

Sample Temperature in a MAS probe



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Bruker BioSpin Billerica, USA
Bruker Users Meeting China, July 23th – 26th 2019



Software - EDTE



Brucker TopSpin 3.0 on WB502 as Sebastian Wegner

Start Acquire Process Analyse Publish View Manage

Create Dataset Find Dataset Open Dataset Paste Dataset Read Pars.

Temperature Control Suite

Temperature Monitoring Record Correction Configuration Log Help

VTU State: ✔ On

Channel	Regulation State	Stability	Current Temperature	Target Temperature	Heater Power
1 1.9 mm MAS BB/1H H0815/12	✔ Steady	✔ Always Stable	300.0 K	300.0 K (100.0 K, 423.2 K) Set...	1.8 % (max. 99.3 % of 169.1 W)

	State	Gas Flow	Target Gas Flow	Standby Gas Flow
Probe Gas	✔ Operating	998 lph	1000 lph Set...	200 lph Set...

VTU State: ✔ On | Probe Temperature: 300.0 K | Probe Regulation State: ✔ Steady | Recording: ✘ Off | Probe: 1.9 mm MAS BB/1H H0815/12

Amplifier Control Acquisition information FID Flash MAS spin rate Probe Temperature Spooler Time

no acquisition running 0 Hz 300.0 K ✔ On ✔ Reg. State ✘ Stopped 10:42 Mar 14

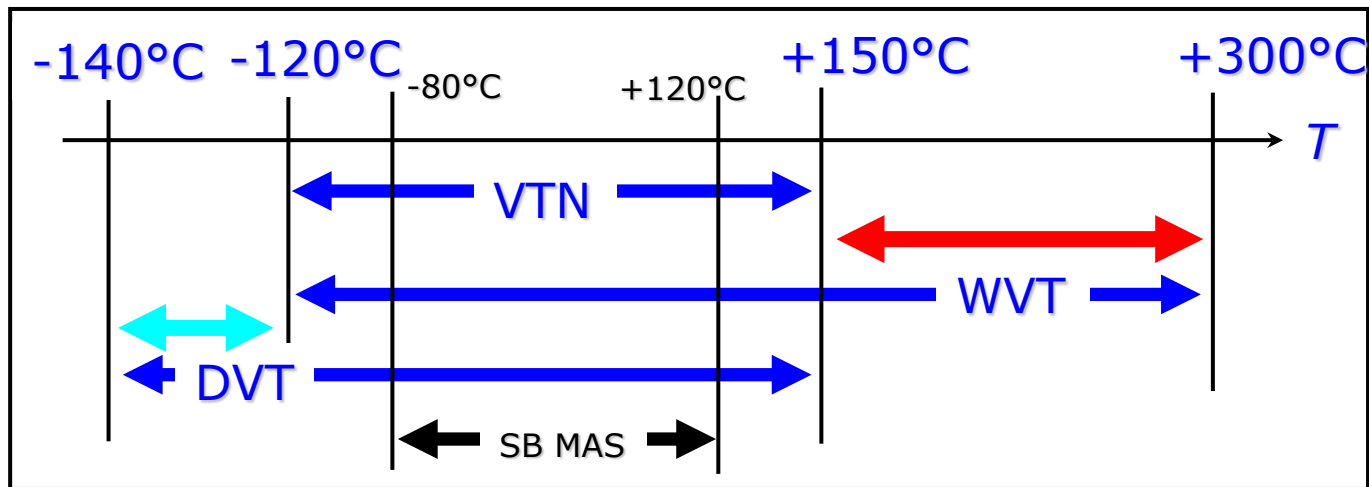
Probe Temperature
300.3 K
✔ On ⚠ Reg. State

Probe Temperature
295.9 K
✔ On ⚠ Reg. State

VT ranges of WB MAS probes

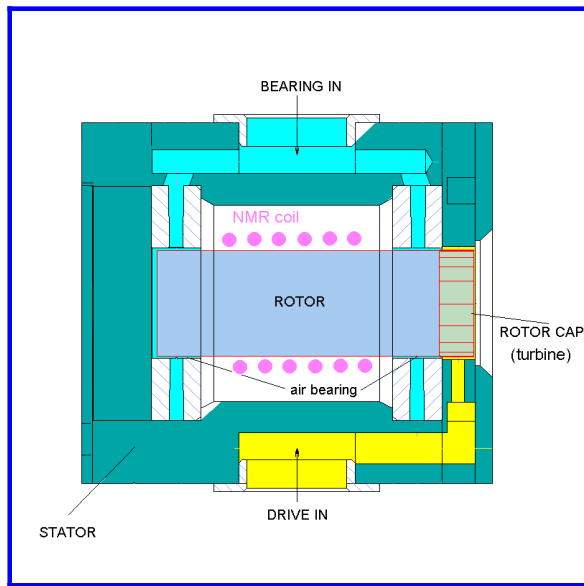


- VTN** : Variable Temperature Normal (BN-Stator)
WVT : Wide Variable Temperature (MgO-Stator)
DVT : Direct Variable Temperature (BN-Stator)

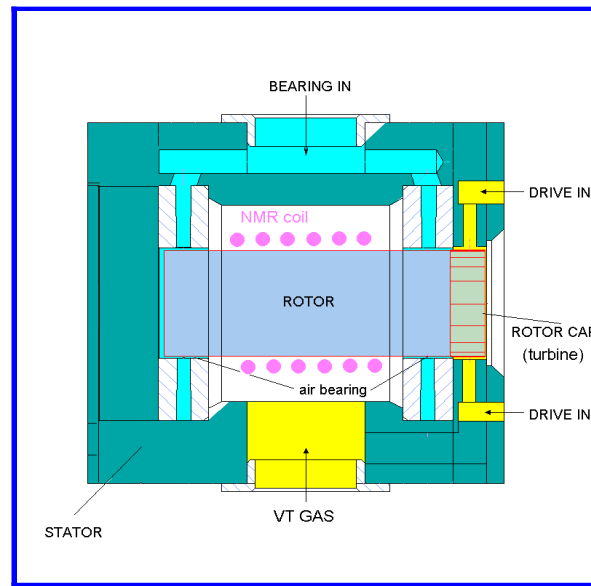


Exception: 2.5 mm probes: $-30^{\circ}\text{C} \leftrightarrow +70^{\circ}\text{C}$

VT – probe design

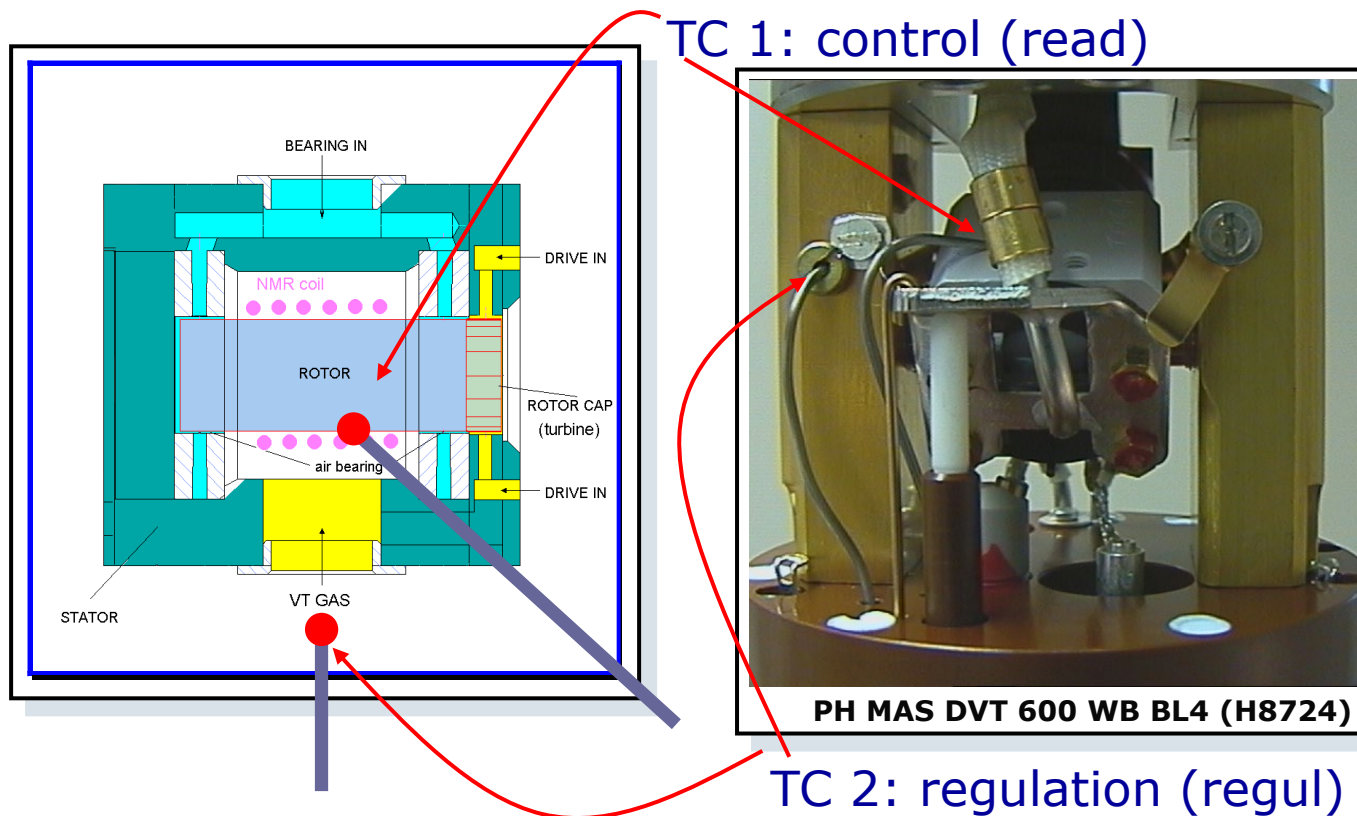


VTN / WVT
bearing gas for temperature
regulation



DVT
separate VT gas line

VT – DVT design



Sample Temperature in a MAS probe



NMR Thermometer:

$$\text{Lead Nitrate Pb(NO}_3\text{)} \quad T = \square \cdot 0.753 \frac{\text{ppm}}{\text{K}}$$

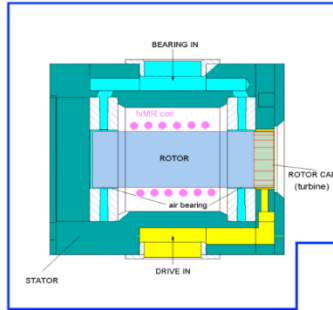
Bielecki, A. et al, J. Magn. Reson. 116, 215 – 220, 1995

Sample Temperature in a MAS probe

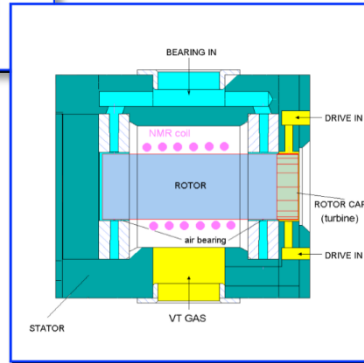


-VT design: Stator Designs

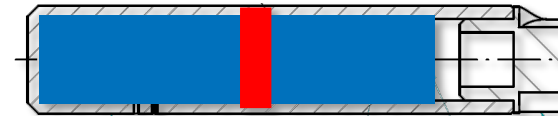
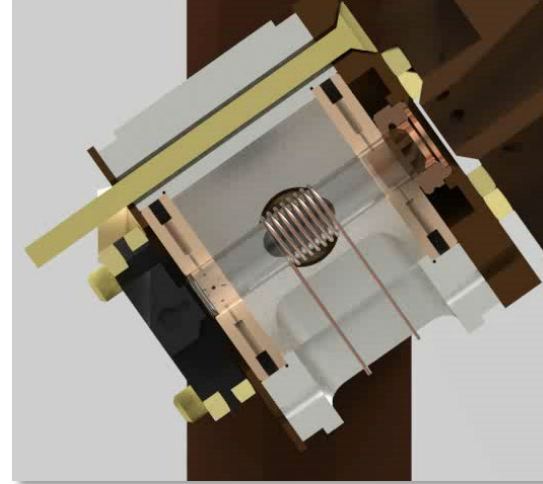
- Thermocouple locations remote from rotor



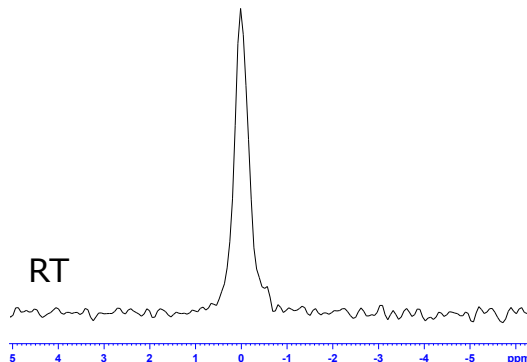
VTN



DVT

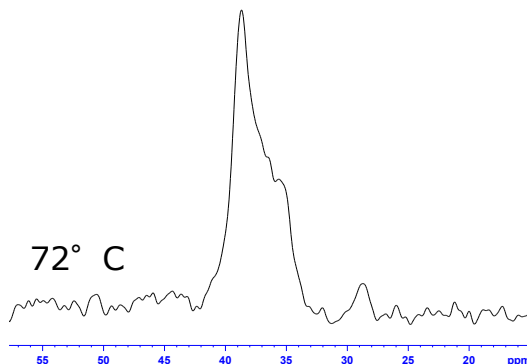


Thermal Gradient: Center Packed Rotor



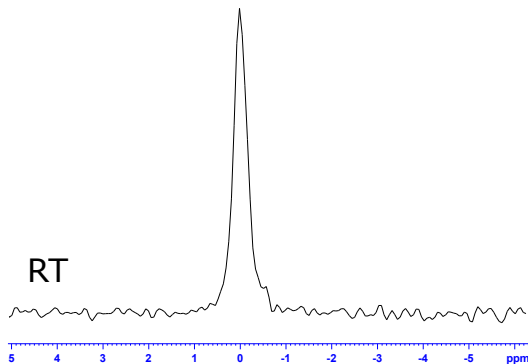
- **Leadnitrate at room temperature:**

FWHM: 0.34ppm / <1K



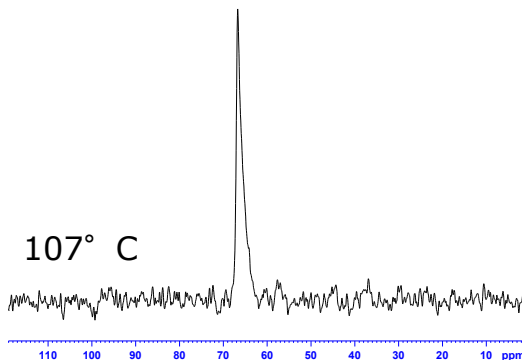
- **Leadnitrate at 72° C:**
FWHM: app. 5ppm / 6K
- **Flow Rate: 500l/h**

Thermal Gradient Center Packed Spinner



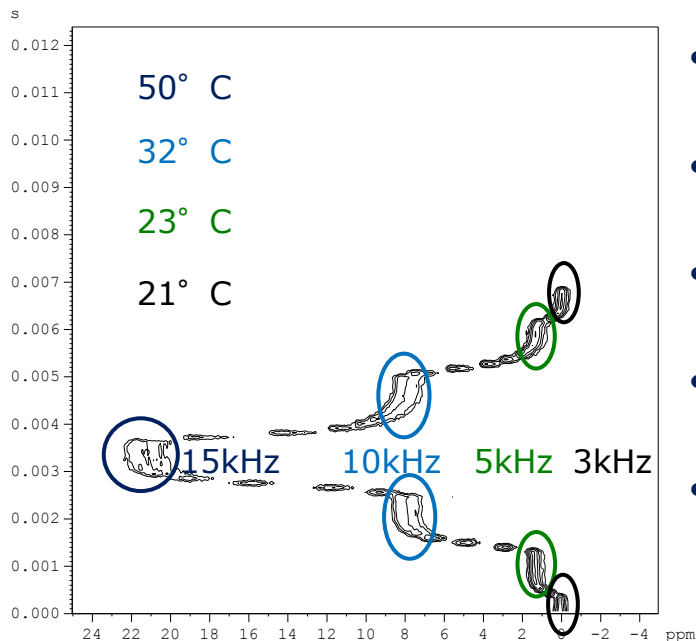
- **Leadnitrate at room temperature:**

FWHM: 0.34ppm / <1K



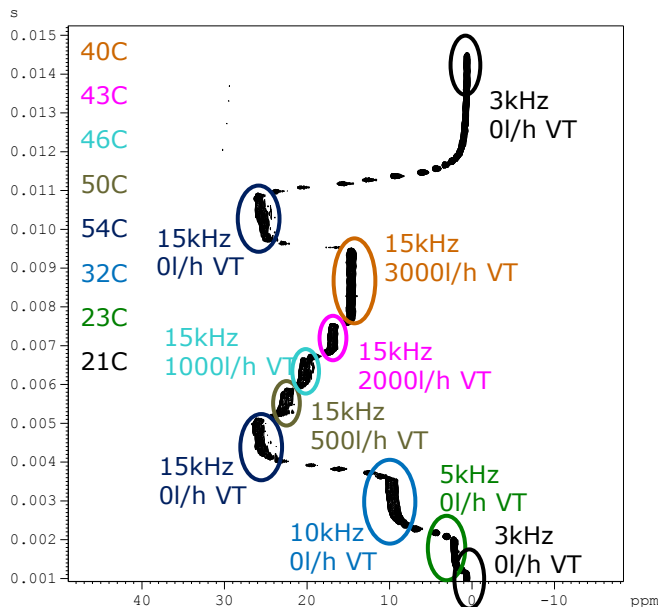
- **Leadnitrate at 107° C:**
FWHM: app. 2ppm / 2K
- **Flow Rate: 3000l/h**

Influence of magic-angle spinning on the temperature



- Center packed sample (4 mm, ZrO_2 powder)
- 21° C at 3 kHz (room temperature, referencing)
- Lead nitrate for temperature calibration, 0.753 ppm/K
- Spin rate was changed within running experiment
- Maximum temperature difference about 30 K above RT

Influence of magic-angle spinning and VT gas on the temperature

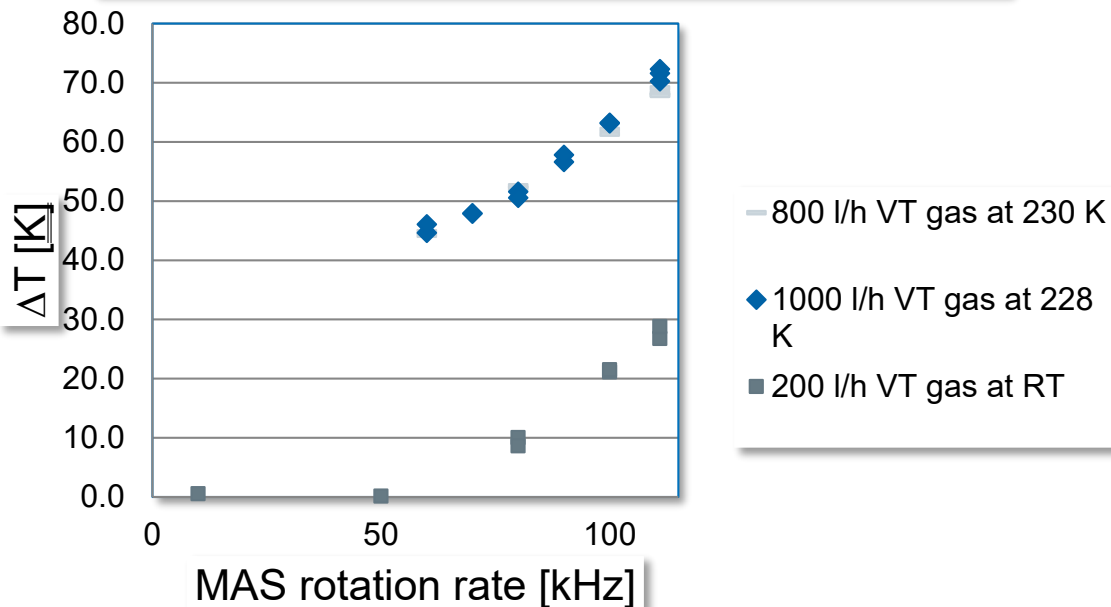


- Center packed sample (4 mm, ZrO_2 powder)
- 21° C at 3 kHz (room temperature, referencing)
- Lead nitrate for temperature calibration, 0.753 ppm/K
- Spin rate was changed within running experiment and VT gas flow was adjusted
- Maximum temperature difference about 34 K above RT

The DVT Problem



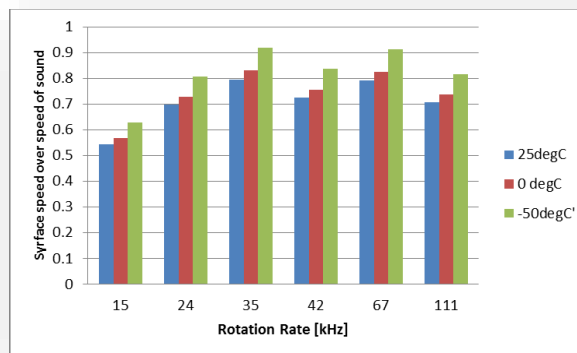
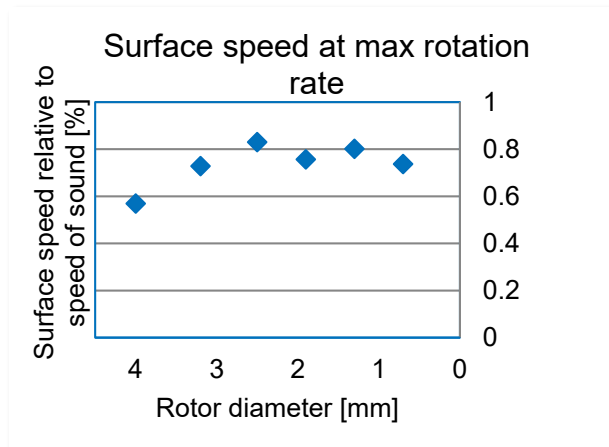
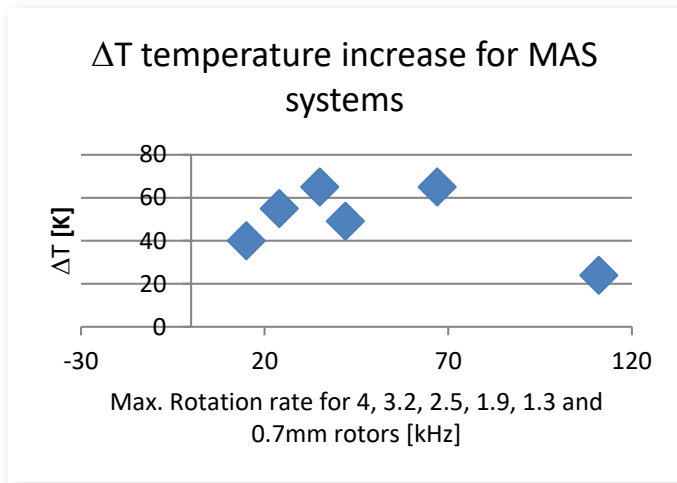
Sample temperature ΔT increase with MAS rate
850MHz SB



Sample Temperature in a MAS probe



- Frictional heating
 - Surface speed and speed of sound



Sample Temperature in a MAS probe



–NMR Thermometers

- Lead Nitrate $\text{Pb}(\text{NO}_3)_2$ $T = \square \cdot 0.753 \frac{\text{ppm}}{\text{K}}$

Bielecki, A. et al, J. Magn. Reson. 116, 215 – 220, 1995

- Stannates, $\text{Sm}_2\text{Sn}_2\text{O}_7 + \text{SnO}_2$ $T = \frac{8.87 \cdot 10^4}{204 - \delta_{\text{CS}}} \text{ approx: } T \cong \square \cdot 1 \frac{\text{ppm}}{\text{K}} + \delta T$

Grey, C.P., et al, J. Magn. Reson. A. 101, 299 – 306, 1993.

- *KBr*

– Chemical shift $T = \square \cdot 0.024 \frac{\text{ppm}}{\text{K}}$

– T_1 -experiment $T = \sqrt{\frac{5330}{T_1 - 0.0145}} T = \sqrt{\frac{5330}{T_1 - 0.0145}} + \delta T$

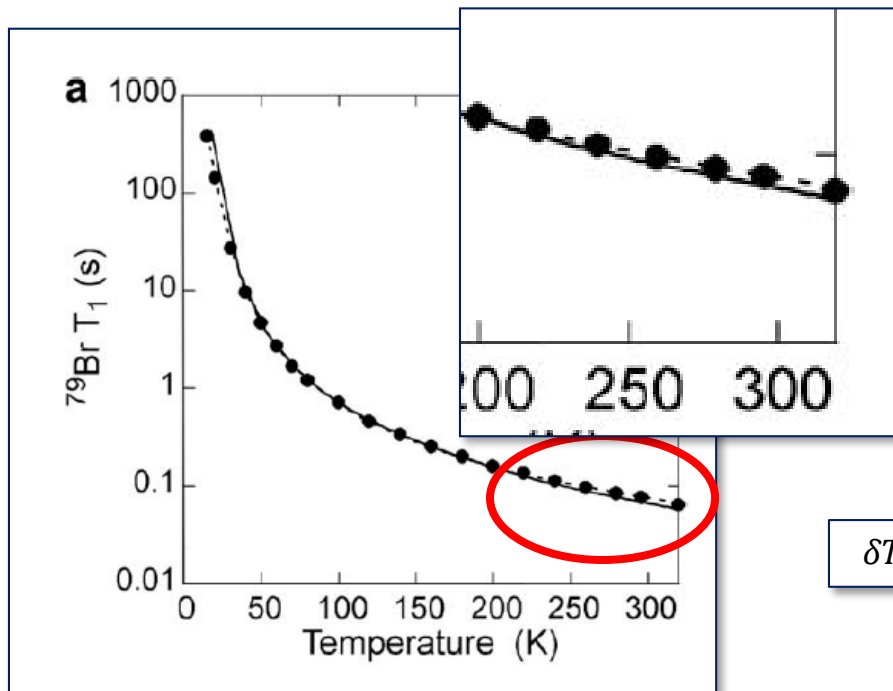
Thurber, K.R., et al., J. Magn. Reson. 196, 84–87, 2009.

Sarkar, R., et al., J. Magn. Reson. 212, 460–462, 2011

Sample Temperature in a MAS probe



$$T_1 = 0.0145 + 5330T^{-2} + (1.42 * 10^7)T^{-4} + (2.48 * 10^9)T^{-6}$$



$$T_{T_1} = \sqrt{\frac{5330}{T_1 - 0.0145}}$$

$$T = \sqrt{\frac{5330}{T_1 - 0.0145}} + \delta T$$

$$\delta T = T_{read} - T_{T_1}$$

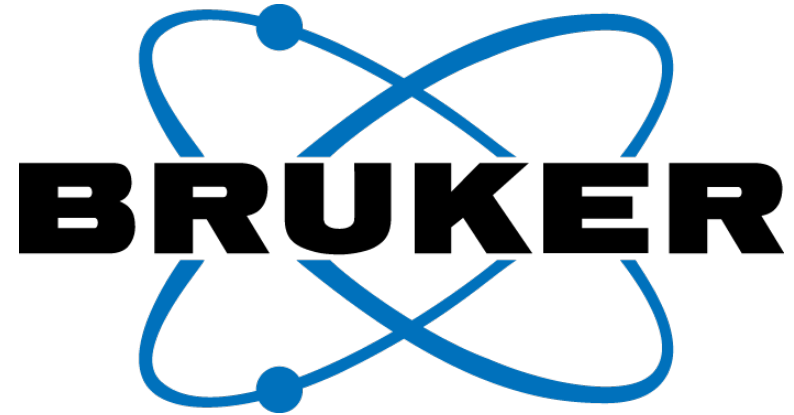
Thank you!



谢谢

结束





Innovation with Integrity