PHOENIX NMR

Elevating your science

MAS NMR Probes for ultrafast MAS: challenges for UHF

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My background

1987-1991	Colorado State University, Chemistry undergraduate, work-study with Prof. Gary Maciel designing and machining Double Rotation (DOR) spinning systems.
1992-1998	University of Washington, Seattle, Physical Chemistry Graduate program with Prof. Gary Drobny. Development of 200, 400 and 750MHz SSNMR probes
1999-2010	Varian Inc., Fort Collins Colorado, Engineering team leader focused on R&D development of SSNMR probes from 400-900MHz.
2011-2015	Agilent Technologies, senior scientist and project manager for SSNMR probe development, beginning 2013 focused on project definition and management for full NMR probe development, liquids, solids and all “In-The-Bore” components.
Present	PhoenixNMR, Principal owner and scientific lead focused on solid state NMR probes, accessories and ??.

Drivers for UltraFastMAS (UFM)

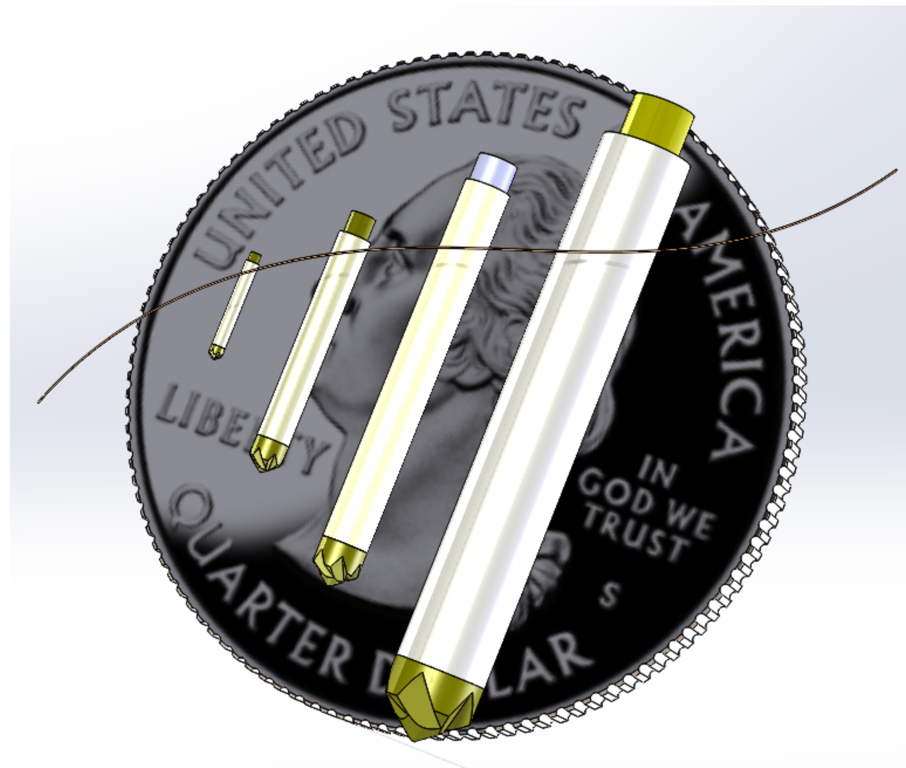
- ^{1}H Indirect detection
  - Functional at ~40kHz
  - Still improving beyond 110kHz
- Ideal for samples of limited mass, < 1mg
- Biosolids – 1st spinning sideband of carbonyls in relatively unpopulated region of 2D. Preferably outside spectral region entirely

Field	1st SSB, inside spectrum	1st SSB, Outside spectrum
600 MHz	13.3 kHz	22 kHz
800 MHz	17.7 kHz	29 kHz
1.2 GHz	26.6 kHz	44 kHz
1.5 GHz	33.3 kHz	55 kHz

Mechanical challenges of UFM

In One Word - **SIZE**

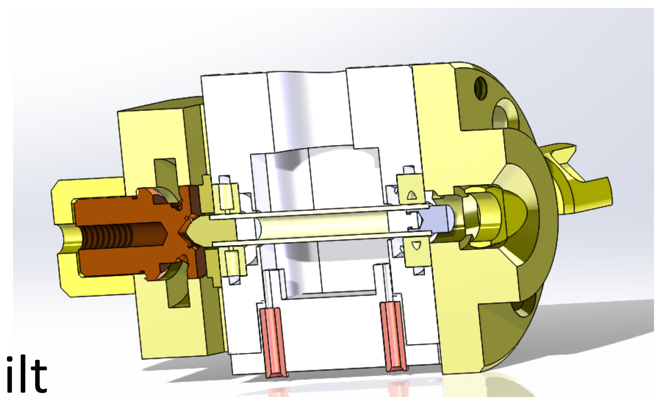
- Plastic parts are extremely precise, not viable for plastic injection molding and are VERY difficult to machine
- Materials requirements are stringent
- Sample packing/handling techniques, “If you make it, they will pack it” attitude insufficient for a national user lab
- Can the parts survive the packing process? Agilent 1.2mm drive tip & cap can be easily damaged by the user
- Are single use rotors an option? i.e. rotor with integral drive tip and a single cap?
- Spinning controller major limitation – mass flowrates challenge available I/P valves, reaction time limits, spin speed detection



0.5mm (140kHz?), 1.2mm (60kHz), 1.6mm (40kHz) and 3.2mm (25kHz) sample rotors pictured over a US Quarter with a human hair laying over all.

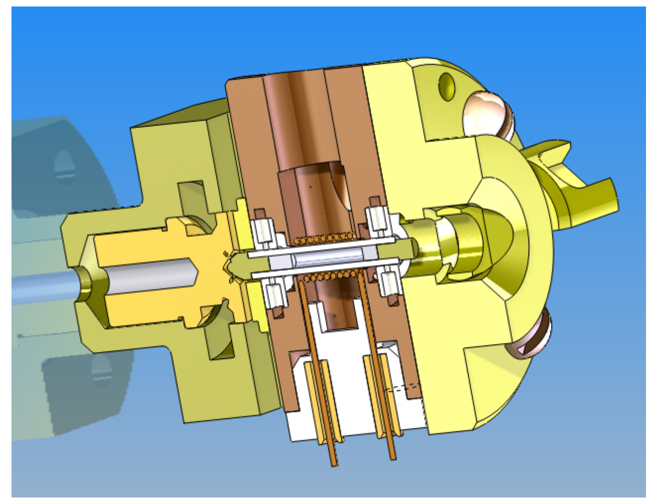
FM(1.6mm) probe example – An ideal case

- Technical
  - Usable variable temperature range ~-30 to +100 C
  - H-(^{31}P to ^{13}C)-(^{13}C to ^{15}N) triple resonance
  - 8 to 40kHz spin rate
  - Supported by speed controller
- Manufacturing
  - High Yields, >80 in the field
  - Yield failures spread throughout probe
  - Minimal rework hours, entirely production built
  - No RF breakdown 'arcing' failures



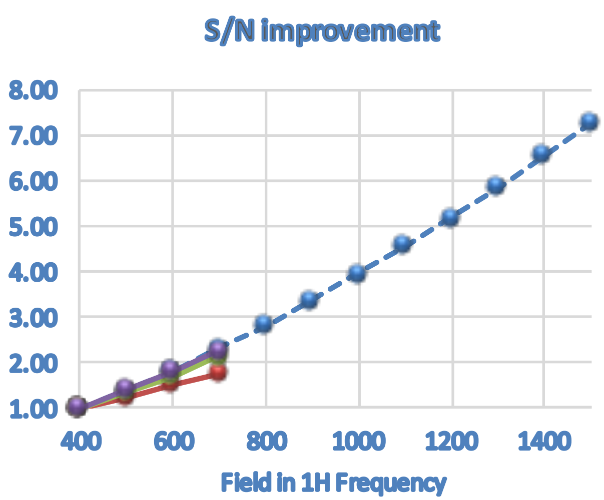
UFM(1.2mm) probe example – A struggle

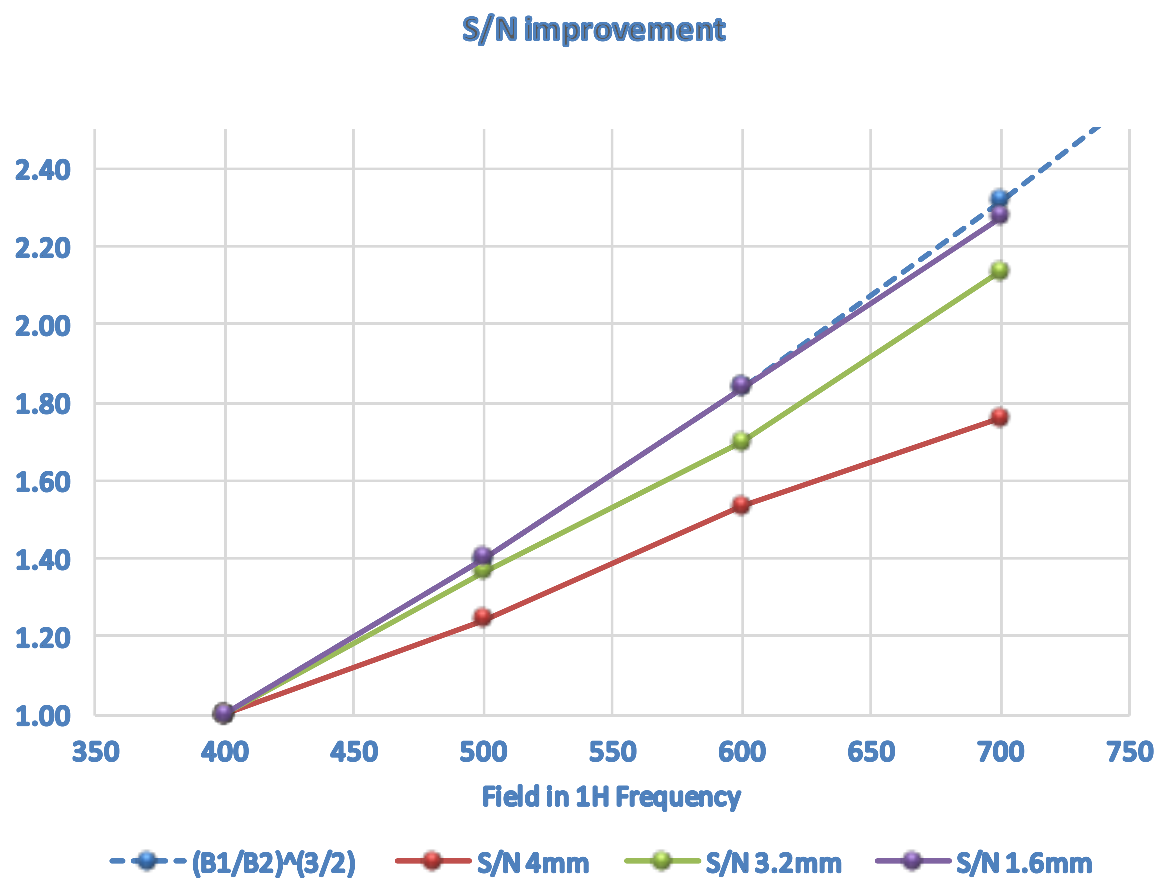
- Technical
  - Usable variable temperature range ~-15 to +50 C
  - H-(^{31}P to ^{13}C)-(^{13}C to ^{15}N) triple resonance
  - 10 to 60kHz spin rate
  - Not supported by speed controller
- Manufacturing
  - Very problematic, low yields, 30-40 in the field
  - All failures associated with spinning stability
  - Never have RF breakdown failures
  - Rework hours excessive, module 90% R&D effort



Sensitivity

- Higher field -> higher sensitivity $(B_a/B_b)^{3/2}$
- Large rotors result in “compromises” as field increases, 3/2 power is not met!





UHF tuning

The Good news

- Distributed (transmission line) H/F, H&F tuning structures ideal for operation beyond 1GHz
- Resonator Designs for <3.2mm more easily realized at UHF
- Low frequency tuning structures for ^{13}C and below good to ~1.2GHz
- Dedicated probe heads for LG, and ^{31}P are an option.

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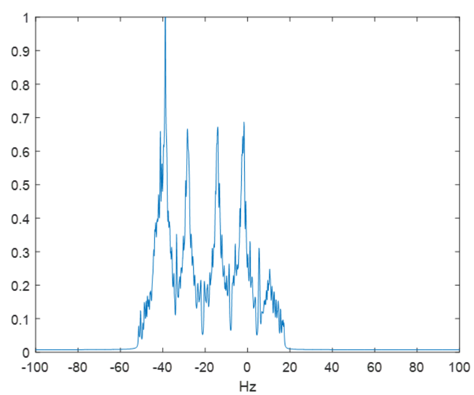
The bad news

- ^{31}P tuning with high inductance solenoids will be difficult. Tradeoff's with ^{13}C performance.
- Resonator designs for larger coils (>=3.2mm ID) will be difficult to realize and inefficient above 1GHz
- Crossed coil stray coupling increasingly difficult as frequency increases due to stray capacitance
- Low F tuning structure must get smaller, parasites and losses will dominate > 1GHz

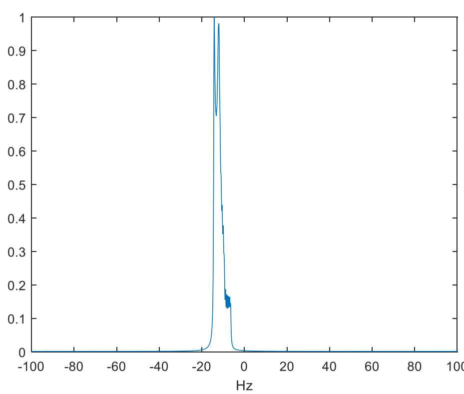
Raw (unshimed) B_0 field homogeneity

We currently use Matlab code to evaluate probe head and spinning module designs for raw B_0 homogeneity impacts.

- Simplifies installation, probe is more easily shimmed
- Reduces probe to probe variation in line shape
- A key to developing probes for UHF



Probe design from early 2000's



Current 1.6mm Phoenix Probe Head

UHF summary

- High frequencies favor smaller rotors
  - 3.2mm < 0.9GHz
  - 1.6mm < 1.2GHz
  - 1.2mm < 1.5GHz
- RF structures must scale in size, good news for magnets, 54mm RT bore will be ideal for SSNMR above 1GHz
- Sensitivity gains depend on the development of smaller, faster spinners.
- Amplifier power levels drop with UFM modules

Business perspectives

- Extremely low product numbers
  - This is a major part of why Agilent left the market
  - 1 per year? How many different flavors? Low-E, static, UFM, Low Gamma – Never the same probe for the manufacturer -> continual high level R&D investment, Engineers build the probes
  - This is a long term, low direct return research program
- Where to do probe development?
  - Bench development can only solve fundamental questions – resonance frequency, spinning stability, variable temperature operation, tuning ranges
  - What about line shape, RF field strengths, power requirements, user interface (ultimately how friendly/fragile is it?)
  - Customers/Funding agencies expect fully functional probes when the magnet comes to field
    - Projects must be multi-step, 1st conservative probe to get system functional followed by fully functional high capability probe.

What is needed?

- High reliability and easily used UFM spinning systems
  - CFD simulation software, 4/5 axis precision milling centers
  - Advanced speed controllers
- Methods of sample packing for UFM rotors that are user friendly
  - Academic partners, look at cell manipulation tools/techniques
  - Single use rotor systems?
- Highly reliable wide VT range probes supporting UFM modules
  - -50 to +50 Celsius is a must, lower desired
- New UHF/HFM coil systems for biological samples (Low-E)
  - Likely a crossed coil type design, similar to work from NHMFL and others
- Application of solenoid UHF/UFM coil systems for materials sciences (Mid - Low Gamma)
  - Current single coil designs optimized for $<^{13}C$
- Overall miniaturization of RF circuit

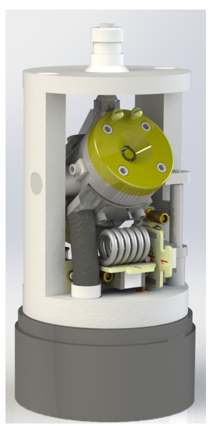
PhoenixNMR

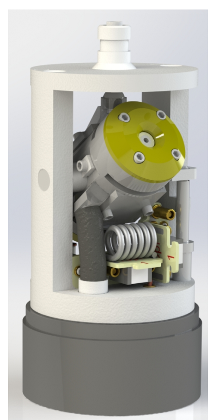
- Team
  - Chuck Mullen, Mech. Engineer 29 yrs in NMR
  - Mario Incitti, Probe specialist 15 yrs in NMR
  - John Stringer, COO/CTO, 23 yrs in NMR
  - John Heinrich, CEO, 34 yrs in MR, NMR
- 5000 sqft manufacturing/office space in LVLD Colorado
  - 400,500,600 NB magnets with single console for NMR test & development

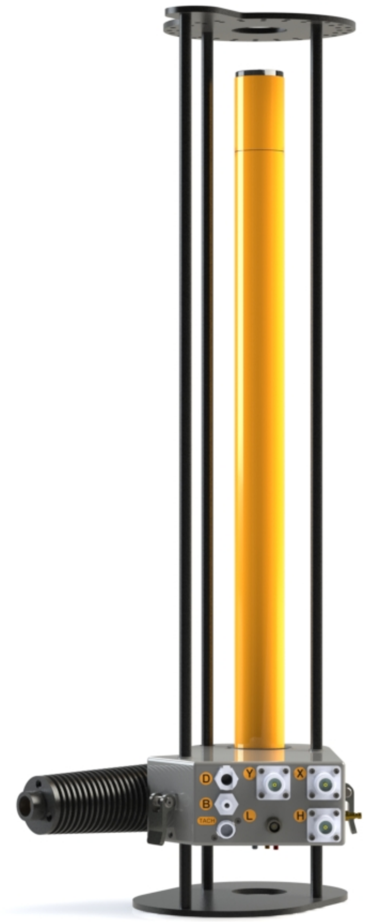



PhoenixNMR

- Modular probe design – configure your probe for your science today
  - Select the probe head based on your science
    - 1.6mm, 3.2mm, 4.0mm, Static
  - Mate the Probe Head to your Probe Base and start collecting data
    - 400MHz to 1Ghz
    - HXY, HFXY, HXY+lock
- VT from bottom, all connections to probe on single probe face
- Fully broadband designs with true HX modes for maximum S/N
- ^{31}P to ^{14}N tuning in DR mode, ^{31}P to ^{13}C, ^{13}C to ^{15}N in TR mode
- Optional Low gamma add on, tune continuously from ^{14}N to ~10MHz







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