

# Preliminary Experimental Results from a $^1\text{H}$ / $^{13}\text{C}$ / $^{15}\text{N}$ CryoMAS<sup>TM</sup> Probe for Solids NMR at 500 MHz

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**The goal: improve performance in NMR spectroscopy** of inhomogeneous systems and many solids by dramatically improving the S/N of MAS VT NMR probes. NMR cryo-coil probes achieve their improvement in SNR from both reduced noise temperature and improved Q, (in spite of reduced filling factor). Nearly an order-of-magnitude increase in SNR is ultimately expected, resulting in nearly two orders of magnitude reduction in signal averaging time in both high-power and high-resolution MAS experiments. The design will initially allow the **sample VT range from 90 K to 400 K** while the **critical rf coils and capacitors are kept at 25-35 K** using primarily a high vacuum for insulation.

Most of the mechanical engineering challenges to building a CryoMAS<sup>TM</sup> probe with full-range VT capability and automatic sample change have been met. We have built and successfully tested a prototype CryoMAS probe in our 500 MHz WB spectrometer. We present results from bench tests and preliminary NMR tests on the probe, which validate the probe and coil design. The initial NMR tests showed a factor-of-four increase in the SNR for the  $^{15}\text{N}$  channel upon cooling the circuit while using a room temperature preamp. Similar improvement in S/N was seen on the  $^{13}\text{C}$  channel. Cooling the preamp is expected to give another factor-of-two increase in the SNR. We present details on preamp development with a discussion on the challenges and possible solutions.

## PROBE DESIGN

A prototype triple-tuned CryoMAS probe is shown in **Figure 1** with the vacuum-tight shield can removed. A long side-arm (similar to cryo probes for liquids NMR) is used to connect the probe to a closed-circuit cryocooler. A small tube at the top of the MAS spinner mates with an intelligent pneumatic sample changer that gently shuttles the rotor from the probe to the top of the magnet. The probehead, where the MAS spinner and rf circuit are located, is evacuated to a high-vacuum ( $\sim 10^{-4}$  mTorr) using an oil-free vacuum pumping system.

Cooling of the sample coil (L1 in the DT circuit shown in **Figure 2**), is achieved through a pair of high-Q alumina disc capacitors, shown in **Figure 3**. The thermally conductive capacitors (see **Figure 3**) are grounded to a cold plate on one side and connected to the sample coil via heavy, short copper leads for high thermal conduction as shown in **Figure 4**. The copper sample coil L1 is magnetically compensated with aluminum for high  $B_0$  field homogeneity within the sample.

A copper cold-finger-type heat exchanger is connected to a thermally isolated cold plate (grounded), which is cooled to a base temperature of  $\sim 20$  K by the closed-circuit cryocooler. This cold plate acts as a heat sink for the conductive heat losses from the MAS spinner and the rf feed-throughs. A second heat exchanger cools the radiation shields surrounding the rf circuit to  $\sim 50$  K, which also serve as cold rf shields further lowering the eddy-current-induced noise.

## THERMAL INSULATION

The probe head is sealed and evacuated to a high vacuum to eliminate convective heat transfer between the warm and cold surfaces. As several o-ring seals are used, it is necessary to continuously pump the probe using a high-vacuum pumping system. Additional pumping capacity is inherent to the probe as the cold finger and helium plumbing act as a cryo-pump. The high-vacuum design requires all the MAS gas connections in the spinner to be hermetic. To achieve this all metal joints are soldered and the metal-to-ceramic joints in the spinner are made with a specially formulated soft epoxy with low outgassing characteristics.

Conduction losses are minimized by careful design. The coilform is made of a low conductivity ceramic (zirconia), which makes minimum contact with warmer surfaces for mechanical support. **This design allows for a 270 K temperature gradient between sample coil and the RT ends with only 0.8 watts heat loss.**

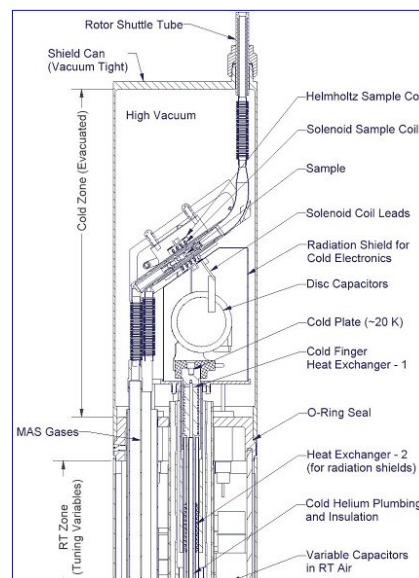
Radiation is minimized by surrounding the cold parts with polished copper radiation shields at  $\sim 50$  K.

## SPINNER DESIGN

One key element of the probe design is the spinner assembly for a 3 mm (outside diameter) rotor that can spin up to 25 kHz, allow for automatic change of rotors, and maintain a sample temperature ranging from 80-400° K while the RF coils wrapped around its outside are kept at  $\sim 35^\circ$  K. A cross section drawing of the spinner assembly is shown in **Figure 5**. Due to the constraints imposed by the provisions for automatic sample eject and vacuum between the stator and the cold RF coil, the rotor is driven from one end only. The design is similar to what we have used in a 4-mm solids probe with auto sample exchange. **Tests of the 3-mm cryo-spinner have achieved 18 kHz.**



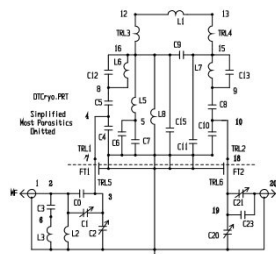
**Figure 1. Prototype CryoMAS probe.**



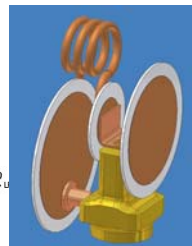
**Figure 4. A cross section of the CryoMAS probehead**

## CryoMAS DESIGN GOALS

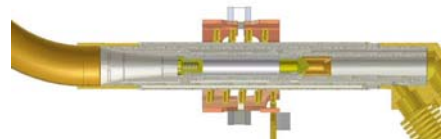
- 10 X S/N of 3.2 mm probes
- $^1\text{H}$  /  $^{13}\text{C}$  /  $^{15}\text{N}$
- Room Temperature MAS
- Automatic sample exchange
- Very stable 25 kHz MAS
- Extended VT range
- Ultra low rf heating
- High Resolution
- Robust, reliable operation
- Rapid cool down & warm up



**Figure 2. Double tuned circuit for  $^{13}\text{C}$  /  $^{15}\text{N}$**



**Figure 3. Disc capacitors**



**Figure 5. A cross section of the MAS spinner showing the inner LF/MF solenoid and outer  $^1\text{H}$  segmented saddle coil.**

## CIRCUIT and COLD PREAMPS

The decoupler noise problems seen with the previous coil design, which used a  $^1\text{H}$  inner cross coil and an outer solenoid, were solved by moving the  $^1\text{H}$  coil to the outside, with the MF and LF on the inner solenoid. This also reduces peak voltages on the LF/MF and improves both Q and filling factor.

To realize most of the S/N benefit (that which comes from the reduced noise temperature) the preamps and front-end filters must be cooled to achieve total NF (including filter and cable losses) below 0.25 dB. A novel preamp based on an enhancement-mode pseudomorphic high-electron-mobility transistor (E-PHEMT) is being developed. Detailed circuit simulations indicate it should have unconditional stability, gain above 20 dB, out-of-band rejection greater than 60 dB, and NF below 0.2 dB at 125 MHz, for cooling to only  $\sim 180$  K. Preliminary tests appear to confirm this, and further development is in progress.

## TEST RESULTS

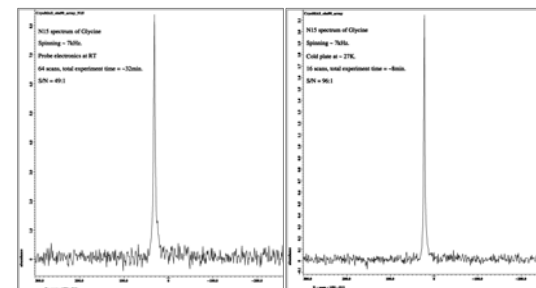
Tests were performed on the CryoMAS probe in our 500 MHz spectrometer. Smooth and stable MAS was attained to 18 kHz. Tests confirmed that the sample could be maintained at RT at speeds between 1 kHz to 18 kHz without affecting the sample coil temperature which was at  $\sim 25$  K. The probe was evacuated and cooled down to 25 K in less than 5 hours.

Power handling tests were done on the probe and revealed that the uncoated disc capacitors used in the prototype were inadequate for high power. Later experiments showed that disc capacitors with a conformal coating would handle over 3.5 kV. With other coil and circuit improvements, it now appears field strengths of 70 kHz on all three channels will be possible.

For single pulse  $^{15}\text{N}$  glycine experiments, a 400% increase in signal to noise ratio was obtained by cooling the sample coil and circuit to  $\sim 25$  K, while spinning the RT sample at 7 kHz.

The factor-of-four increase in sensitivity was obtained using RT preamps with a NF = 1.0 dB. As the average noise temperature of the probe is about 35 K, about 60% increase in S/N is expected by using cooled preamps with NF = 0.25 dB.

The initial NMR spectra obtained using RT preamps are shown in **Figure 6**.



**Left: coils at RT, 64 scans, S/N = 49:1. Right: coils at 30 K, 16 scans, S/N = 96:1. Both: RT glycine sample,  $^{15}\text{N}$ , 10  $\mu\text{s}$  pw90, 11.7 T, 7 kHz MAS**

**Figure 6.  $^{15}\text{N}$  NMR spectra showing  $\sim 4\text{X}$  gain in S/N using standard, RT preamp. Another 60% gain in S/N is expected with a cold preamp.**

## CONCLUSIONS

An enhancement of a **factor of four** in S/N ratio for room temperature MAS was demonstrated upon cooling the sample coil and circuit to 25 K while using RT preamps. Another **60% gain** is readily possible by using cooled preamps with a NF = 0.25 dB instead of RT preamps of NF = 1.0 dB.

The next version should also achieve an additional 30% gain in S/N from other circuit changes. The net result is that the next-generation CryoMAS probe is expected to have 8 times the S/N of a state-of-the-art triple-tuned MAS probe of similar sample ( $\sim 40$   $\mu\text{L}$ ).

## REFERENCES

1. W. A. Anderson, "High Q Normal Metal NMR Probe Circuits," presented at the 42<sup>nd</sup> ENC, Orlando FL, 2001.
2. FD Doty, G Entzminger, J Kulkarni, K Pamarthi, JP Staab, "RF Coil Technology for Small-Animal MRI", *NMR in Biomedicine*, 20(3):304-325, 2007.
3. FD Doty, J Kulkarni, C Turner, G Entzminger, A Bielecki, "Using a cross-coil to reduce RF heating by an order of magnitude in triple-resonance multinuclear MAS at high fields", *J. Magn. Reson.*, 182 (2006), 239-253.

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