NMR

Variable Temperature Measurements using CPMAS iProbes

Innovation with Integrity

Introduction

Solid-state NMR experiments are frequently conducted at temperatures that differ from ambient temperature. This application note describes the specific procedures and precautions for variable temperature measurements using Bruker's CPMAS iProbes, which provide a high degree of automation. But the described routines can also be adapted for non-iProbe solid-state probes.

Using iProbes, variable temperature experiments can also be performed automatically using IconNMR. If measurements at temperatures outside of the range of approximately -10 to 50 °C are carried out, users must be careful to select a rotor drive cap from a suitable material, configure the gas supply lines correctly, and to set the shim cooling or heating appropriately.

Drive Cap Selection

The general sample temperature range for CPMAS iProbes is -80 to 200 °C. However, when using Kel-F drive caps, which are well suited for repeated use and commonly used for 4 mm rotors, the temperature range is limited to approximately -10 to 50 °C. In other words, the variable temperature range is limited not only by the probe specification but also by the selection of the drive cap material. Table 1 shows various cap materials, their constituent elements and the allowable temperature range for each cap.

Drive Cap Material	**Kel-F**	**Vespel**	**Zirconium Oxide**
Constituent Elements	C, F, Cl	C, H, O, N	Zr, O
Temperature Range	-10 - 50 °C	-30 - 80 °C (*)	-140 - 700 °C

Table 1: Drive cap materials, constituent elements and allowable temperature range for each cap.

(*) For LTMAS and DNP applications, special tight-fit rotors sets are available which enable experiments over the whole VT range applied in LTMAS & DNP

Gas Line Configuration in Solid-State NMR

Figure 1 shows a schematic diagram of the recommended gas line routing for CPMAS iProbes. For magic angle spinning (MAS) experiments, several gas flows are typically required: the bearing gas flow for the air bearings, the drive gas flow to spin the rotor with the MAS turbine, VT gas to control the temperature of the sample, frame cooling to prevent heat buildup in the probe, and shim cooling to cool the room temperature shim stack. In the case of a CPMAS iProbe, the bearing and VT gas are combined in one line and are connected to the bearing port of the probe with a Johnston connector. When operating at temperatures below room temperature, the combined bearing / VT gas flow must be cooled by a suitable chiller like Bruker's BCU-I or II.

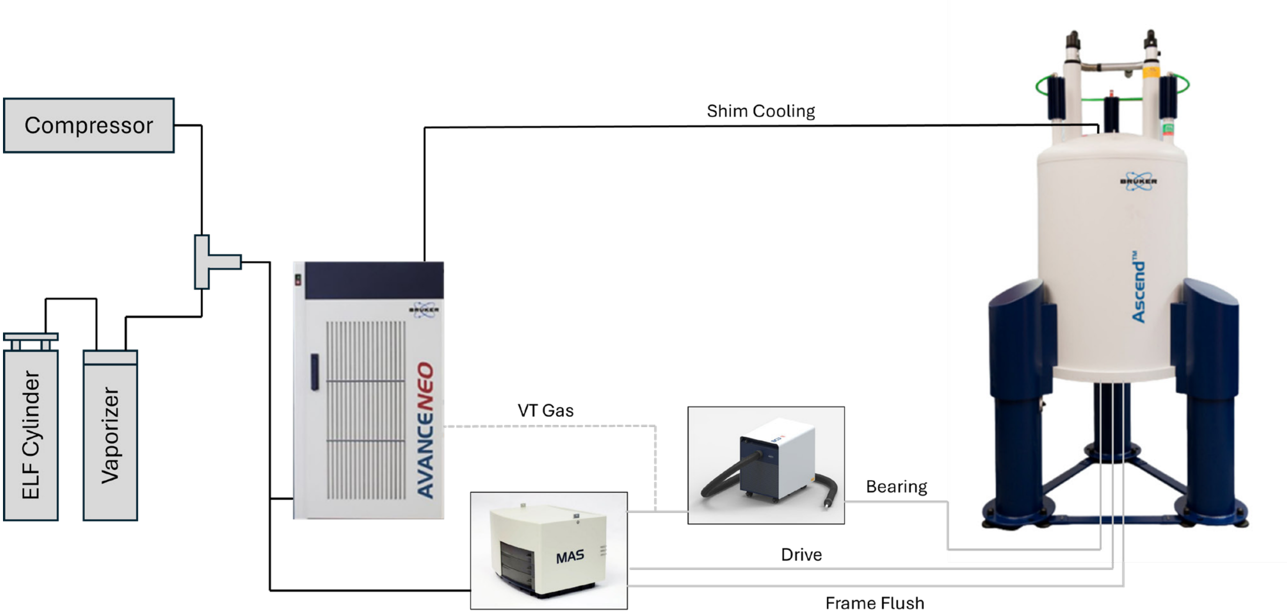


Figure 1: Schematic diagram of the recommended gas line configuration for CPMAS iProbes. The dotted line represents a tube which connects the output of the MAS3 unit to the console to ensure that the console senses the presence of VT cooling gas.

In experiments around room temperature, compressed air from a compressor can often be used for the gas supply, but when the temperature is above 70 °C or below 0 °C, dry N_2 gas should be used, as the use of dry N_2 gas helps to avoid oxidation of components inside the probe at higher temperatures and condensation at lower temperatures. Many NMR labs are equipped with a compressed N_2 supply of 6 bar or more. If such a N_2 supply is not available, a N_2 gas generator as shown in Figure 2 is needed. A N_2 gas generator consists of an Evaporator Liquid Flask (ELF) cylinder filled with liquid N_2 and a vaporizer. In the setup shown in Figure 2, two ELFs are used, but one will often be sufficient. It is convenient to use a three-way valve as shown in Figures 1 and 3 to switch between compressed gas from a compressor and dry N_2 gas from a vaporizer.

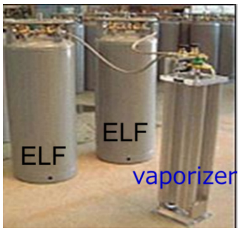


Figure 2: N_2 gas generator

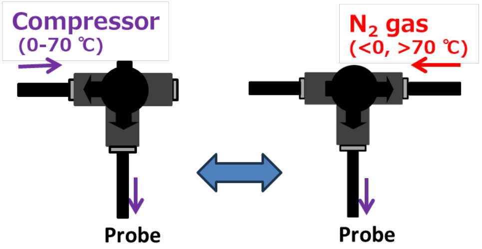


Figure 3: Three-way valve

Please note that there are many ways to generate the required gas flows. In this application note, we don't discuss the various gas source options. In the following, the presence of a gas installation compatible with Bruker's site-planning specifications will be assumed.

Use of a Cooler for Measurements Below Room Temperature

To perform experiments below room temperature, it is necessary to cool the VT and bearing gas streams with one of the coolers shown in Figure 5. There are different types of coolers:

- The Smart Cooler BCU I can cool VT gas to -40 °C with a maximum flow rate of 50 NL/min. As a rule of thumb, the sample temperature will drop to around 0 °C at a MAS speed of 5 kHz.
- The Smart Cooler BCU II can cool VT gas to -80 °C with a maximum flow rate of 60 NL/min. The sample temperature will drop to around -40 °C at 5 kHz MAS. For solid-state NMR, the BCU II is typically used.
- A LN_2 heat exchanger can be used to cool the VT gas by passing it through a bath of liquid N_2 in a dewar at 77 K. The sample temperature can be lowered to -150 °C. The number of turns of the heat exchanger needs to be selected depending on the target temperature.

Each of the coolers above can be connected to Bruker's CPMAS iProbes with a Johnston connector.

The BCUs make low temperature experiments easy and convenient since temperature control settings can be adjusted directly from TopSpin. The LN_2 heat exchanger enables lower sample temperatures than the BCUs, but is less convenient to use as the liquid N_2 in the dewar needs to be refilled when the level runs low.

Smart Cooler BCU I -40/50

Smart Cooler BCU II -80/60

LN_2 Heat Exchanger

Figure 5: Different Types of VT Gas Coolers

Shim Coil Cooling

In variable temperature NMR experiments, it is recommended to let gas flow through the annular gap between the room temperature shim stack and the magnet bore. At high temperatures, this helps to maintain the temperature of the shim stack below the allowable maximum. At low temperature, this helps to avoid freezing of the O-rings of the magnet bore, which could lead to degradation of the magnet's isolation vacuum and result in a quench. The gas supply to the shim stack is shown in Figure 6. If the shim coil temperature drops below 5 °C or rises above 80 °C, TopSpin issues a warning. The shim coil temperature can be displayed in the TopSpin status bar. The shim gas flow settings can be adjusted as follows:

1. Run "ha" from the TopSpin command line
2. From the window with the Ethernet addresses, open the web interface of the BSMS
3. When the BSMS Service Web opens, click "Variable temperature"
4. Click "VT Control" and then "Auxiliary Gas Flow"
5. When the window shown in Figure 7 opens, ensure that "auto" is selected for "Shim Gasflow Mode" (be sure to click the "Set" button when making a change). This setting will adjust the gas flow to the shim coil automatically depending on the shim coil temperature.

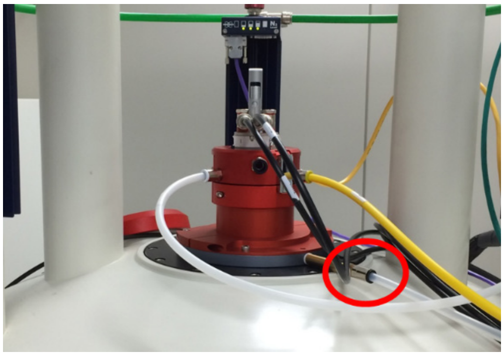
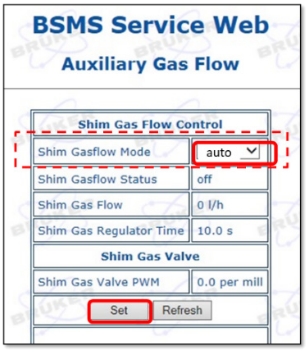


Figure 6: Shim cooling piping to magnet



BSMS Service Web

Auxiliary Gas Flow

Shim Gas Flow Control	
Shim Gasflow Mode	auto
Shim Gasflow Status	off
Shim Gas Flow	0 l/h
Shim Gas Regulator Time	10.0 s
Shim Gas Valve	
Shim Gas Valve PWM	0.0 per mill

Figure 7: Auxiliary gas flow window

In the case of high temperature measurements exceeding 120 °C for extended periods of time, it is effective to intentionally cool the shim cooling gas. Such a setup is schematically shown in Figure 8. This method of connecting a BCU-I unit is intended for situations where a dedicated high-flow flush line for shim cooling is not available. Ideally, the system should always be flushed with room-temperature cooling gas with a sufficiently high flow rate to ensure efficient thermal management during extended high-temperature experiments.

If such a high-flow gas supply cannot be provided, the procedure described here may be used as an alternative. However, it is essential that the system is not left unattended during the thermal equilibration phase, and that temperatures are closely monitored throughout the experiment.

In particular, the temperatures of the magnet flanges and the shim coil must not fall below the specified safety thresholds. Detailed information on these limits can be found in the respective manuals for the shim and magnet systems. Additionally, do not connect a BCU-II unit using full cooling power. Excessive cooling can cause the magnet flanges to reach critically low temperatures.

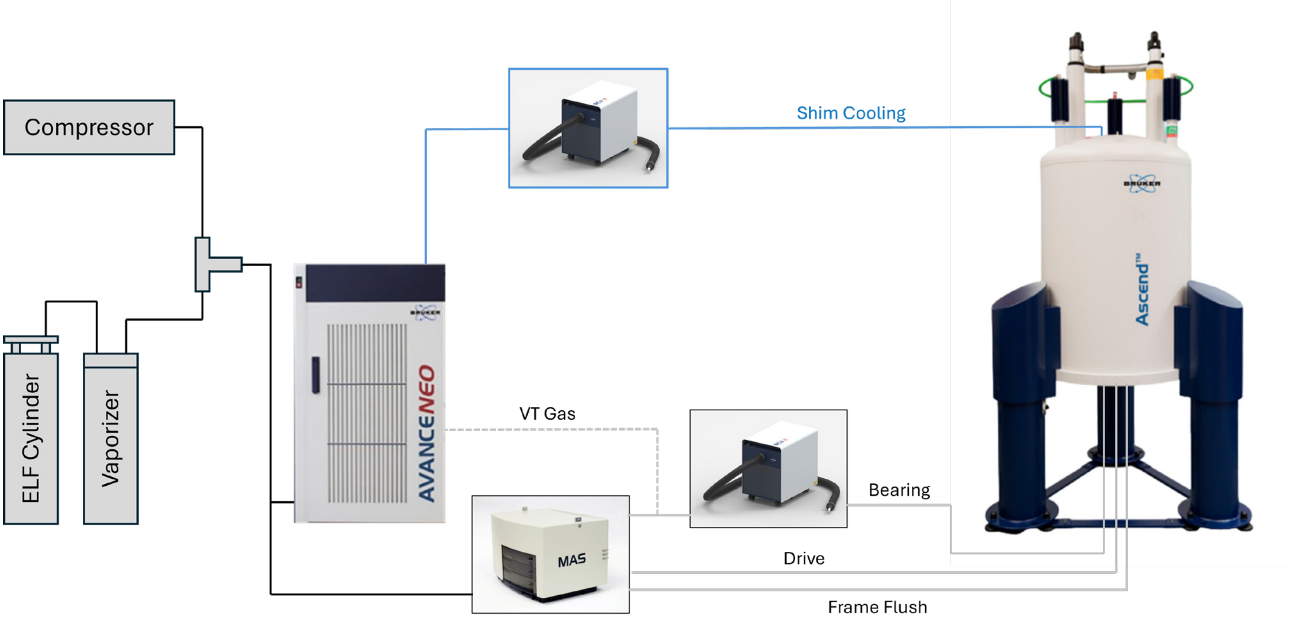


Figure 8: Schematic diagram of how to use a BCU to cool the shim cooling gas.

Figure 9 shows the evolution of the shim coil temperature as a function of time when the VT temperature is set to 200 °C and the sample is rotated at 5 kHz in a CPMAS iProbe. The shim coil cooling gas was cooled with a BCU-I, as shown in Figure 10, by connecting the BCU-I outlet directly with the shim cooling tube. Depending on form of the BCU, this can be done using a ball joint or a Johnston coupling adapter.

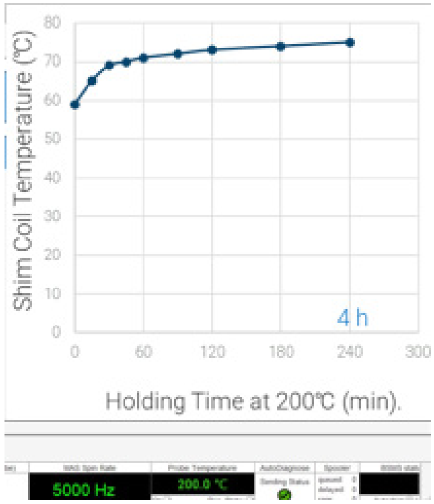


Figure 9: 200°C holding time vs Shim Coil Temp.

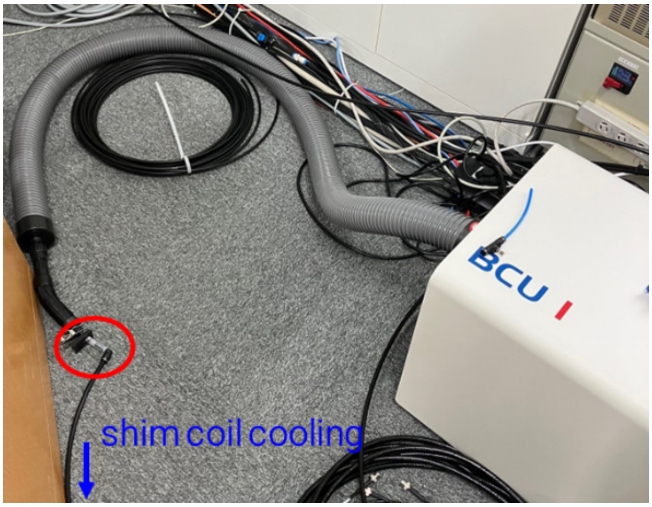


Figure 10: Use the BCU-1 for Shim

From Figure 9, it can be seen that the temperature of the shim coil slowly increases at a rate of about 1°C/hour after 60 minutes. Since 80 °C is the upper allowable limit for the shim coil temperature, it is estimated that NMR measurements at 200 °C for at least 8 hours are enabled by this simple setup. If room temperature gas had been used for shim coil cooling, the maximum experimental time would have been about 20 minutes.

Summary of Necessary Equipment for Each Temperature Range

As mentioned above, depending on the target sample temperature, it is necessary to select the appropriate rotor cap, configure the gas supply lines accordingly, choose a suitable cooler, and adjust the settings and possibly the setup for shim coil cooling.

Table 2 summarizes the equipment required for each temperature range. While Vespel and Kel-F caps are only suitable for experiments in certain temperature ranges, zirconium oxide caps are suited for the whole temperature range, but are not available for all rotor diameters. Dry N_2 gas can be used at all temperatures. However, at around room temperature, it is often cheaper and more convenient to use air from a compressor. For experiments below room temperature, a heat exchanger can be used as a cooler at any temperature, but it is much more convenient to use a BCU in the temperature range where the cooling power of the BCU is sufficient. For shim coil cooling and heating, it is usually sufficient to set the "Auxiliary Gas Flow" to "auto" in the BSMS service web; when high temperatures up to 200 °C are required, consider cooling the gas stream which is used for shim cooling.

Temperature Range	Cap	Gas Supply	Cooler	Shim Coil Cooling & Heating
-80 °C to -40 °C	Zirconium Oxide	N_2	heat exchanger	Use of dedicated gas line is ideal.
-40 °C to -30 °C	Zirconium Oxide	N_2	heat exchanger or BCU-II	Auto
-30 °C to -10 °C	Zirconium Oxide or Vespel	N_2	heat exchanger or BCU-II	Auto
-10 °C to -0 °C	Zirconium Oxide, Vespel, or Kel-F	N_2	heat exchanger or BCU-II	Auto
0 °C to 25 °C	Zirconium Oxide, Vespel, or Kel-F	N_2 or compressed air	heat exchanger or BCU-I or II	Auto
25 °C to 50 °C	Zirconium Oxide. Vespel, or Kel-F	N_2 or compressed air	no need	Auto
50 °C to 70 °C	Zirconium Oxide or Vespel	N_2 or compressed air	no need	Auto
70 °C to 80 °C	Zirconium Oxide or Vespel	N_2 or compressed air	no need	Auto
80 °C to 120 °C	Zirconium Oxide	N_2	no need	Auto
120 °C to 200 °C	Zirconium Oxide	N_2	no need	Use of chilled cooling gas is recommended

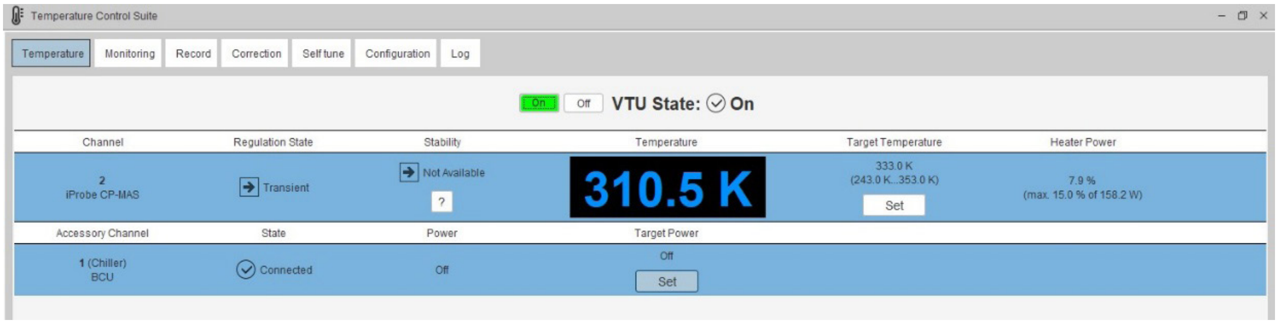
Table 2: Equipment recommended for each temperature range

Variable Temperature Experiment in Practice

Once the equipment for an experiment in the desired temperature range has been prepared, insert the MAS rotor into the probe. Set the sample temperature in the "Temperature Control Suite" in TopSpin. The "Temperature Control Suite" can be launched by clicking on the temperature display in the status bar of the TopSpin, or by running "edte" from the command line of the TopSpin.

Figure 11 shows the "Temperature Control Suite". To start the temperature control, the desired temperature needs to be entered and the button "On" needs to be clicked. In case the temperature control turns off immediately after switching "on", click the "Configuration" tab and ensure that "gas mode" is set to "external" as shown in Figure 12.

To lower the sample temperature to below room temperature, click "Set" for the "Target Power" of the chiller as shown in Figure 11 and select "Low", "Medium" or "Strong" according to the target temperature. Note that it typically takes approximately 15 minutes for the temperature to drop.



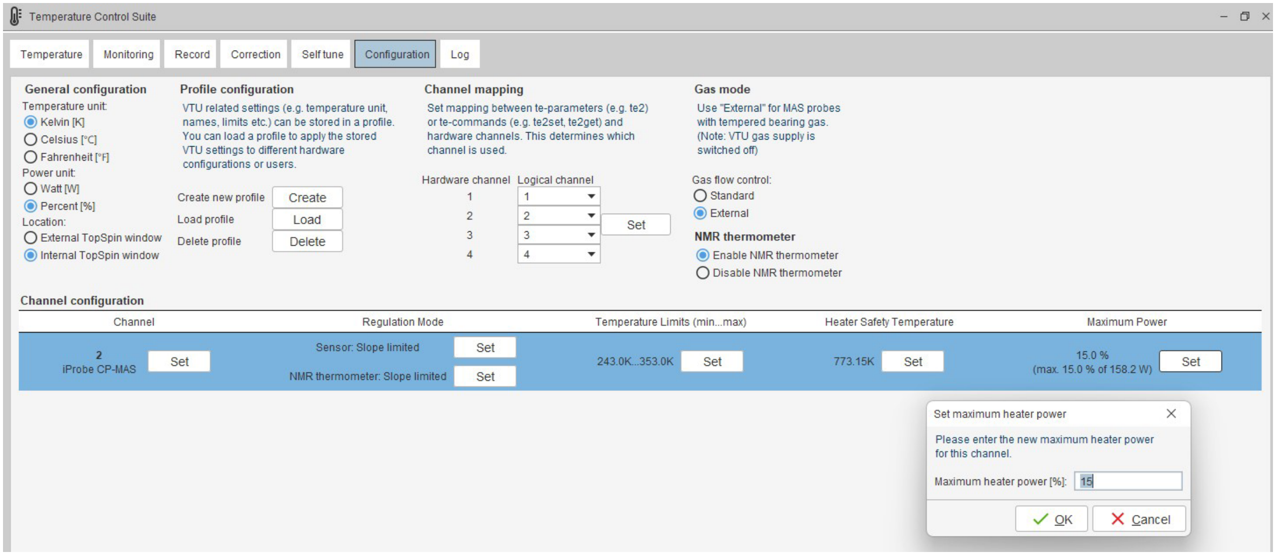
VTU State: ✓ On

Channel	Regulation State	Stability	Temperature	Target Temperature	Heater Power
2 iProbe CP-MAS	→ Transient	→ Not Available	310.5 K	333.0 K (243.0 K...353.0 K)	7.9 % (max. 15.0 % of 158.2 W)

Accessory Channel	State	Power	Target Power
1 (Chiller) BCU	✓ Connected	Off	Off

Figure 11: Temperature Control Suite

The maximum applicable "heater power" shown in Figure 11 is best set modestly to avoid large overswings in the temperature regulation behavior. It is recommended to start with 10% or less and then gradually increase the heater power setting. To set the heater power, click "Set" under "Maximum Power" shown in Figure 12.



General configuration

Temperature unit:
● Kelvin [K]
○ Celsius [°C]
○ Fahrenheit [°F]

Power unit:
○ Watt [W]
● Percent [%]

Location:
○ External TopSpin window
● Internal TopSpin window

Profile configuration

VTU related settings (e.g. temperature unit, names, limits etc.) can be stored in a profile. You can load a profile to apply the stored VTU settings to different hardware configurations or users.

Create new profile
Load profile
Delete profile

Channel mapping

Set mapping between te-parameters (e.g. te2) or te-commands (e.g. te2set, te2get) and hardware channels. This determines which channel is used.

Hardware channel	Logical channel
1	1
2	2
3	3
4	4

Gas mode

Use "External" for MAS probes with tempered bearing gas. (Note: VTU gas supply is switched off)

Gas flow control:
○ Standard
● External

NMR thermometer

● Enable NMR thermometer
○ Disable NMR thermometer

Channel configuration

Channel	Regulation Mode	Temperature Limits (min...max)	Heater Safety Temperature	Maximum Power
2 iProbe CP-MAS	Sensor: Slope limited NMR thermometer: Slope limited	243.0K...353.0K	773.15K	15.0 % (max. 15.0 % of 158.2 W)

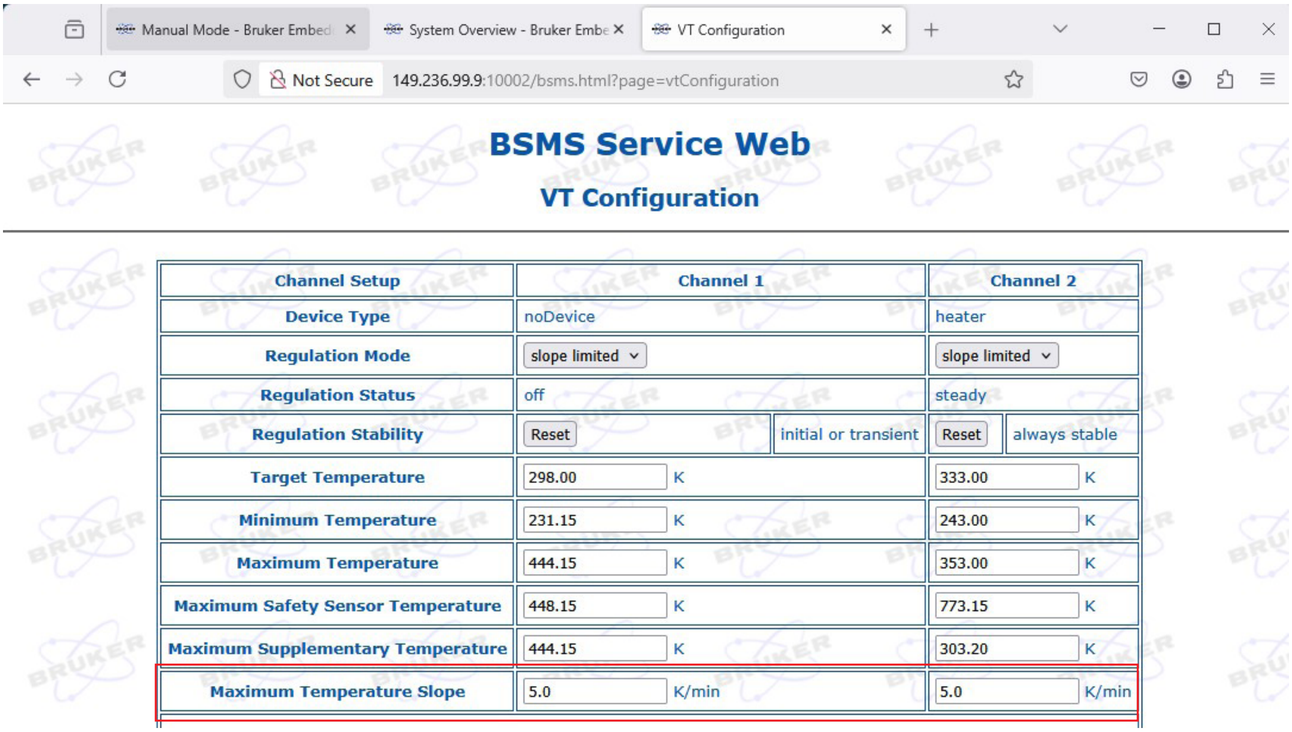
Set maximum heater power

Please enter the new maximum heater power for this channel.

Maximum heater power [%]: 15

Figure 12: Maximum Heater Power Setting

To prevent a sudden rise in temperature, it is recommended to select “Slope limited” in the “Regulation Mode” on the screen shown in Figure 12. This prevents the temperature from rising faster than at a certain rate. The maximum slope for “Slope limited” can be set in the “VT Configuration” window of the BSMS Service Web as shown in Figure 13 (run “ha” → open “BSMS” → open “Variable Temperature” → open “VT Control” → open “VT Configuration”).



BSMS Service Web

VT Configuration

Channel Setup	Channel 1	Channel 2
Device Type	noDevice	heater
Regulation Mode	slope limited	slope limited
Regulation Status	off	steady
Regulation Stability	Reset initial or transient	Reset always stable
Target Temperature	298.00 K	333.00 K
Minimum Temperature	231.15 K	243.00 K
Maximum Temperature	444.15 K	353.00 K
Maximum Safety Sensor Temperature	448.15 K	773.15 K
Maximum Supplementary Temperature	444.15 K	303.20 K
Maximum Temperature Slope	5.0 K/min	5.0 K/min

Figure 13: Temperature Control Suite

Correcting the Difference between the Display Temperature and the Sample Temperature

It has been demonstrated that the sample temperature increases as the MAS speed increases (due to frictional heating).[1, 2] For a 4 mm rotor, there is data showing a rise of approximately 3 °C at a MAS rate of 5 kHz, 9 °C at 10 kHz and 34 °C at 15 kHz[3]. In particular, samples that contain solvents such as water tend to warm easily. In addition, the decoupling strength and sample properties affect the sample temperature. Since the temperature is detected outside of the spinning rotor, there is a difference between the temperature shown on the display and the actual sample temperature.

To correct this difference, it is recommended to create a plot of sample temperatures calculated from chemical shift thermometers such as KBr and $Pb(NO_3)_2$ against the NMR display temperature. Since the ^{207}Pb chemical shift of $Pb(NO_3)_2$ changes by 0.753 ppm/K,[1] the sample temperature change can be calculated from the ^{207}Pb chemical shift change. It is recommended to generate such a plot for each MAS speed. Figure 14 shows an example plot of the displayed temperature and the actual sample temperature calculated from the chemical shift of $Pb(NO_3)_2$ at a MAS speed of 5 kHz with a 4 mm probe.

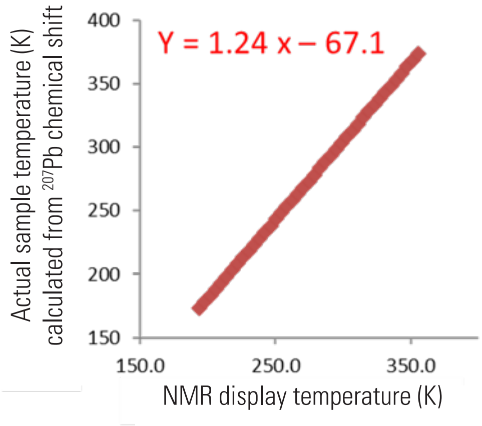


Figure 14: Example of a Temperature Correction Graph

In the case of KBr, the ^{79}Br chemical shift changes with a slope of -0.025 ppm/K.[2] Although the chemical shift change with temperature is small, using KBr has become popular recently because of its low toxicity. In addition, the ^{79}Br T1 relaxation time of KBr also changes with temperature, and the sample temperature can also be calculated using the ^{79}Br T1 relaxation time.

Finally, it has also been shown that the sample temperature varies depending on the location inside the rotor.[1] To achieve a more uniform sample temperature, it is recommended to pack the sample only near the center of the rotor. Center packing a rotor can therefore significantly reduce the temperature gradient, if the reduced volume and the therefore lower sensitivity can be accepted.

References:

1. Bielecki, A. and Brum, D.P. J. Magn. Reason. **1995**, A116, 215-220.
2. Thurber, K.R. and Tycko, R. J. Magn. Reason. **2009**, 196, 84-87.
3. Perrone, B. and Struppe, J. Presentation Material entitled "Variable Temperature & Solid State NMR" in 38th German Users Meeting.

Bruker BioSpin
info@bruker.com

bruker.com

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