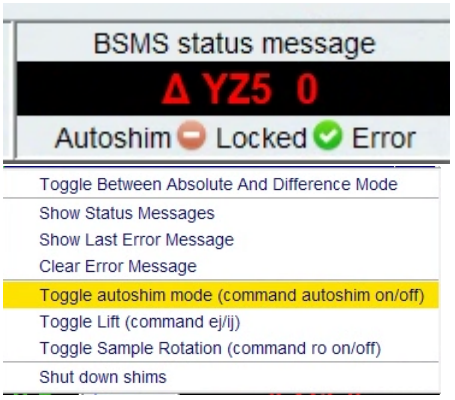

Figure 7: Right click on the BSMS status widget to turn on autoshim

Running experiments at multiple temperatures

Obviously you can simply follow the normal temperature setting process each time, however if for example you want to run a sequence of proton spectra in intervals of 10°C this becomes rather tedious. If you just want to repeat a single experiment, you can use the AU program **`multi_zgvt_topshim`**. This is a locally modified program which takes the entries in a temperature list and repeats the current experiment for each, waiting for sample temperature equilibration and repeating shimming each time. Note that this cannot change any operating conditions except the temperature - if you want to run from room temperature to -50°C, you would have to use maximum chiller power and 1000 l/hr gas from the beginning. In particular if you want to cover high and low temperature ranges, you will need to run these completely separately.

To use this, first create a list of temperatures (in K) with the command **`edlist vt <name>`**, so I might use **`edlist vt ptg`**. Enter the temperature values one per line, and you can add a last line which is 298 to return the temperature back to normal. So for temperatures

293-323 in 10K steps I could use a list as shown in figure 8.

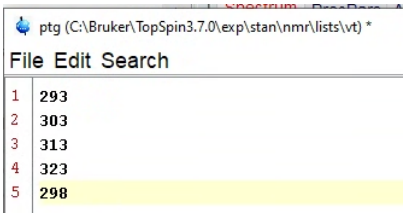

Figure 8: Example VT list with return to room temperature

Once you have created and saved your list, start the program by typing **multi_zgvt_topshim**. Enter the name of your temperature list, and it will ask you to confirm that the highest and lowest temperatures in the list are OK. Enter the number of experiments (it defaults to the number of entries in the list; if you set a lower number it will start from the beginning of the list and use that many entries). It will ask for a temperature equilibration period; 120 (seconds) is probably OK given that we are using slope limited temperature regulation. Once you click OK it will immediately start running the first experiment. Note this will run in the dataset that you called the command from.

If you want to stop the sequence of experiments, it's not sufficient to simply stop the current experiment, you have to kill the multi_zgvt_topshim program. To do this type **show**, and in the active commands popup select the line with module multi_zgvt_topshim, as shown in figure 9 and click kill. OK the resulting error message, and the AU program will stop. You can then close the active commands window.

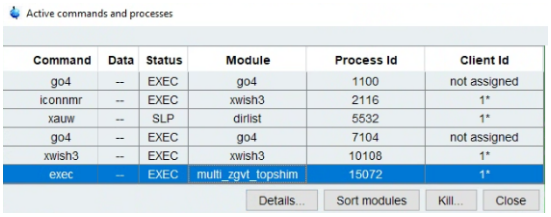

Figure 9: Killing the multi_zgvt_topshim au program

Returning the system to room temperature after long experiments

In order for the system to be completely ready for the next user, it is vital that you return the system to its normal operating state before your booked time ends - if the next user has to wait for a long time for the system to be ready they may be unable to complete required experiments and this may result in a complete waste of the booked time.

Obviously this means allowing enough time for the probe to return to normal temperature. With the slope-limited temperature regulation, this will take at least 1 minute per 5 degrees temperature change. So, if you are operating at 50°C, it will take at least 5 minutes to return to 25°C, and if you are at -50°C it will take at least 15 minutes. This however is not nearly enough time for the whole system to stabilise sufficiently - this is only reflects the temperature of the sample space. Other parts of the probe and the shim system will also change temperature, and with a large thermal mass these return to room temperature rather slowly. During very low temperature operation, the chiller must be set to maximum chilling power, and once this is returned to the normal low power it will take about 20 minutes for the output temperature to stabilise; this applies even if the sample has been at low temperature only very briefly.

From very low temperatures, where the gas flow rate has been increased and the chiller power set to maximum, in order to allow

the system to recover slowly:

- Reduce the gas flow slightly, eg to 800l/hr
- Wait for a couple of minutes - the temperature will increase
- Reduce the gas flow to 600l/hr and wait again
- Reduce the gas flow to 400l/hr and wait again
- Set the target temperature to 273K and wait until this is almost reached (10 minutes)
- Change the chiller power to low - temperature will start to increase
- Once the temperature stops increasing, set temperature to 298K

From high temperatures you only need to make sure the chiller power is set to low (Glengrant); the temperature can simply be set back down and the probe will cool slowly. For temperatures above 50°C you should again allow 1 hour for complete stabilisation of the whole system.

Leaving the system

Once the sample temperature is close to room temperature you can remove your sample. Turn off the shim cooling gas at the needle valve - leaving this on can waste a significant amount of gas. Make final checks:

- Temperature is set to 298K
- Gas flow and chiller settings are as in table 1 or table 2
- On Glengrant, return the sample changer:
- Put the carousel back on
- Rotate the carousel until it falls into the correct position
- Turn the unit on with the button at the front
- Wait until the main light turns green - if it goes red contact the NMR team
- Return samples to the carousel

Tables of settings and calibration data

Range (C/K)	Spinner type	Gas flow	Chiller setting
15-80 / 283-353	Blue or Kel-F	400	low
80-120 / 353-373	Kel-F or ceramic	400	off
0-15 / 273-283	Kel-F or ceramic	400	strong
-50-0 / 223-233	Ceramic	1000	strong

Table 1: Summary of required operating conditions on Glengrant for different temperatures

Range (C/K)	Spinner type	Gas flow
10-80 / 283-353	Blue or Kel-F	535
80-120 / 353-373	Kel-F or ceramic	535
0-10 / 273-283	ceramic	1000

Table 2: Summary of required operating conditions on Auchentoshan for different temperatures

Spectrometer	Set temp	Gas flow	Chiller setting	error (+/- 0.1K)
Glengrant	293k	400	Medium	0K
Glengrant	283K	400	Medium	0K
Glengrant	273K	400	Medium	-2.0K
Glengrant	283K	1000	Maximum	+0.2K
Glengrant	273K	1000	Maximum	+0.1K
Glengrant	263K	1000	Maximum	0K
Glengrant	253K	1000	Maximum	0K
Glengrant	243K	1000	Maximum	-0.2K
Glengrant	233K	1000	Maximum	-0.4K
Glengrant	223K	1000	Maximum	-0.8K

Table 3: Deviations between measured and real sample temperatures. Error value should be added to the displayed temperature to get the true temperature, ie at a displayed temperature of 223K, the real temperature is 222.2K. For intermediate temperatures one can interpolate the errors. Reproduciblilty, assuming sufficient equilibration time, is about +/- 0.1K

References

[1] N. Karschin et al. "Extension and improvement of the methanol-d4 NMR thermometer calibration". In: *Magn Reson Chem* 60.2 (2022), pp. 203–209. DOI: https://doi.org/10.1002/mrc.5216.

[2] Wikipedia. *Proportional–integral–derivative controller — Wikipedia, The Free Encyclopedia*. http://en.wikipedia.org/w/index.php?title=Proportional%E2%80%93integral%E2%80%93derivative%20controller&oldid=1208005380. [Online; accessed 11-March-2024]. 2024.