Sample Temperature in a MAS probe

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

Exception: 2.5 mm probes: -30°C ↔ +70°C
VT – probe design

VTN / WVT
bearing gas for temperature regulation

DVT
separate VT gas line
VT – DVT design

TC 1: control (read)

TC 2: regulation (regul)
Sample Temperature in a MAS probe

NMR Thermometer:

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

Sample Temperature in a MAS probe

–VT design: Stator Designs
  • Thermocouple locations remote from rotor
Thermal Gradient: Center Packed Rotor

- **Lead nitrate at room temperature:**
  - FWHM: 0.34ppm / <1K

- **Lead nitrate at 72°C:**
  - FWHM: app. 5ppm / 6K

- **Flow Rate:** 500l/h
Thermal Gradient Center Packed Spinner

- **Lead nitrate at room temperature:**
  FWHM: 0.34ppm / <1K

- **Lead nitrate 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, ZrO₂ 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 $\Delta T$ increase with MAS rate
850MHz SB

- 800 l/h VT gas at 230 K
- 1000 l/h VT gas at 228 K
- 200 l/h VT gas at RT
Sample Temperature in a MAS probe

- Frictional heating
  • Surface speed and speed of sound

\[ \Delta T \text{ temperature increase for MAS systems} \]

\[ \Delta T [K] \]

\[ -30 \quad 20 \quad 70 \quad 120 \]

Max. Rotation rate for 4, 3.2, 2.5, 1.9, 1.3 and 0.7mm rotors [kHz]

Surface speed at max rotation rate

Surface speed relative to speed of sound [%]

Rotor diameter [mm]

0 0.2 0.4 0.6 0.8 1

0 1 2 3 4 5 6

\[ \text{Surface speed over speed of sound} \]

\[ 0 \quad 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \quad 0.5 \quad 0.6 \quad 0.7 \quad 0.8 \quad 0.9 \quad 1 \]

\[ 0 \quad 15 \quad 24 \quad 35 \quad 42 \quad 67 \quad 111 \]

Rotation Rate [kHz]

25degC, 0 degC, -50degC
Sample Temperature in a MAS probe

-NMR Thermometers

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

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

- KBr
  
  - Chemical shift $T = \Box \cdot 0.024\frac{ppm}{K}$
  
  - $T_1$-experiment $T = \sqrt{\frac{5330}{T_1 - 0.0145}} T = \sqrt{\frac{5330}{T_1 - 0.0145}} + \delta T$

Sample Temperature in a MAS probe

\[ T_1 = 0.0145 + 5330T^{-2} + (1.42 \times 10^7)T^{-4} + (2.48 \times 10^9)T^{-6} \]

\[ T_{T1} = \sqrt{\frac{5330}{T_1 - 0.0145}} \]

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

\[ \delta T = T_{read} - T_{T1} \]
Thank you!

谢谢

结束
Innovation with Integrity