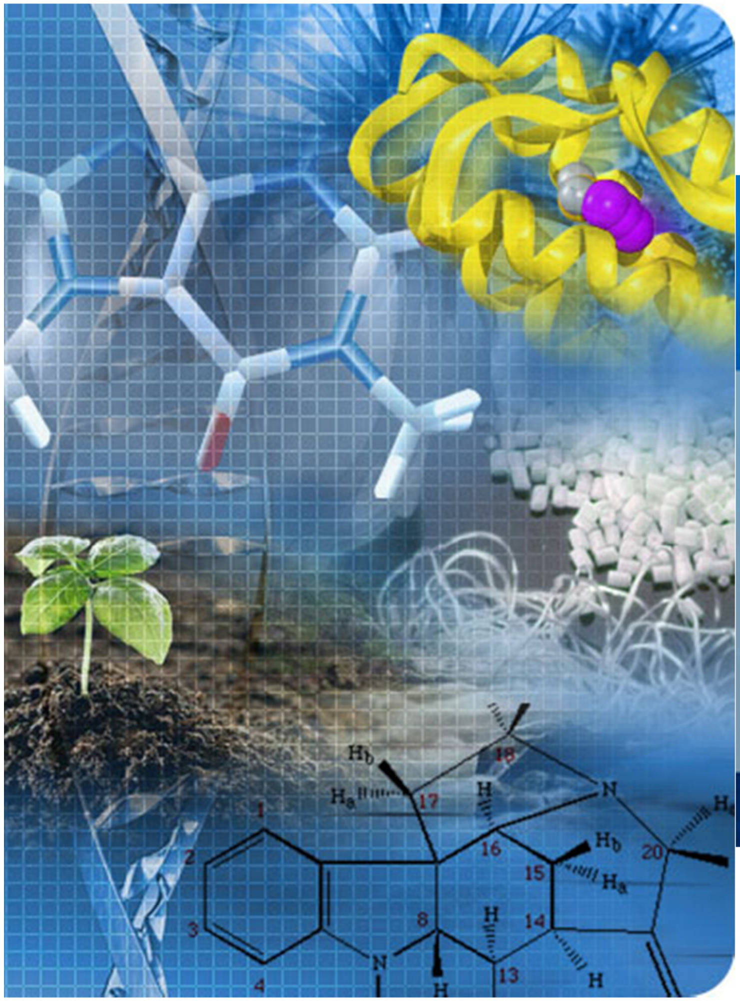


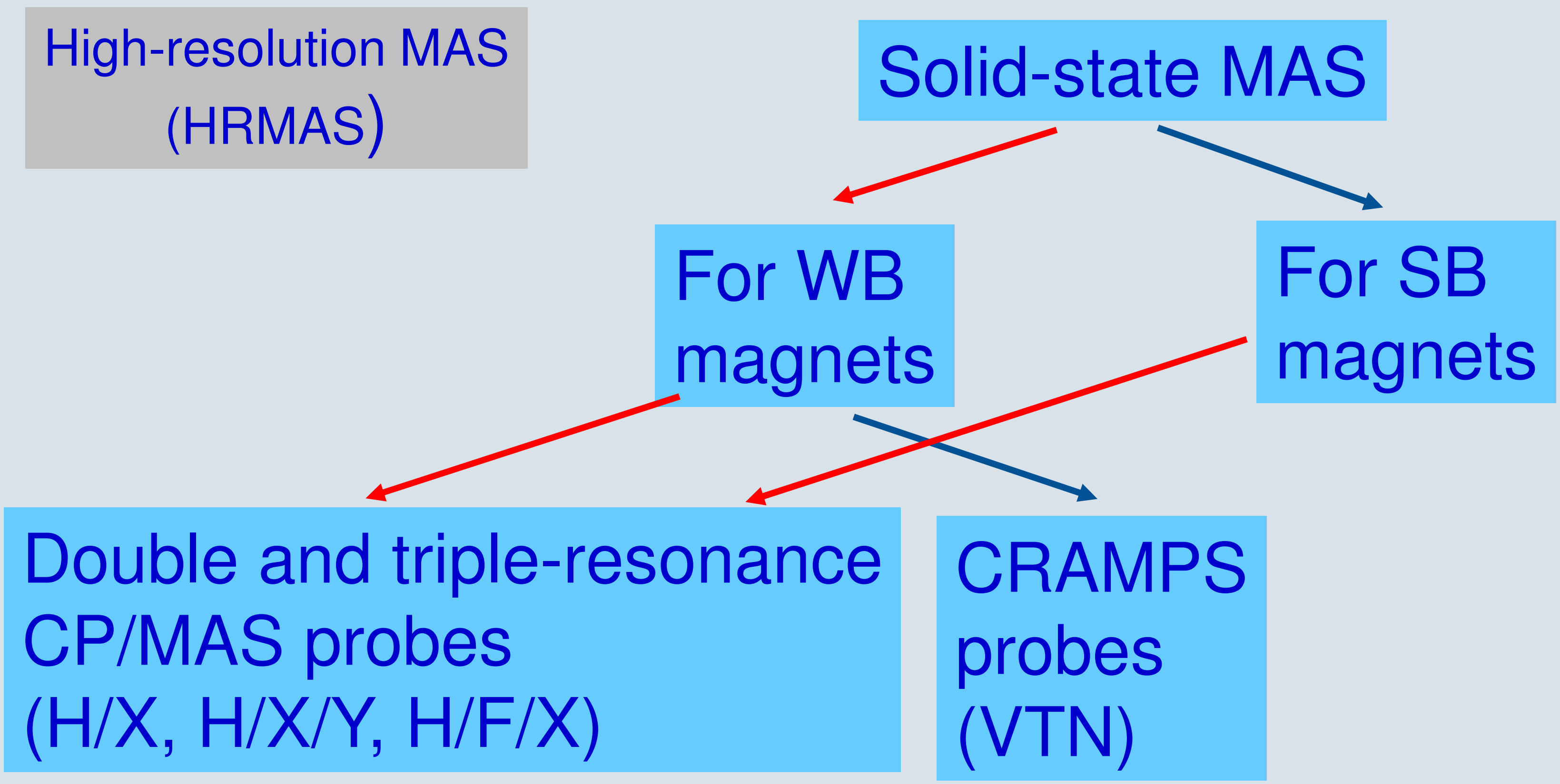
Solid State NMR Hardware
Probeheads, MAS Rotors, RF Filters

Gerhard Althoff
Bruker Biospin GmbH

Overview

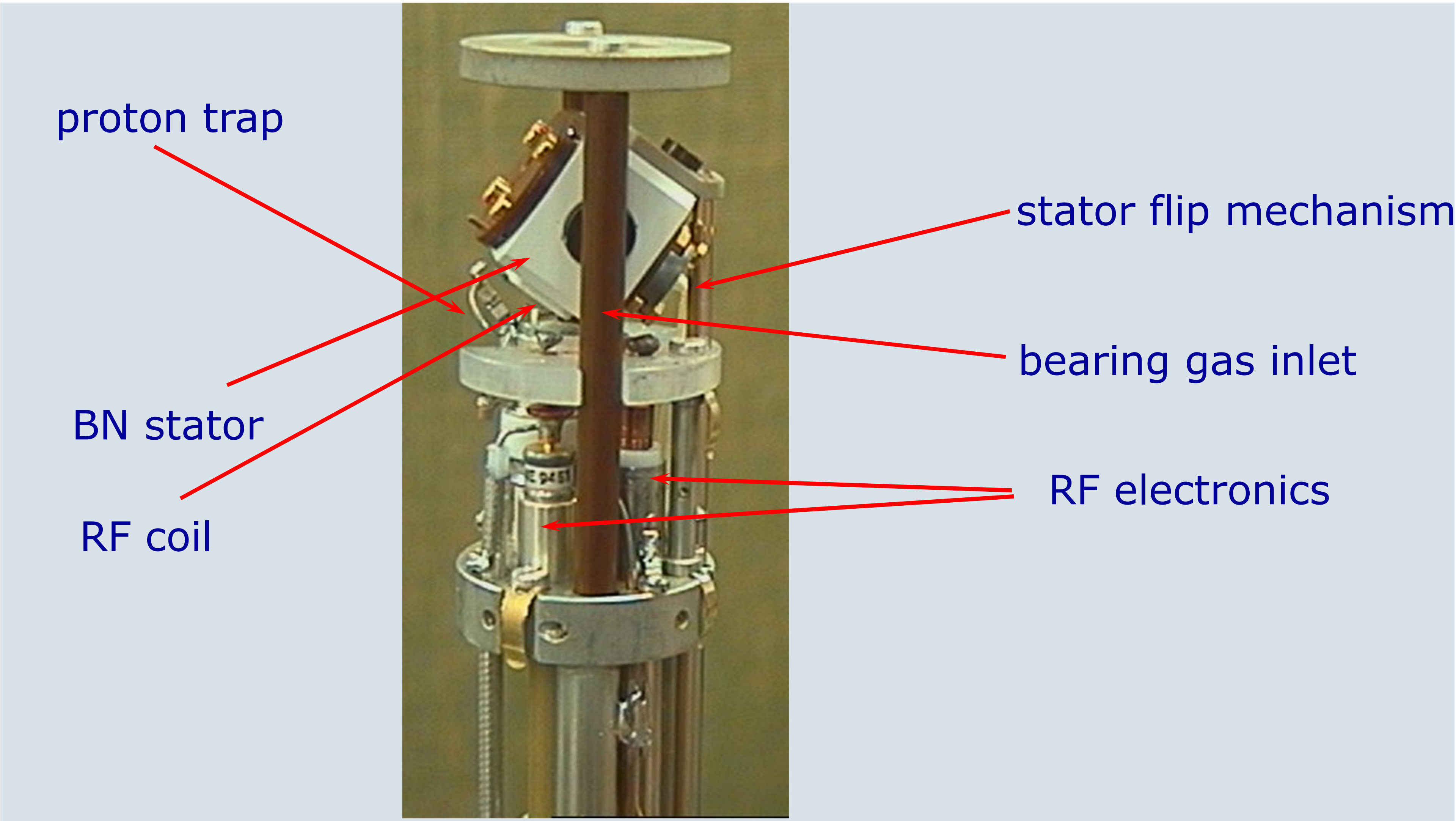
- probe types
- probe design
- Magic Angle Sample Spinning
  - rotor types and applications
  - rotor cap types and applications
  - sample change
- RF handling
  - tuning and matching
  - external RF filters
- temperature control -> dealt with in additional presentation

Types of MAS Probes

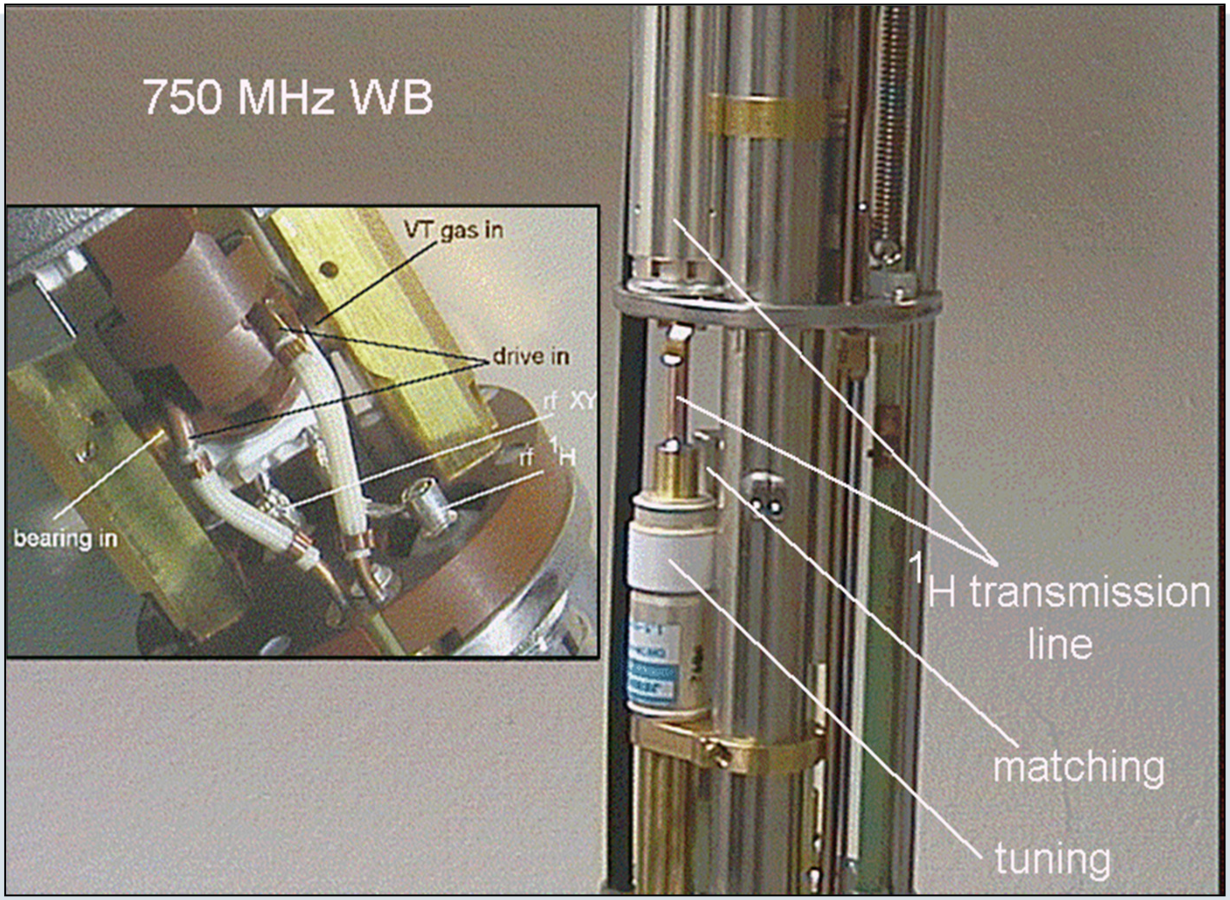


MAS technology
variable temperature features
RF design

Standard Bore (SB) MAS probe



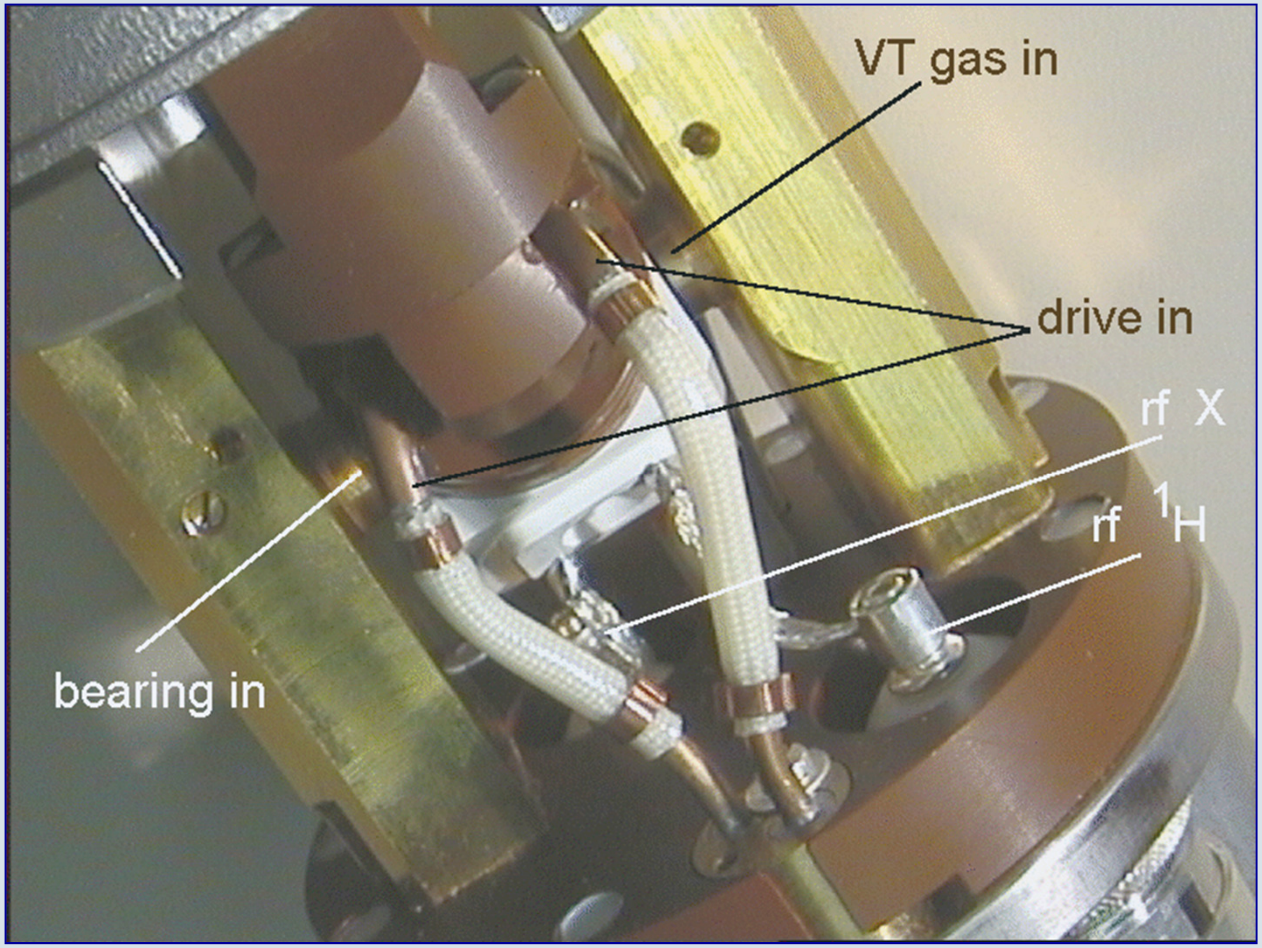
Wide Bore (WB) MAS probe



Principal design of 400-850 MHz WB CP/MAS probes

Wide Bore (WB) MAS probe

close view of
MAS stator
(DVT design)



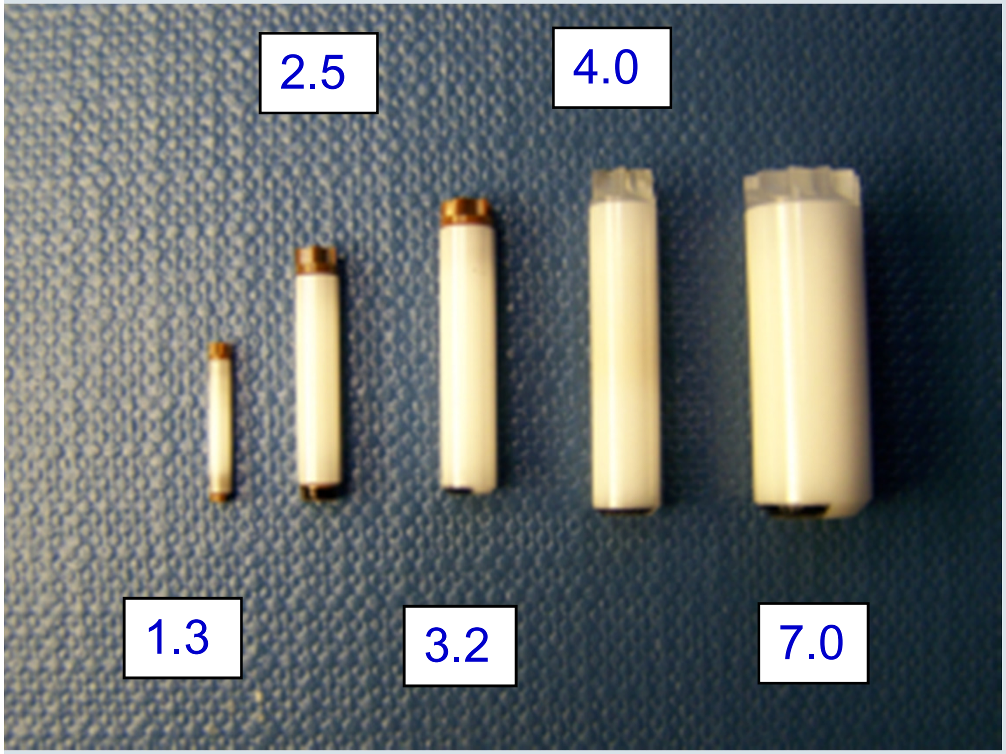
Overview

MAS rotor types and specifications

- sizes and maximum spinning speed
- volume/sample confinement
- cap materials and temperature ranges
- special rotors for special samples/applications

MAS Rotors (Spinners)

MAS rotors with
1.3, 2.5, 3.2, 4, and 7 mm OD



maximum spinning speeds:
1.3 mm: 67 kHz
2.5 mm: 35 kHz
3.2 mm: 24 kHz
4.0 mm: 15 kHz
7.0 mm: 7 kHz

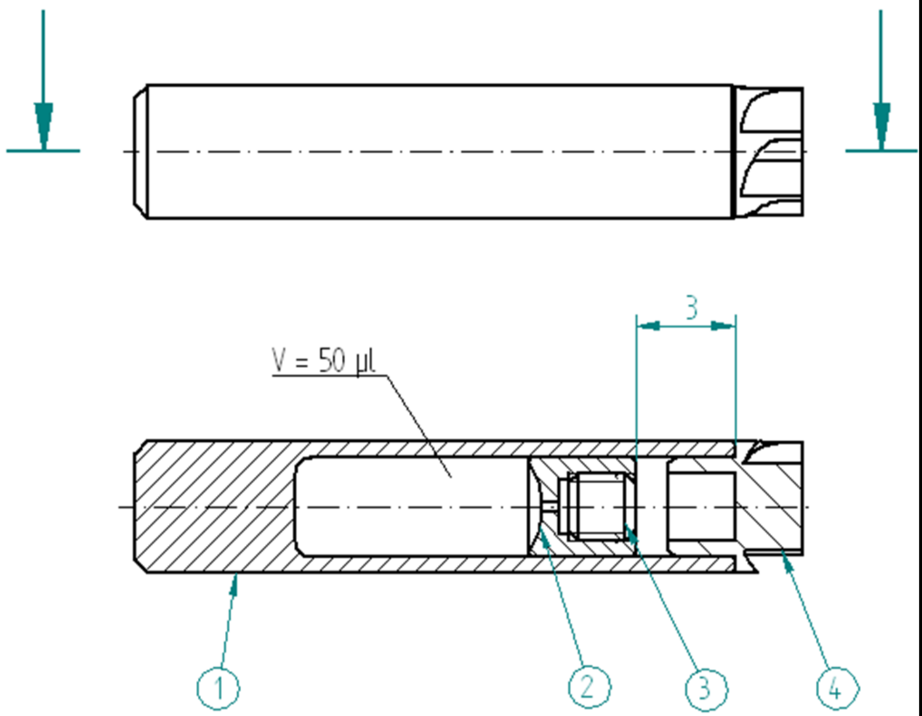
Maximum Spinning Speed

maximum spinning speed of MAS rotors determined by

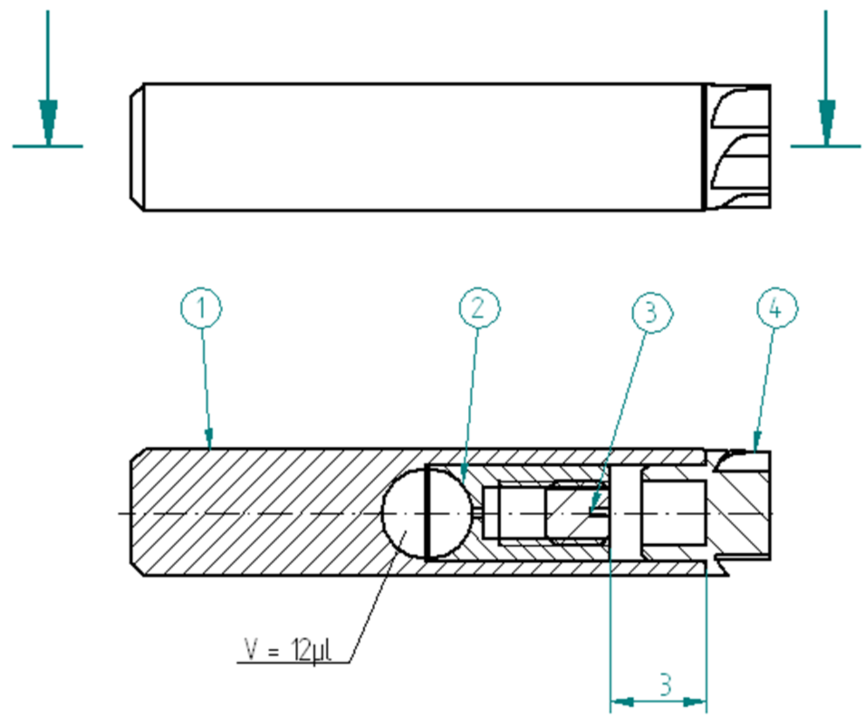
- pressure resistance of rotor material, pressure increases with the square of the spinning speed
- speed of the circumfence must be less than the speed of sound, otherwise stall may occur, circumfence speed increases linearly with the spinning speed

Reduced Volume 4 mm Rotors:HRMAS Type

for high resolution MAS or for high RF homogeneity



50 µl, cylindrical



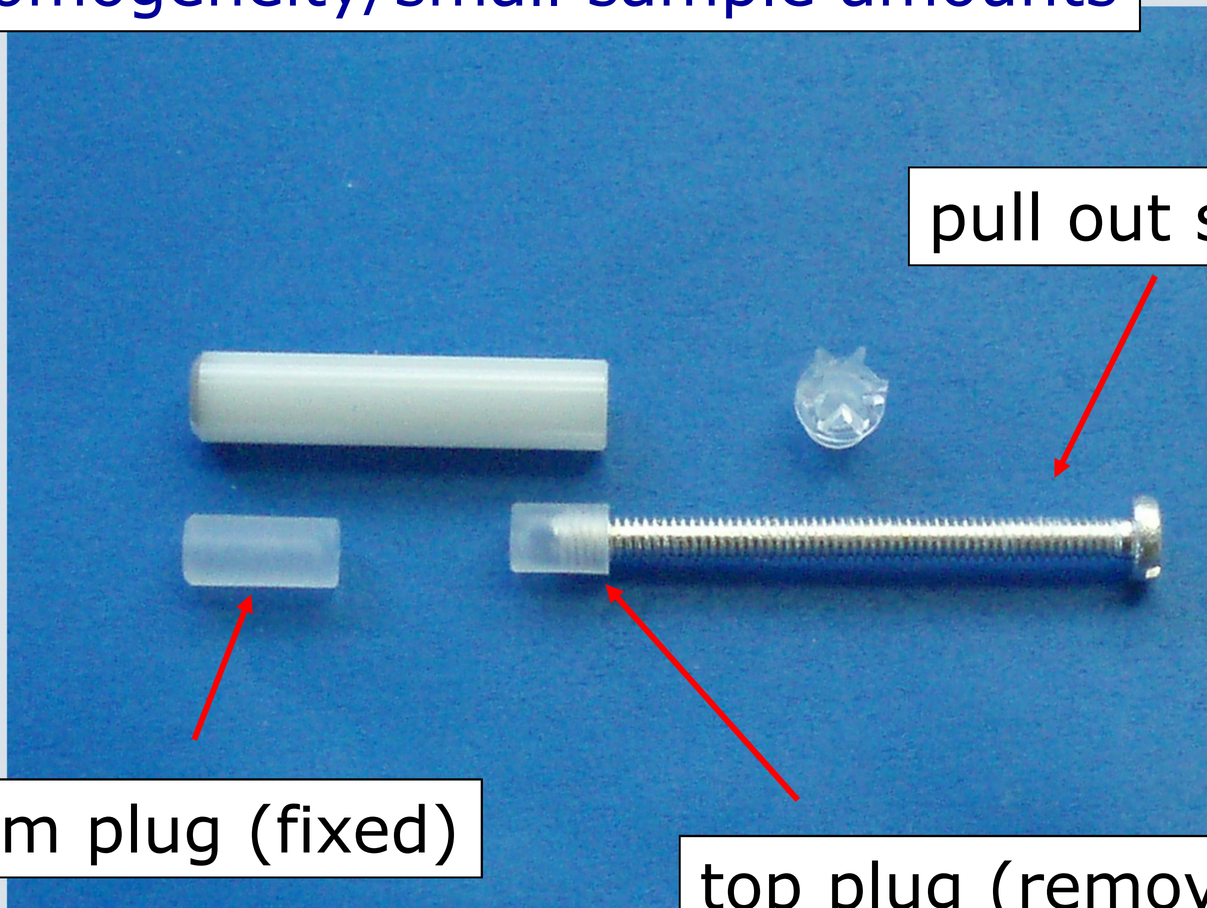
12 µl, spherical

1: rotor with solid bottom; 2: top plug with ventilation hole
3: sealing screw; 4: rotor cap

Reduced Volume 4 mm Rotors: CRAMPS Type

for high RF homogeneity/small sample amounts

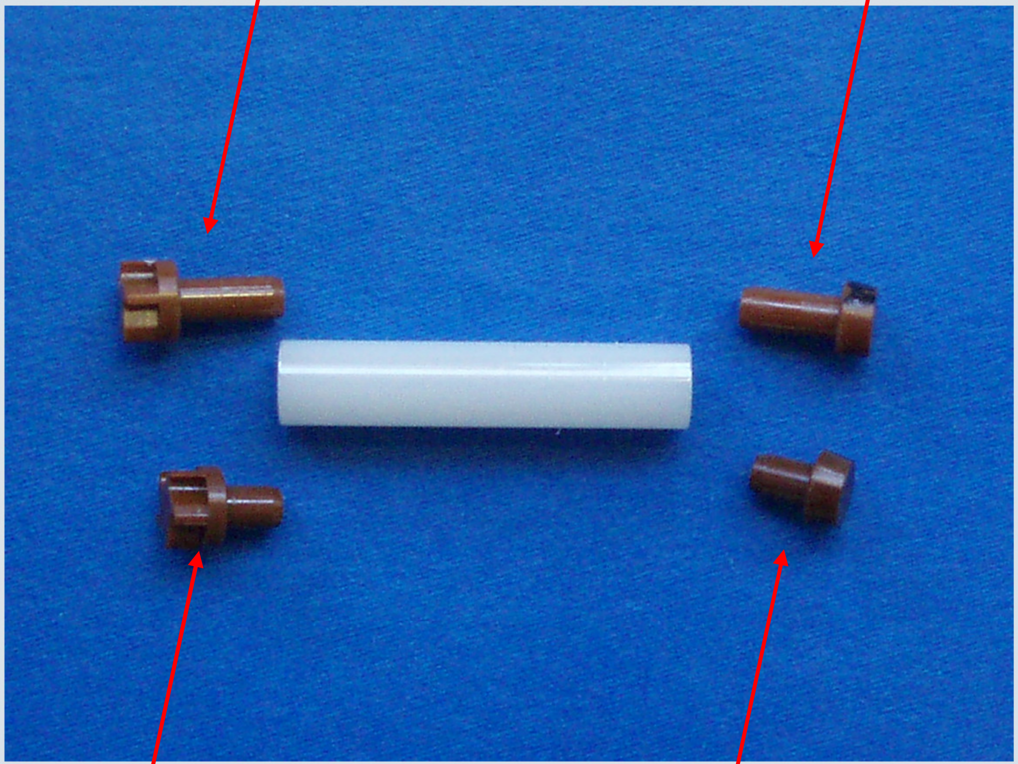
plug materials:
- Kel-F
- Teflon
- polyethylene



also available for 7 mm rotors

Reduced Volume 2.5 mm Rotors I

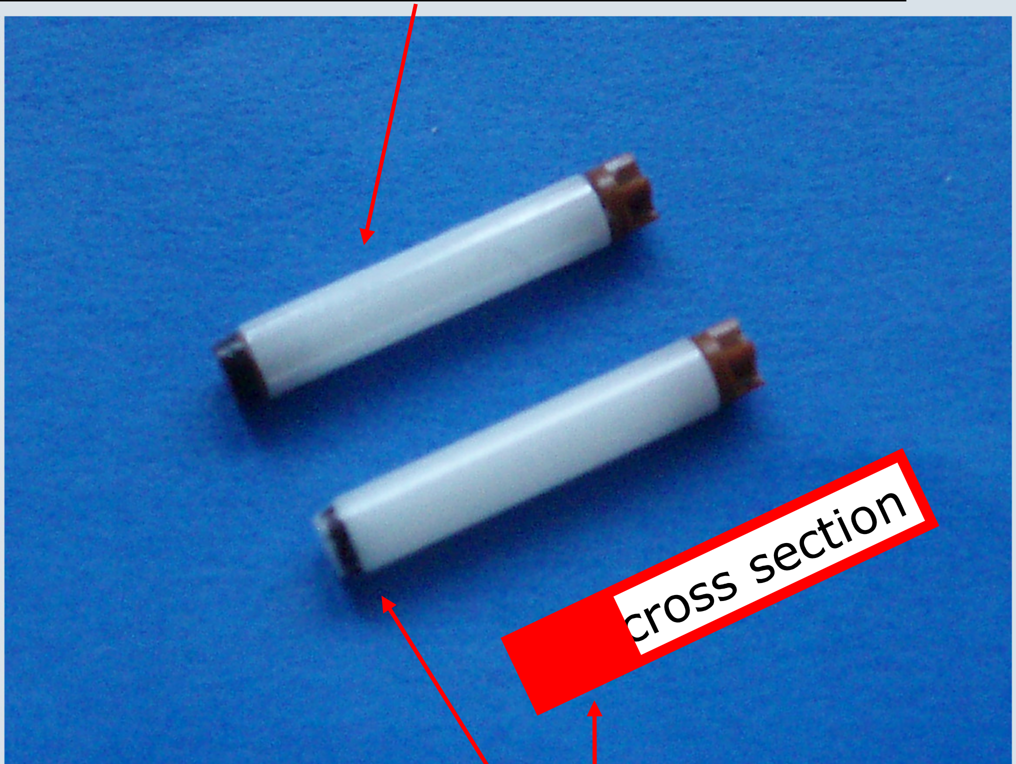
confinement by using long stem plugs



Reduced Volume 2.5 mm Rotors II

confinement by massive rotor bottom

standard top and bottom plug rotor

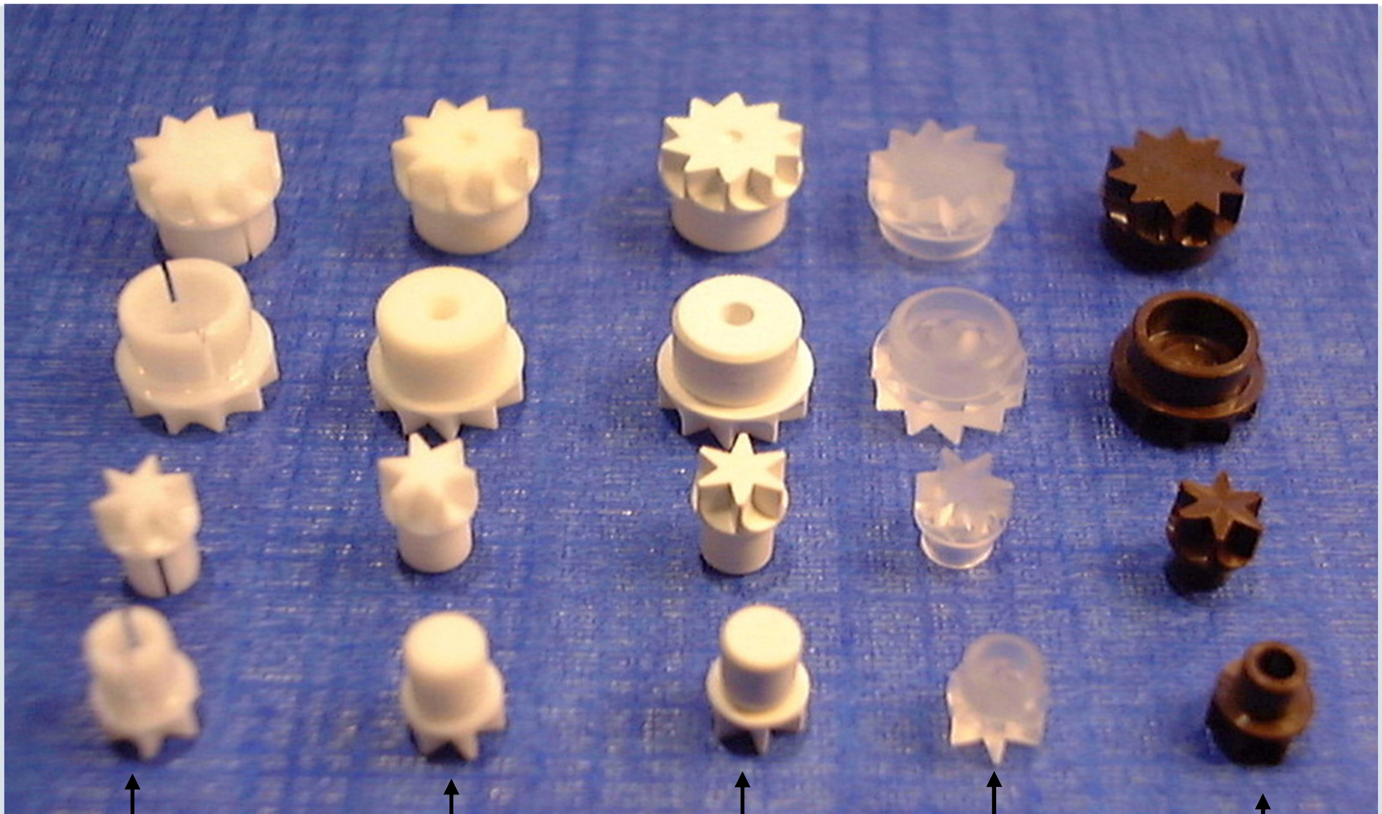


massive bottom rotor

MAS-Spinners, Inserts, and Spinner Caps

diameter	insert/cap for volume reduction	volume within coil
2.5 mm	spinner with bottom cap	11 µl
	with integrated bottom	8 µl
3.2 mm	with integrated bottom	30 µl
	with upper insert and massive bottom	14 µl
4 mm	without insert, with thin bottom	71 µl
	with upper insert and massive bottom	50 µl
	with upper inserts and massive bottom	12 µl
7 mm	without Insert, with thin bottom	240 µl
	"CRAMPS – inserts"	60 µl

VT: Rotor Caps



ZrO_2 Macor BN Kel-F Vespel

VT: Rotor Caps

Kel-F (polymer): ambient temperature ± , (shrinks when cold, softens and deforms when hot), easy pull-out

BN (ceramic): high and low temperature, mechanically delicate, glue in for tight fit

Macor (ceramic): high and low temperature, mechanically delicate, glue in for tight fit

ZrO_2 (ceramic): high and low temperature, mechanically durable, easy pull-out, not so cheap ...

Vespel (polymer): high speed high temperature, easy pull-out

Spinner Caps: Materials and Application Ranges

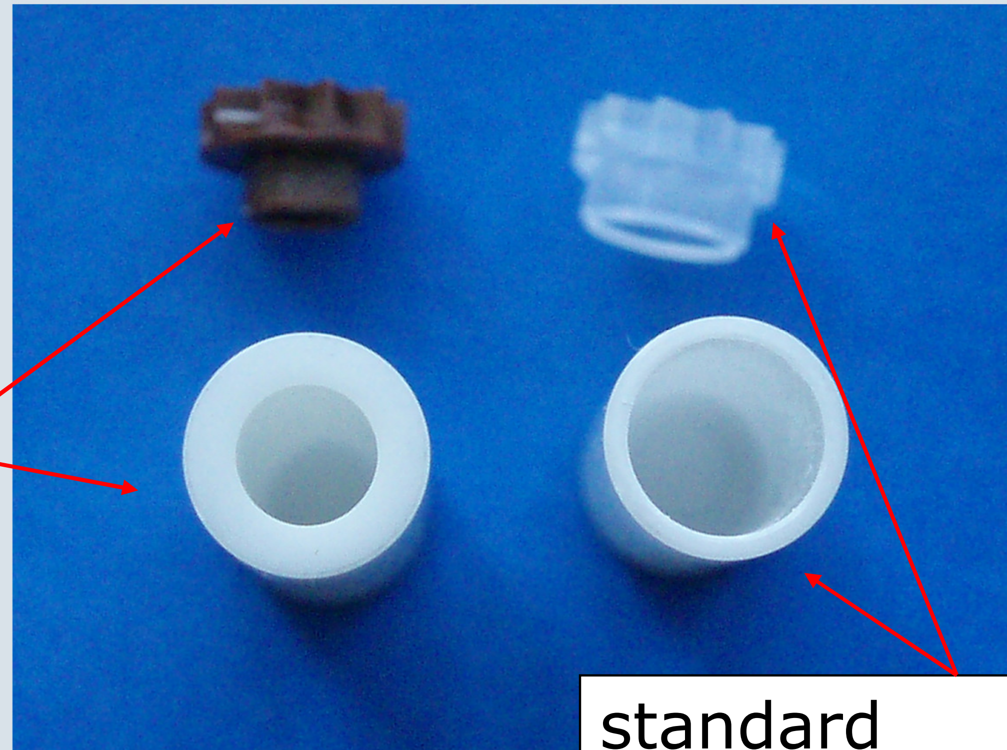
spinner diameter	material of rotor cap	temperature range
2.5 mm	Vespel	-30 ... +80°C
3.2 mm	Kel-F Vespel Zirconia	-10°C ... +50°C -30 ... +80°C -140°C ... +300°C
4 mm	Kel-F Vespel Zirconia Boron nitrid	-10°C ... +50°C -30 ... +80°C -140°C ... +300°C -140°C ... +300°C
7 mm	Kel-F Zirconia, Macor Boron nitrid	-10°C ... +50°C -140°C ... +300°C -140°C ... +300°C

High Speed Rotors

high speed ZrO_2 rotors:

7 mm: $\nu_{rot,max}$= 8 kHz

4 mm: $\nu_{rot,max}$= 18 kHz

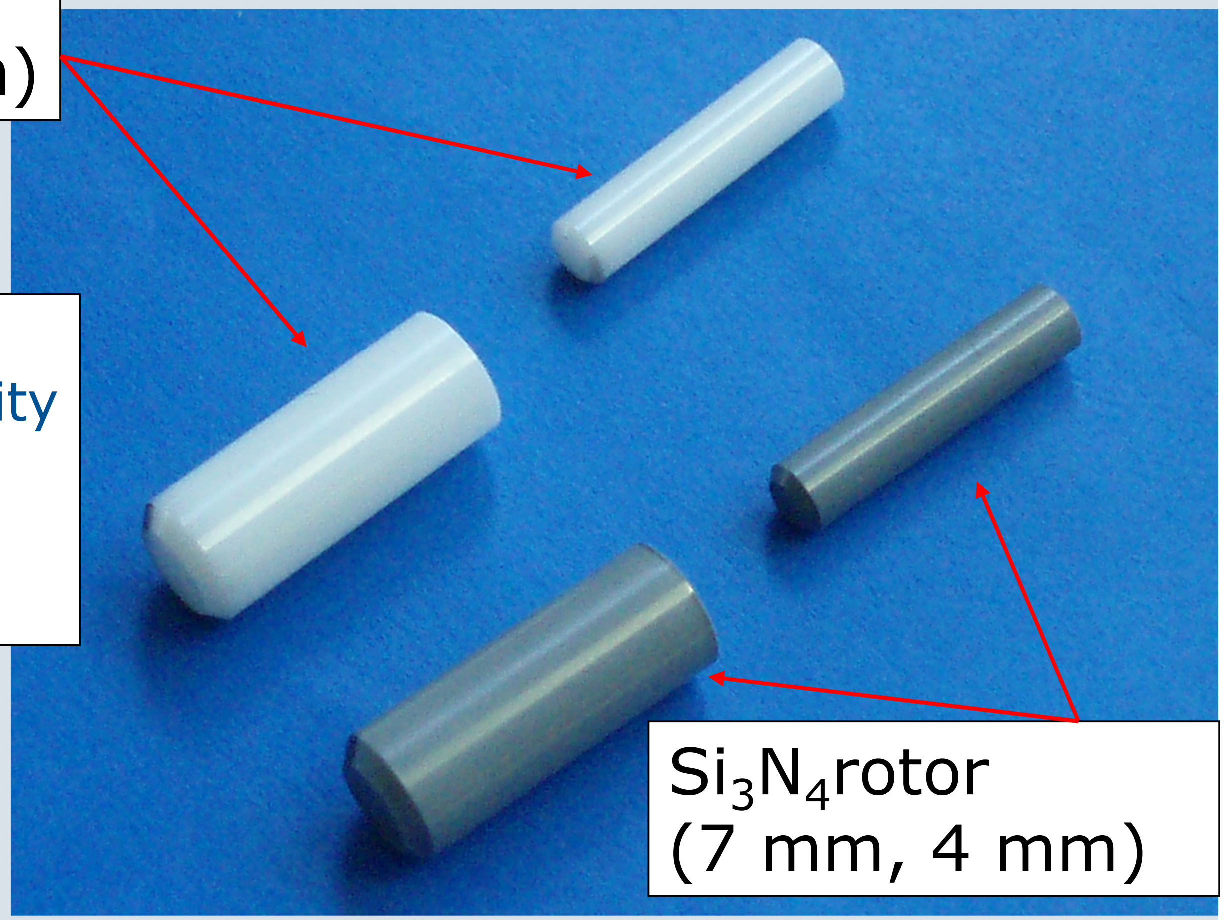


high speed 7mm ZrO_2 rotor/cap

standard 7mm ZrO_2 rotor/cap

increased wall thickness
(reduced active volume)

Si_3N_4 Rotors



main advantage of Si_3N_4:
higher thermal conductivity
(smaller temperature gradients)

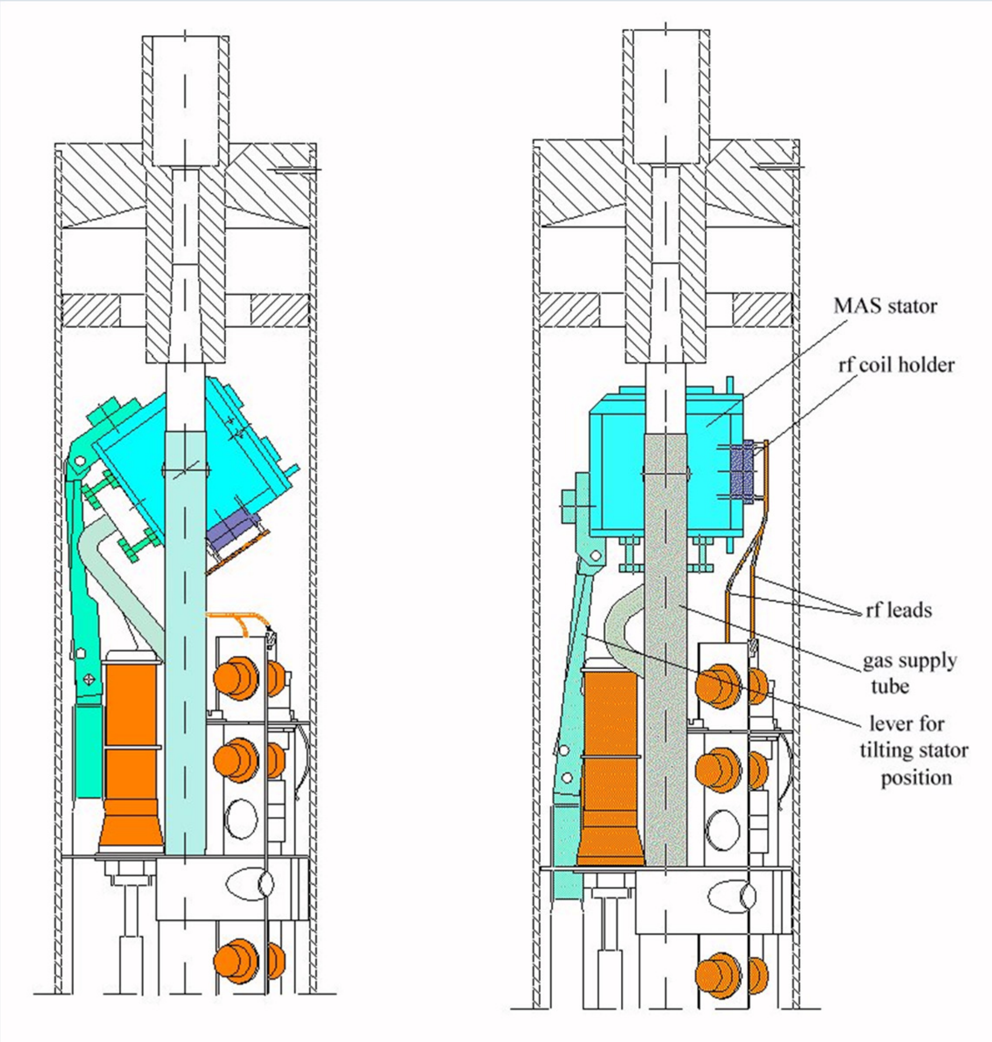
Special MAS Rotors

- sapphire rotors for light excitation
- rotors for laser heating (no bottom, sample in ceramic insert)
- stretch rotors for spinning sealed glass vials
- ...

MAS Rotors Summary

type	*available for*
standard ZrO2	7, 4, 3.2, 2.5 1.3
CRAMPS (Kel-F, PTFE, PE)	7, 4,
massive bottom, top insert	4, 3.2
massive bottom, long stem cap	2.5
high speed	7, 4
Si3N4	7, 4
sapphire	7, 4, 2.5

Sample Insert/Eject for SB MAS Probe



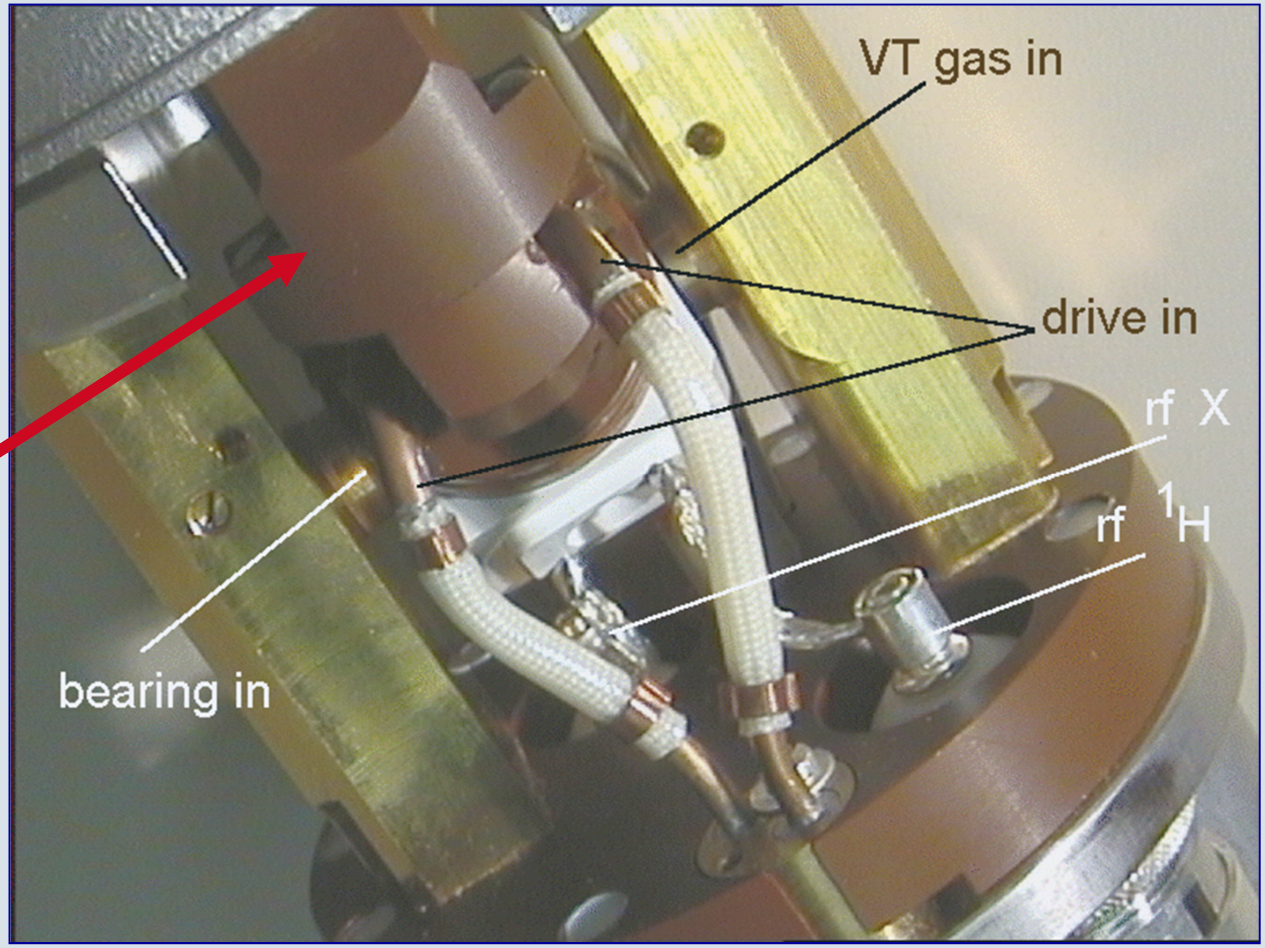
stator flips from the magic angle to the vertical position for eject/insert

exceptions:
2.5 mm (no flip)
3.2 mm (small angle flip)

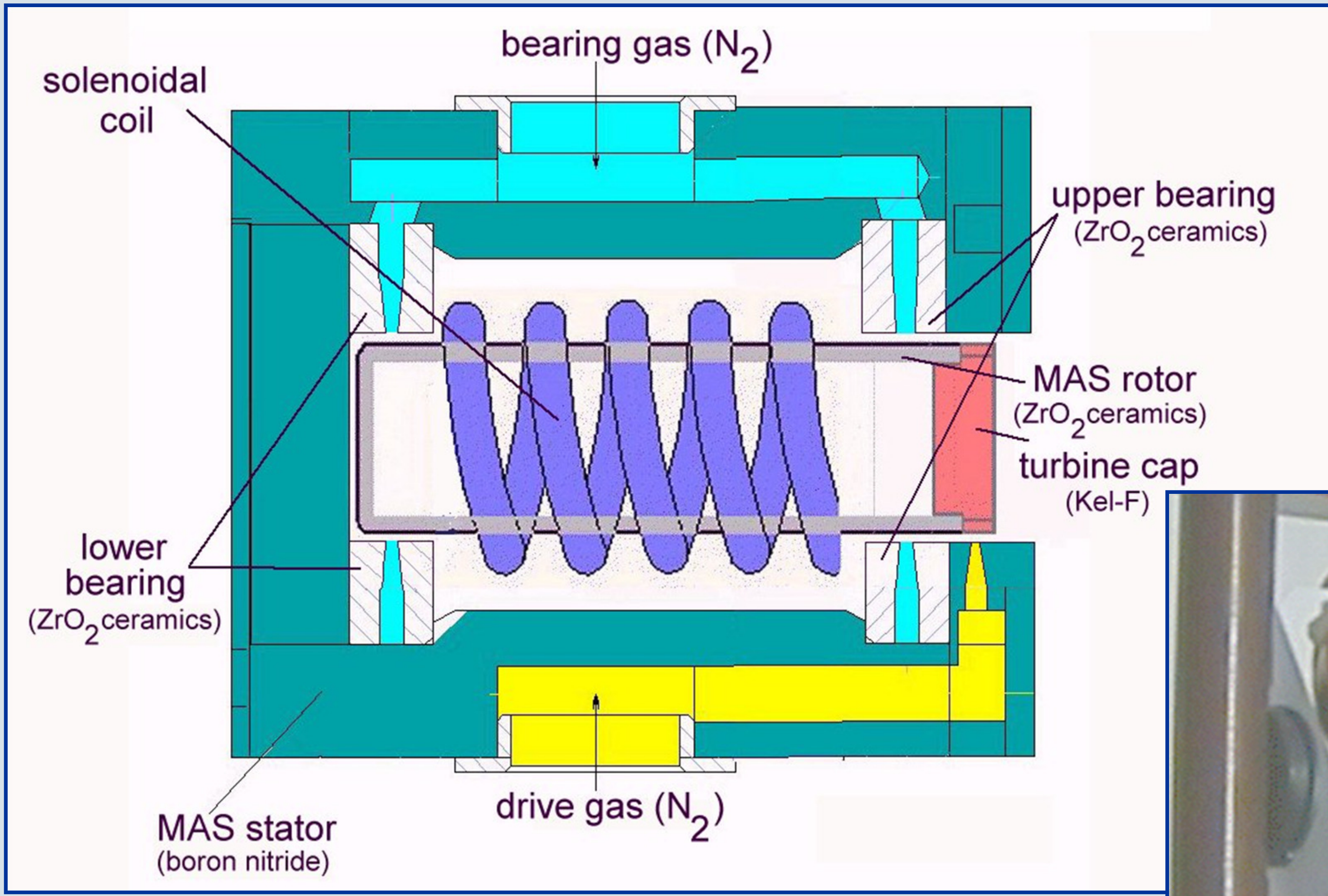
Sample Insert/Eject for WB MAS Probe

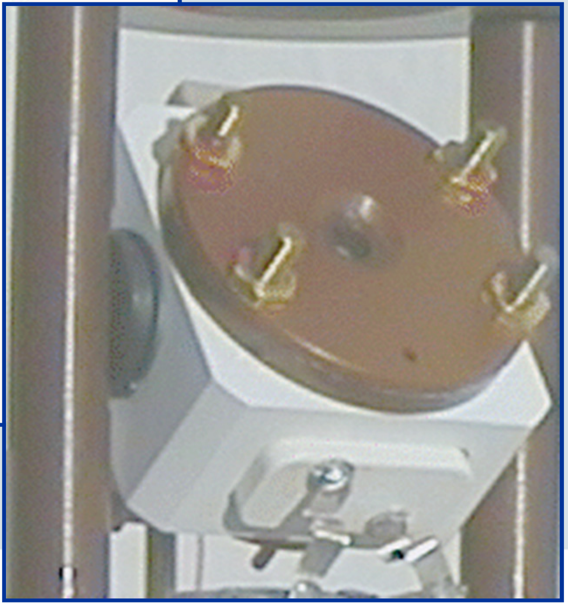
stator is static during sample change (no flip)

sample is guided on its way in or out by a funnel like device

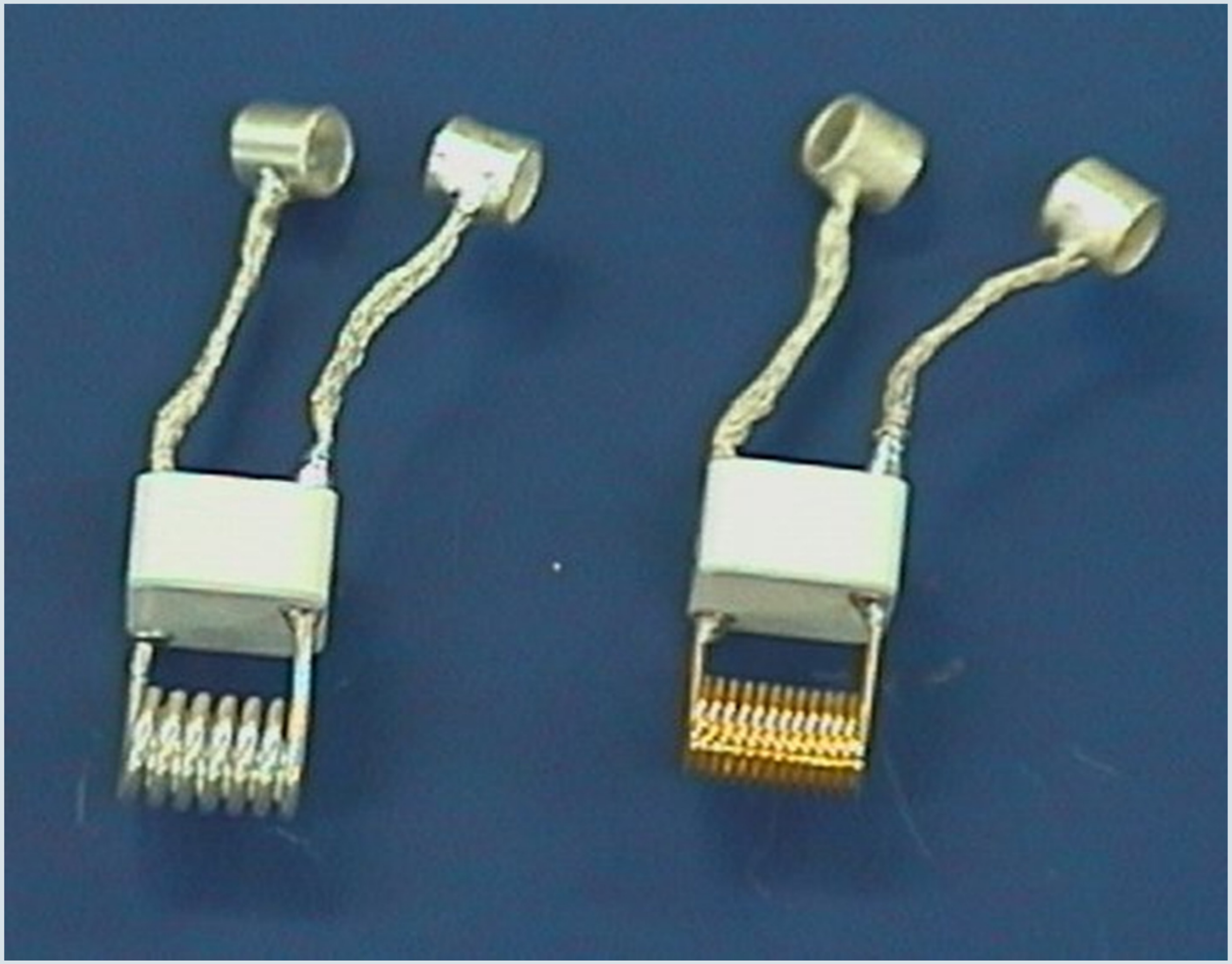


Cross Section View of the MAS Probe Stator





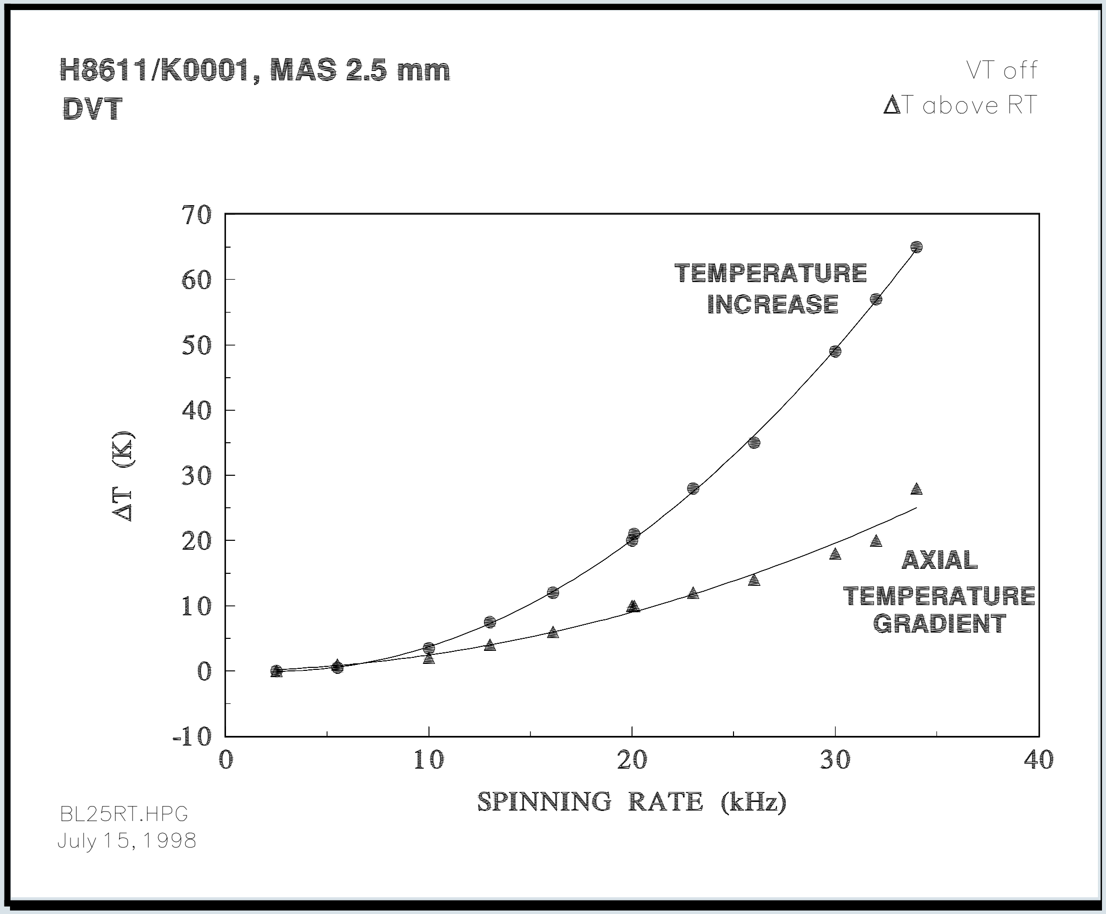
Coils for WB MAS probes



Frictional Heating in Air Bearings

- air bearings are low friction bearing but are not friction free
- friction causes heating of spinner and sample
- effect is small or negligible at slow spinning and becomes important close to the maximum spinning speed
- for sensitive samples: cool the sample appropriately
- for precise temperature control perform a temperature calibration using an NMR thermometer

Frictional Heating in MAS probes



Temperature increase due to air friction for high spinning speeds and accompanying thermal gradients over full zirconia rotors for 2.5mm MAS/DVT.
No cooling or heating gas (VT) applied.

General RF Design of MAS Probes

single Coil design

coil is simultaneously tuned to

one (single resonance probe) frequency

two (double resonance probe) frequencies

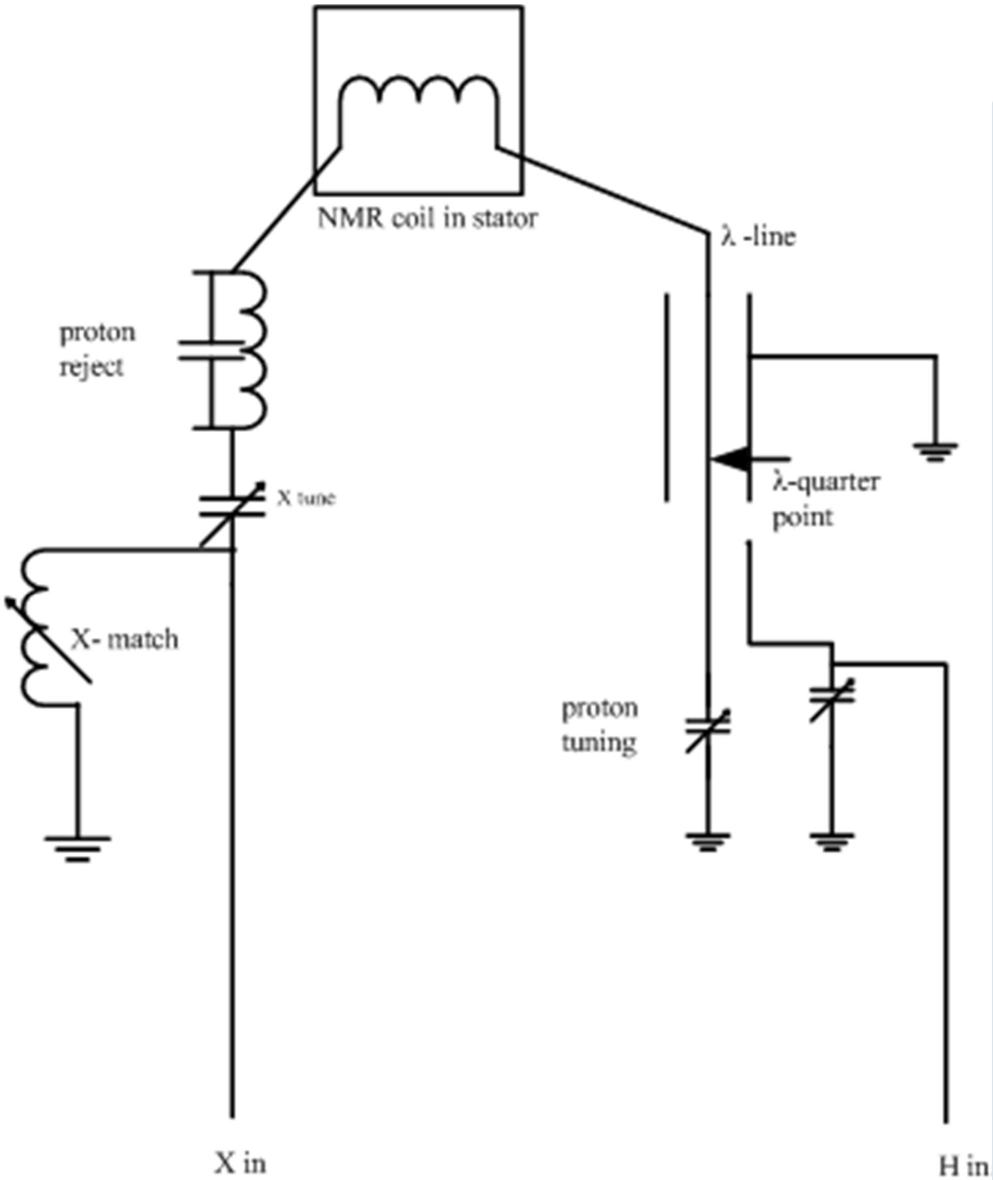
three (triple resonance probe) frequencies

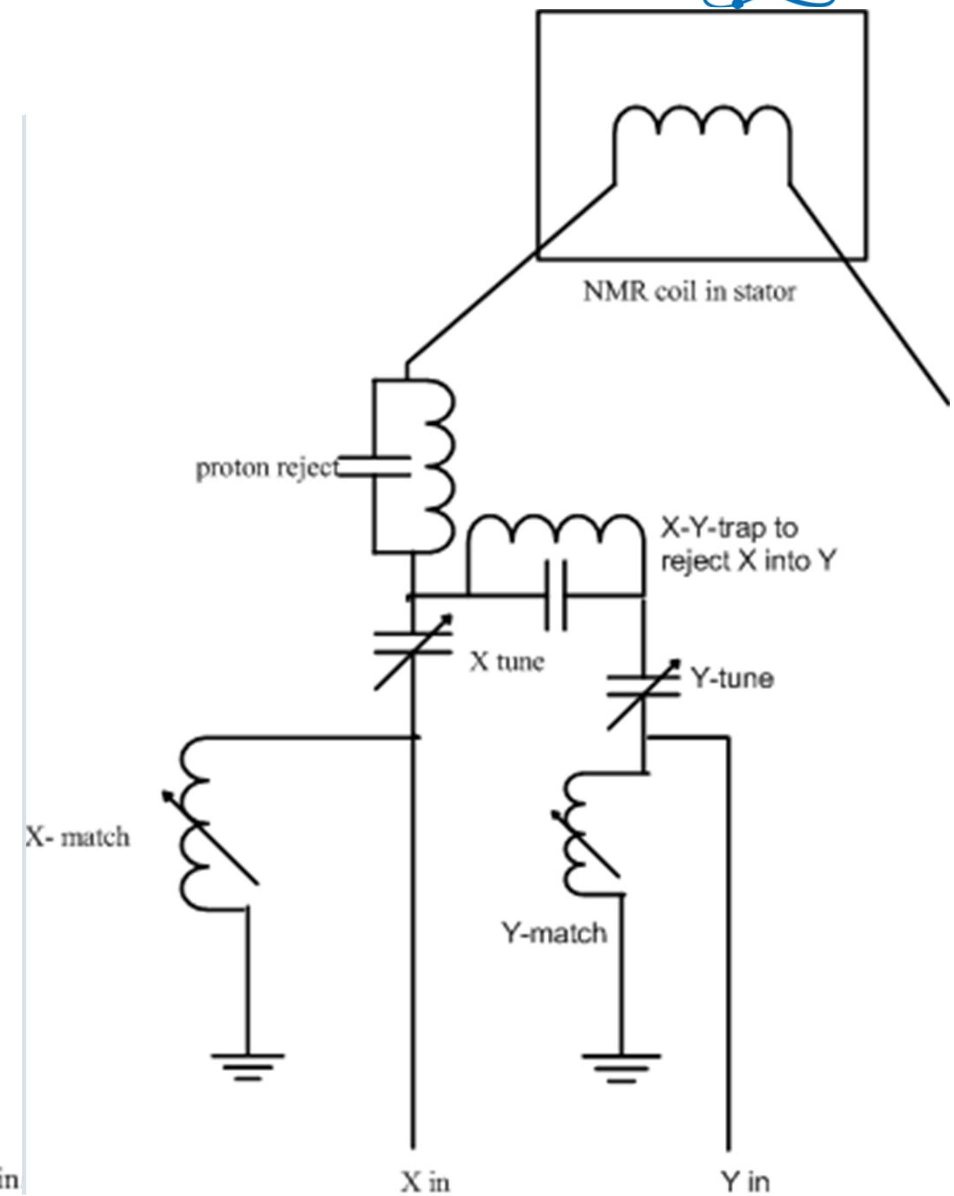
dual Coil design Efree

inner coil is tuned to 1 or 2 frequencies,

outer coil (cavity) is tuned to protons only

RF design of a WB CP/MAS probe





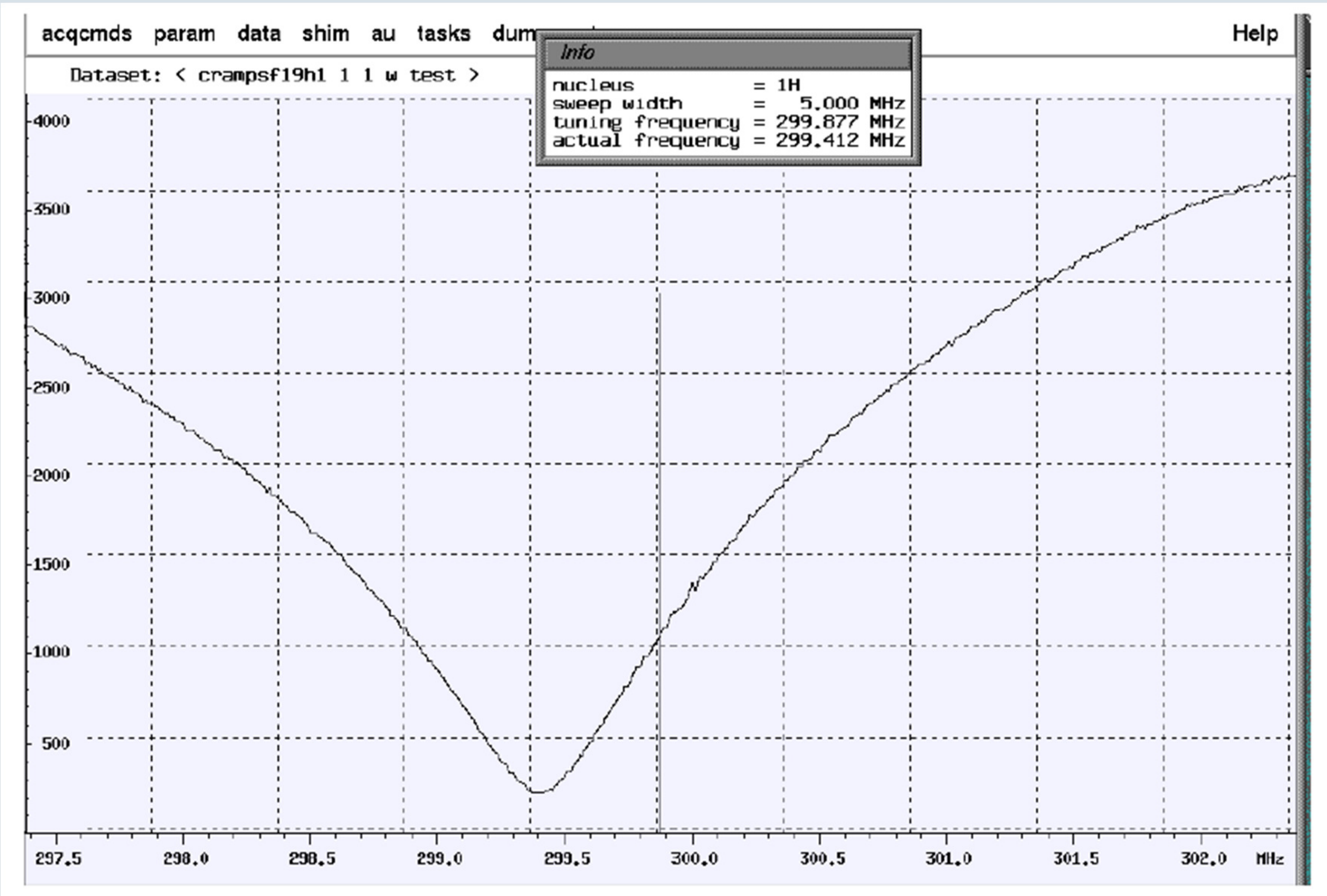
Probe Tuning and Matching

tuning:
adjust the resonance frequency of the probe circuit to the observe frequency (Larmor frequency)

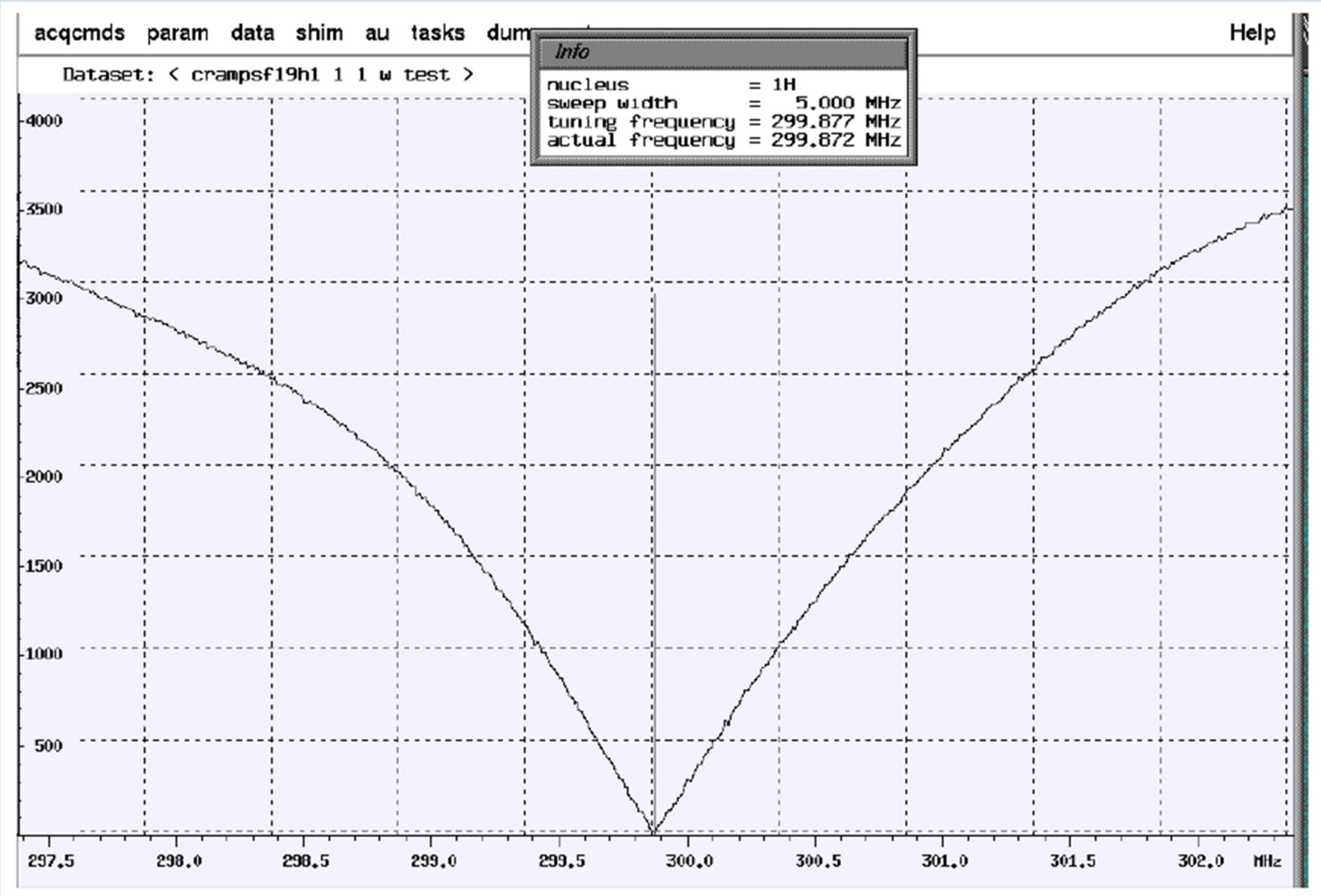
matching:
adjust the probe impedance to the impedance of the other RF components (transmitter, cables, etc.),standard impedance: 50 Ohm

purpose:
maximum power delivered to NMR coil, i. e. maximum B_1 field and minimum reflected power (which could be harmful to other components, e.g. the transmitter)

Wobbler response of a detuned probe

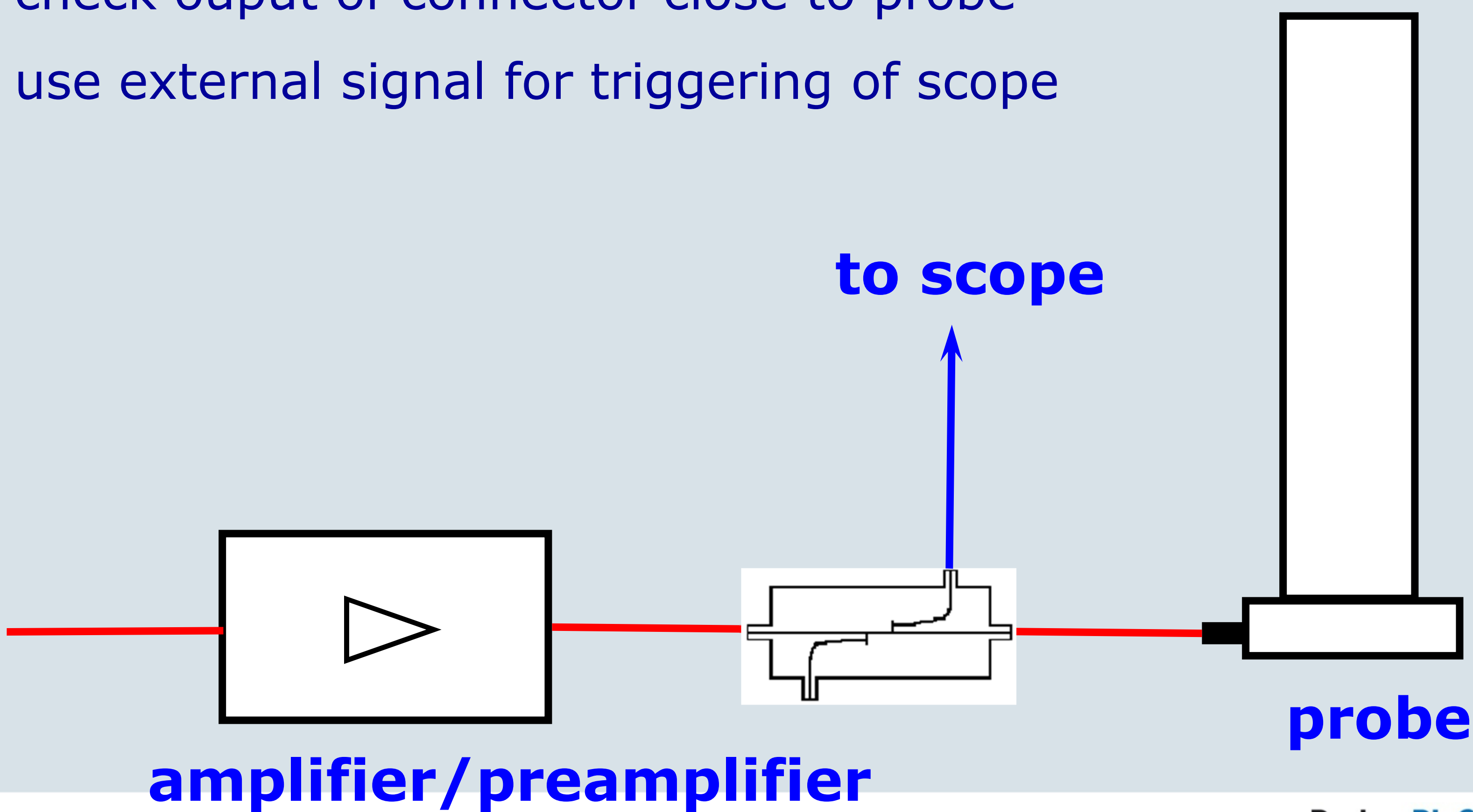


Wobbler response of a tuned probe

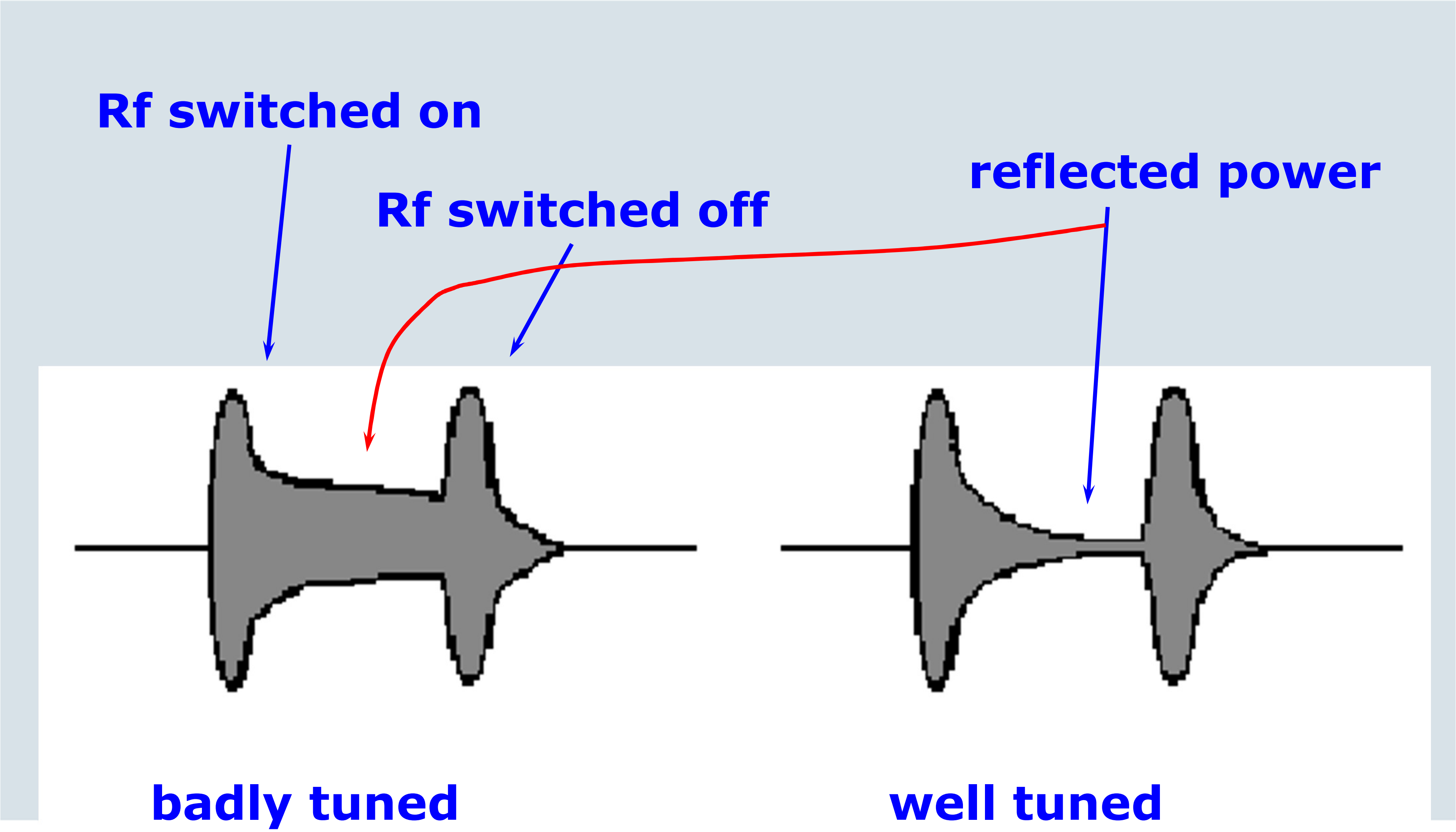


Set-up for probe tuning on the reflected RF power

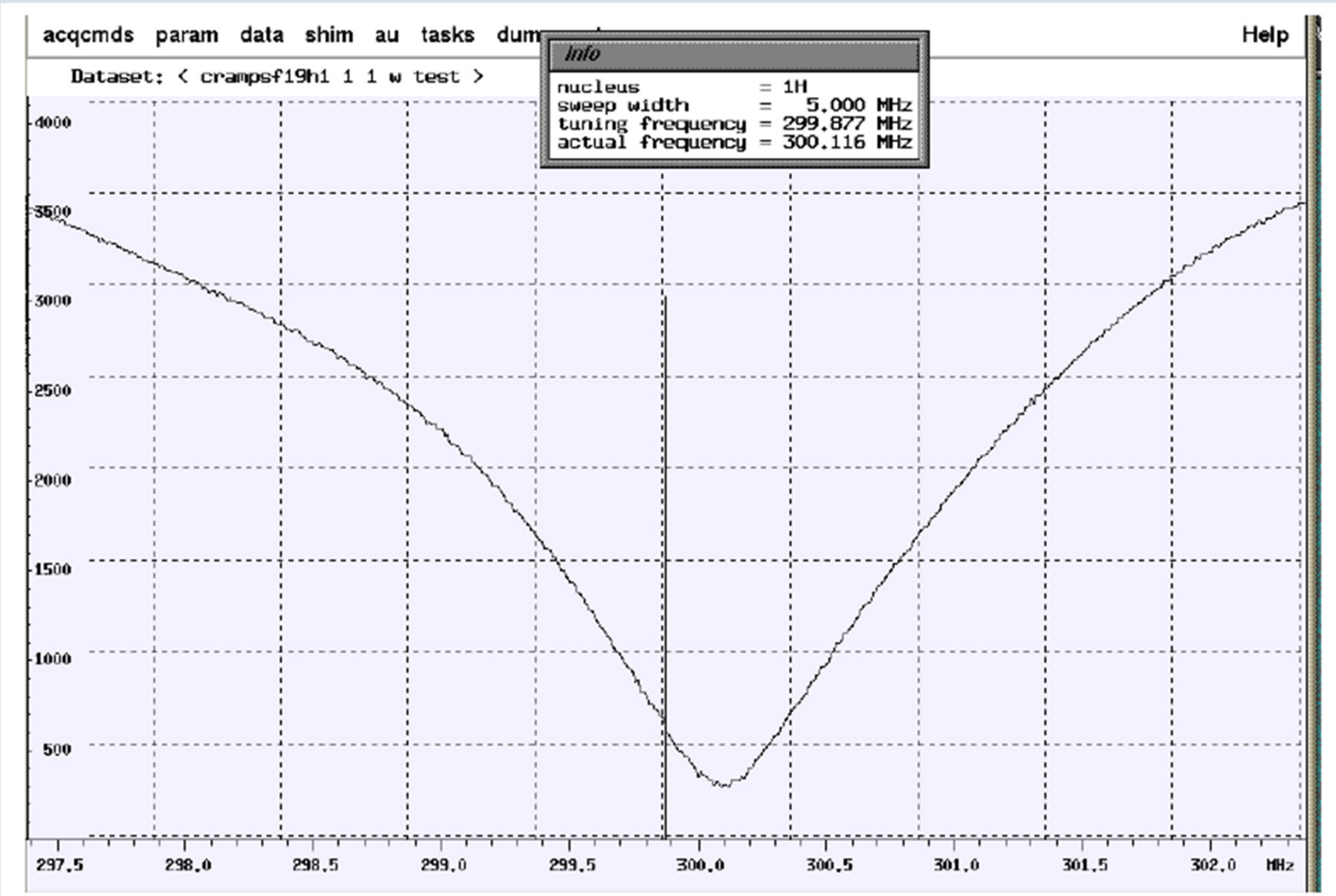
- Connect directional coupler between amplifier and probe
  - check ouput of connector close to probe
  - use external signal for triggering of scope



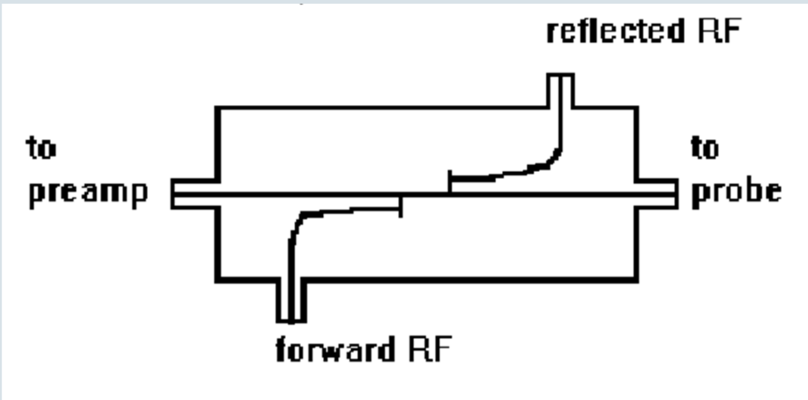
Shapes of reflected pulses



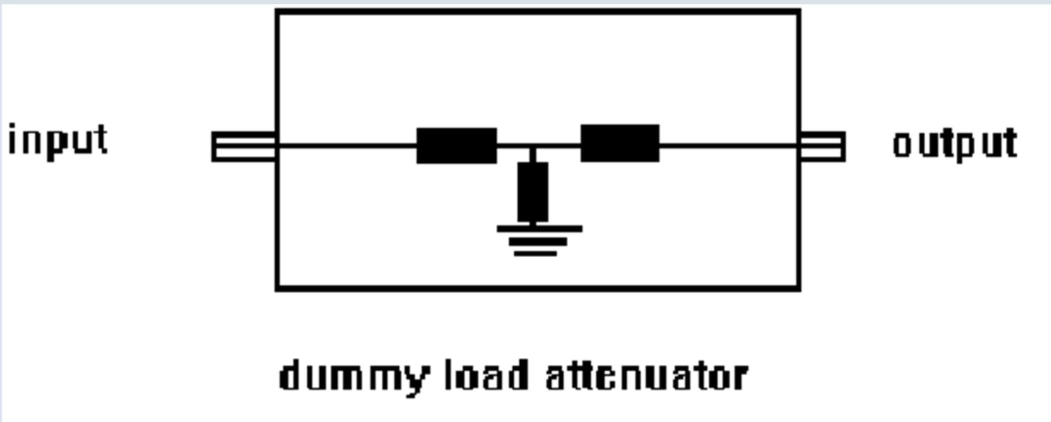
Wobbler response of a probe after tuning on the reflected RF power (if component off 50 Ω or pulse detunes probe)



Some useful equipment



Directional coupler



Dummy load attenuator

Radio Frequency Filters

RF filters for double resonance experiments

- decoupling channel filters
- X-channel filters

RF filters for H/X/Y triple resonance experiments

- X-channel filters
- Y-channel filters

Radio Frequency Filters

RF filters for H/X/Y triple resonance experiments

- X-channel filters
- Y-channel filters

Radio Frequency Filters

Why external RF-Filters?

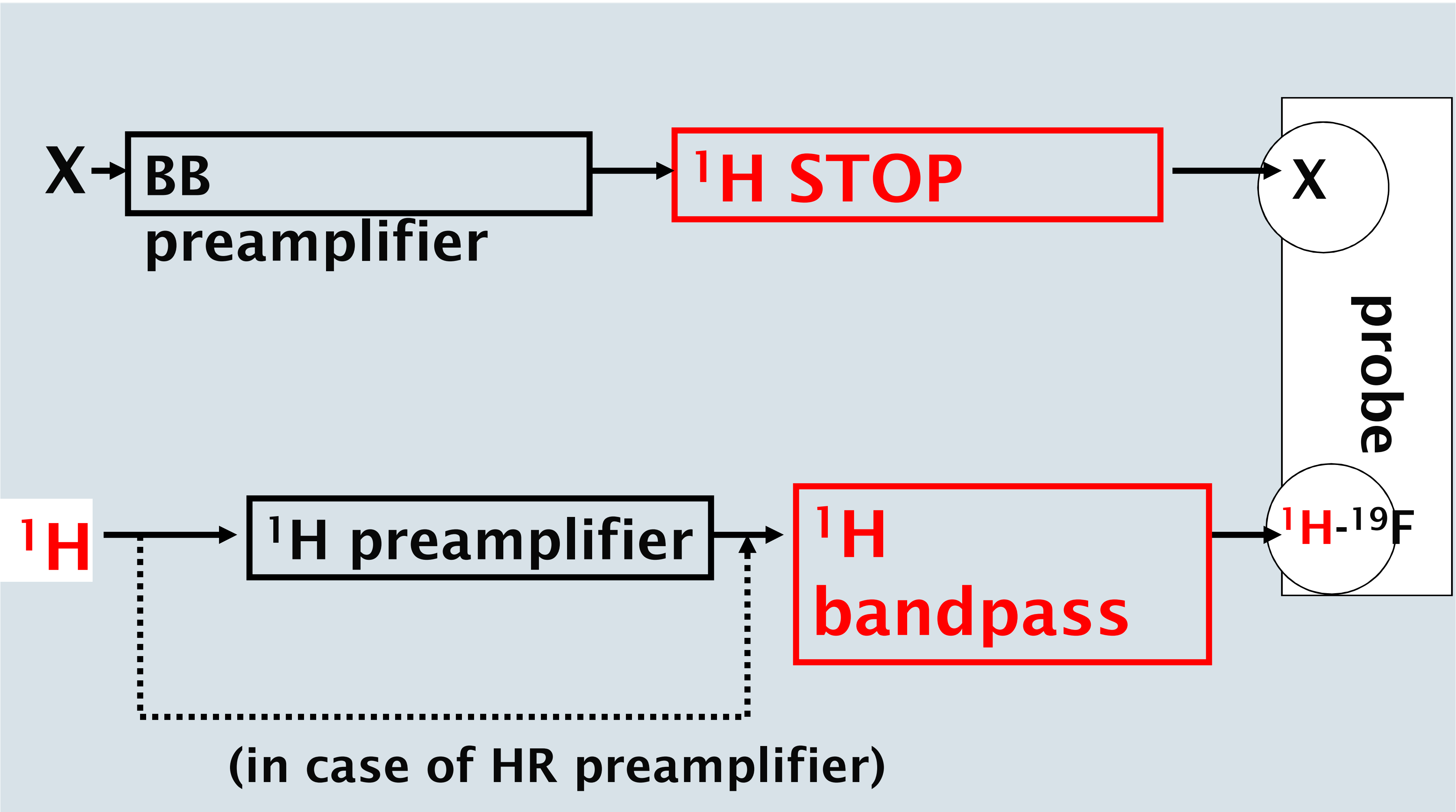
MAS probe: *single* NMR coil, tuned to all Frequencies (H/X, H/X/Y, or even H/F/X/Y). Internal isolation, therefore, comparatively small.

X observe with Y decoupling (or vice versa):
signal: µV to mV range
decoupling: typical values:100 W (=200V_{pp}) to 300 W (343 V_{pp})

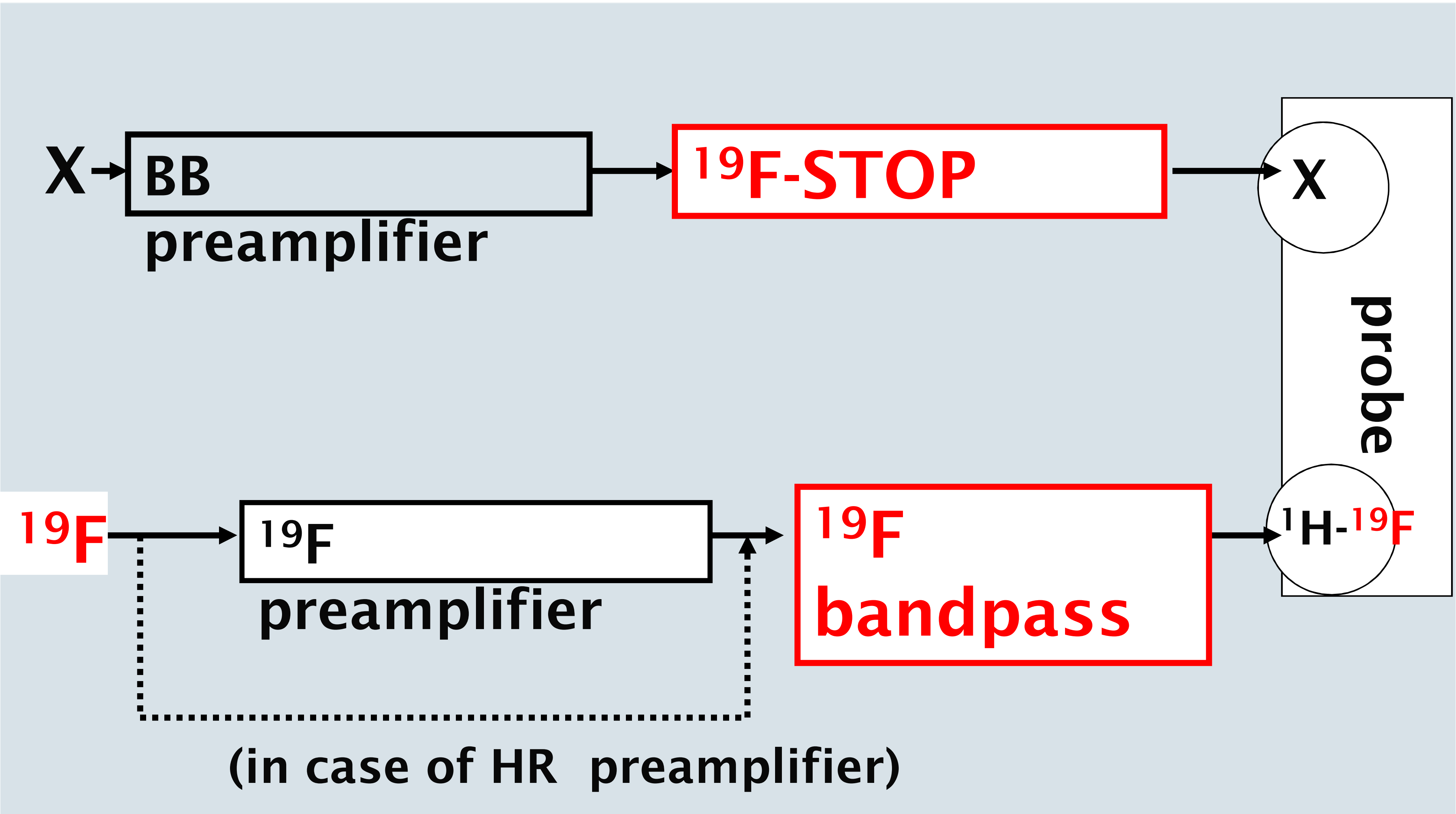
⇒isolation better than 90 dB,

this can be achieved with external filters only

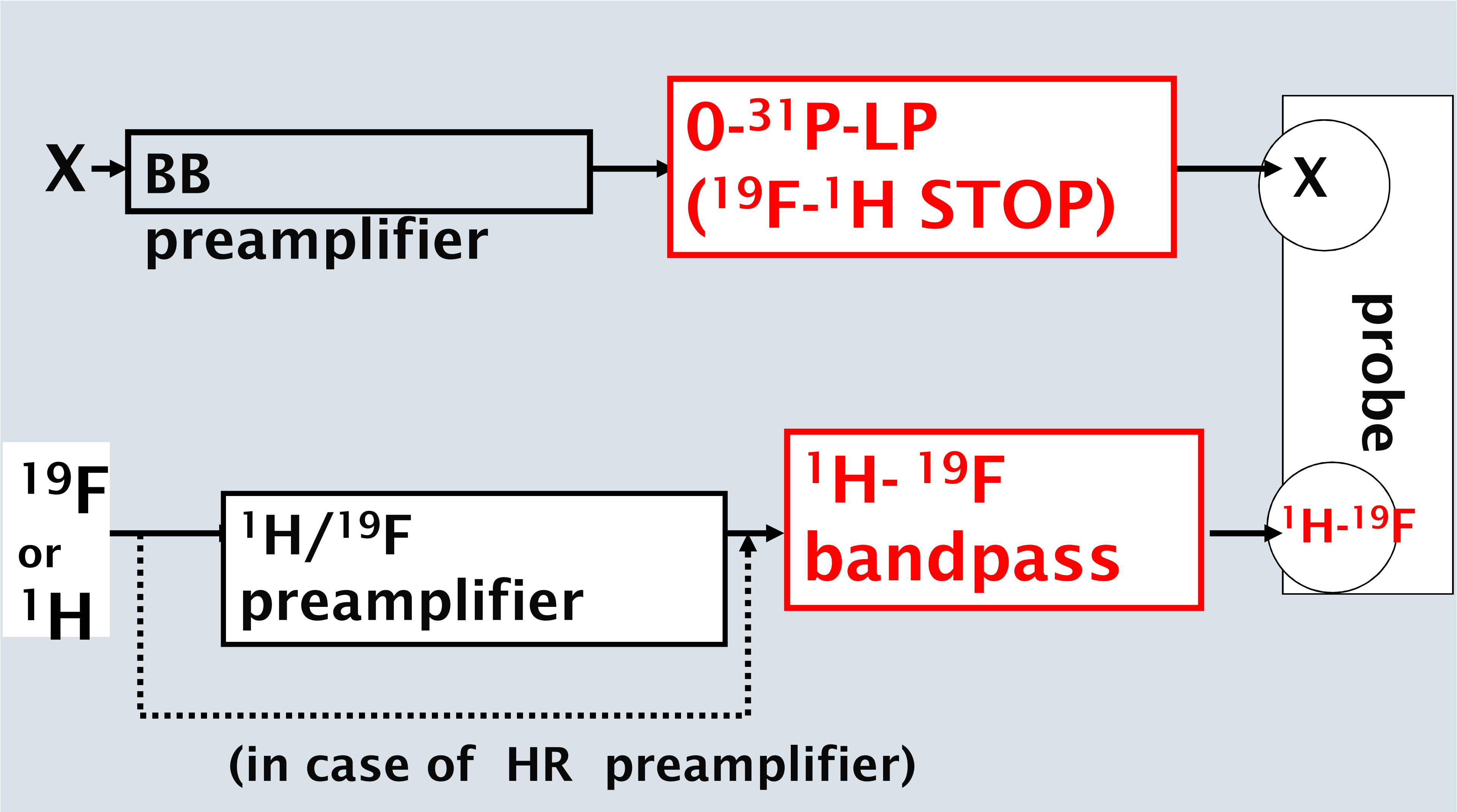
Filters for H-F/X Double Resonance Experiments



Filters for H-F/X Double Resonance Experiments

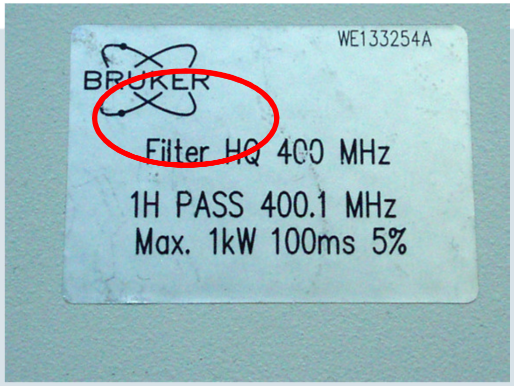


Filters for H-F/X Double Resonance Experiments

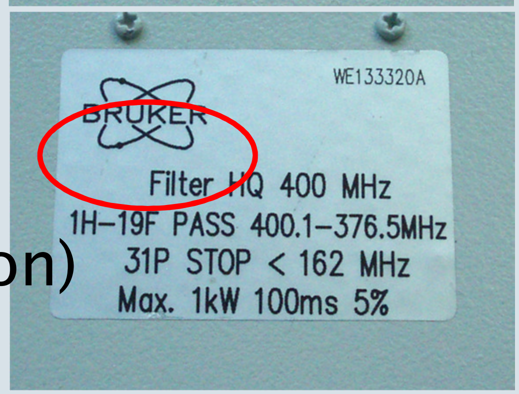


Decoupling Channel RF Filters

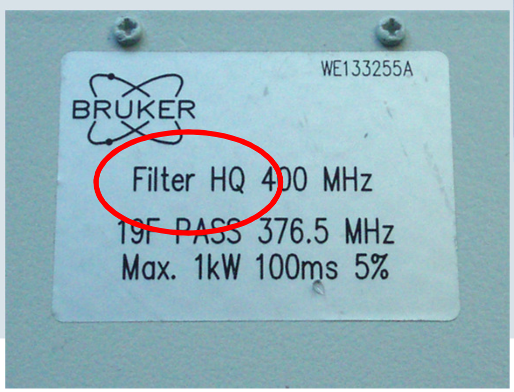
H/X
experiments



H/X or F/X
or H+F/X
(X observation)
experiments

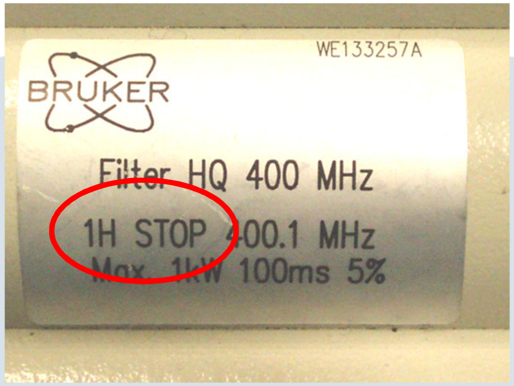


F/X
experiments

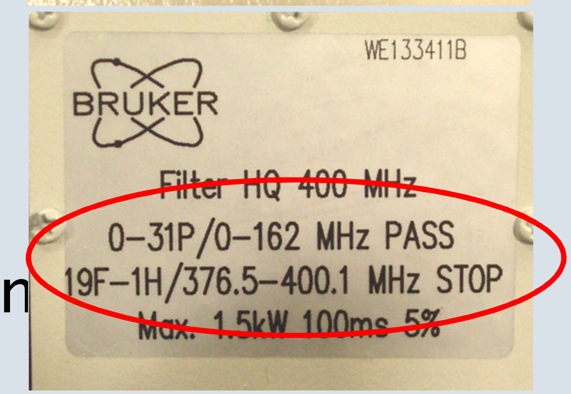


X Channel RF Filters, Double Resonance

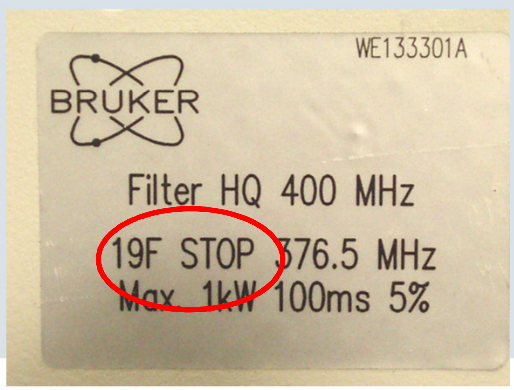
H/X
experiments:

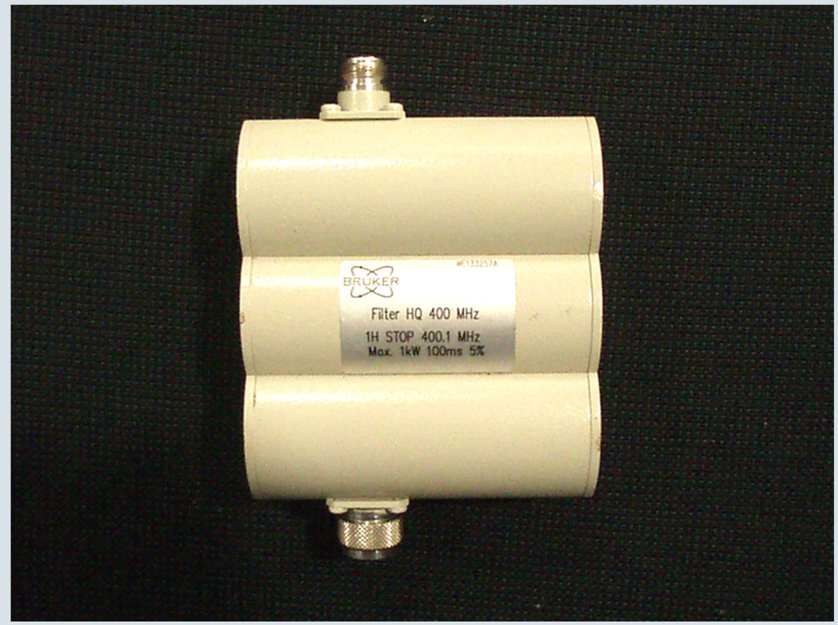


H/X or F/X
or H+F/X
(X observation
experiments

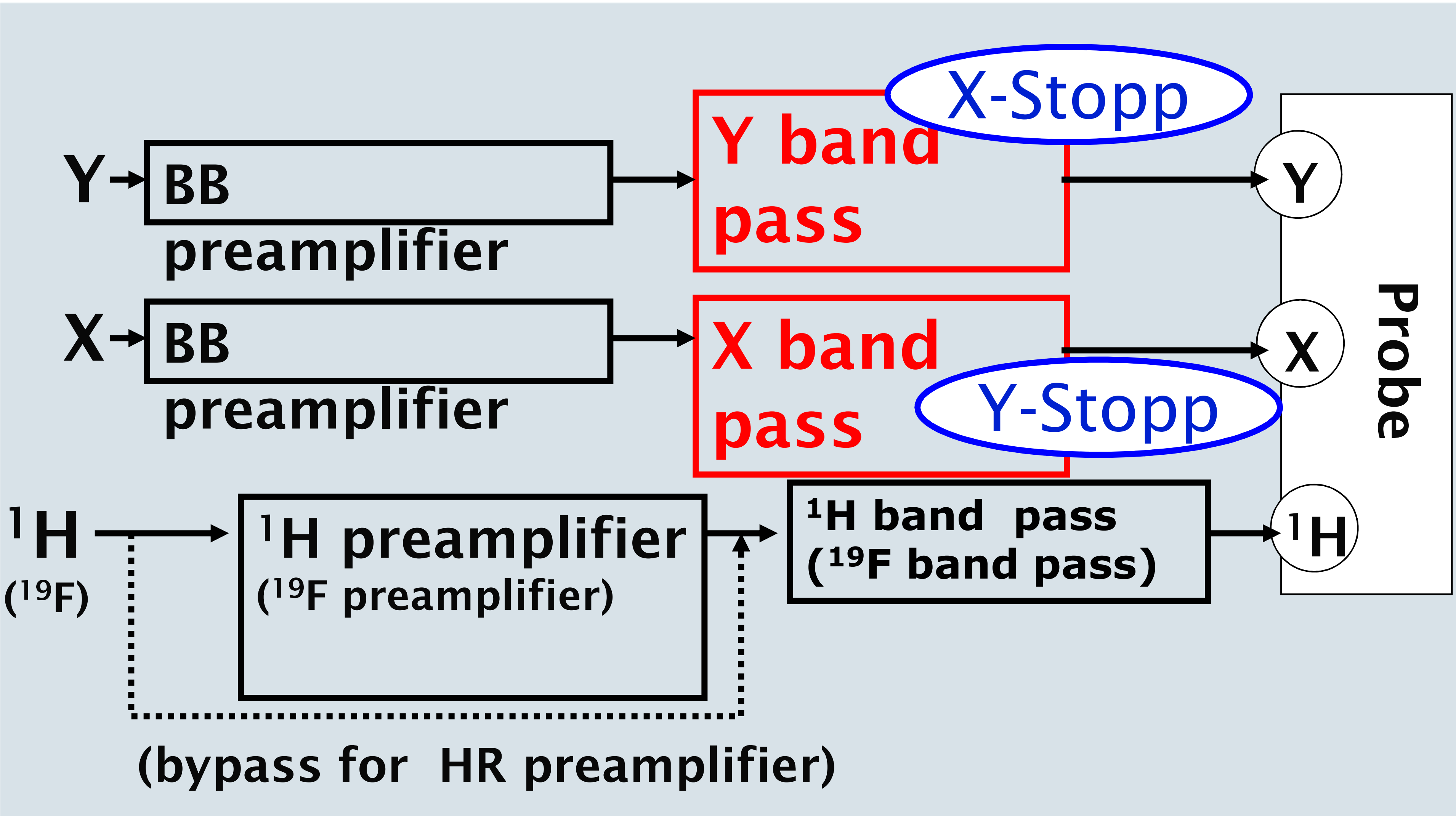


F/X
experiments





RF Filter, Triple Resonance Experiments



Band Pass Filters, Triple Resonance Experiments

band pass filter,
maximum input power: 1 kW
for 100 ms max. duration
at 5% dutycycle,
(order No.: W1346 ...)

^{7}Li-^{31}P

^{71}Ga-^{87}Rb

^{59}Co-^{23}Na

^{29}Si

^{133}Cs-^{2}H

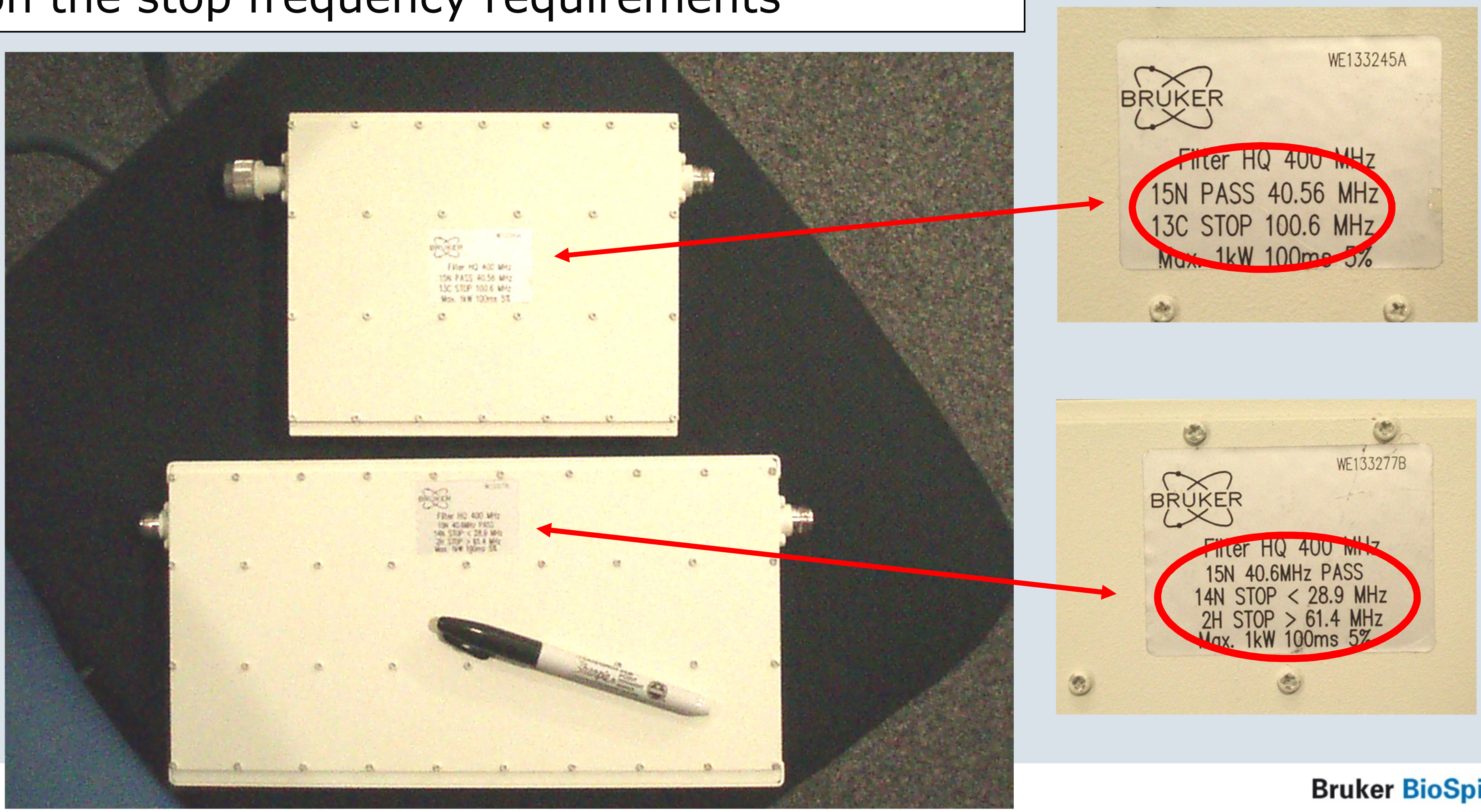
^{15}N

^{14}N

0-15N LP available

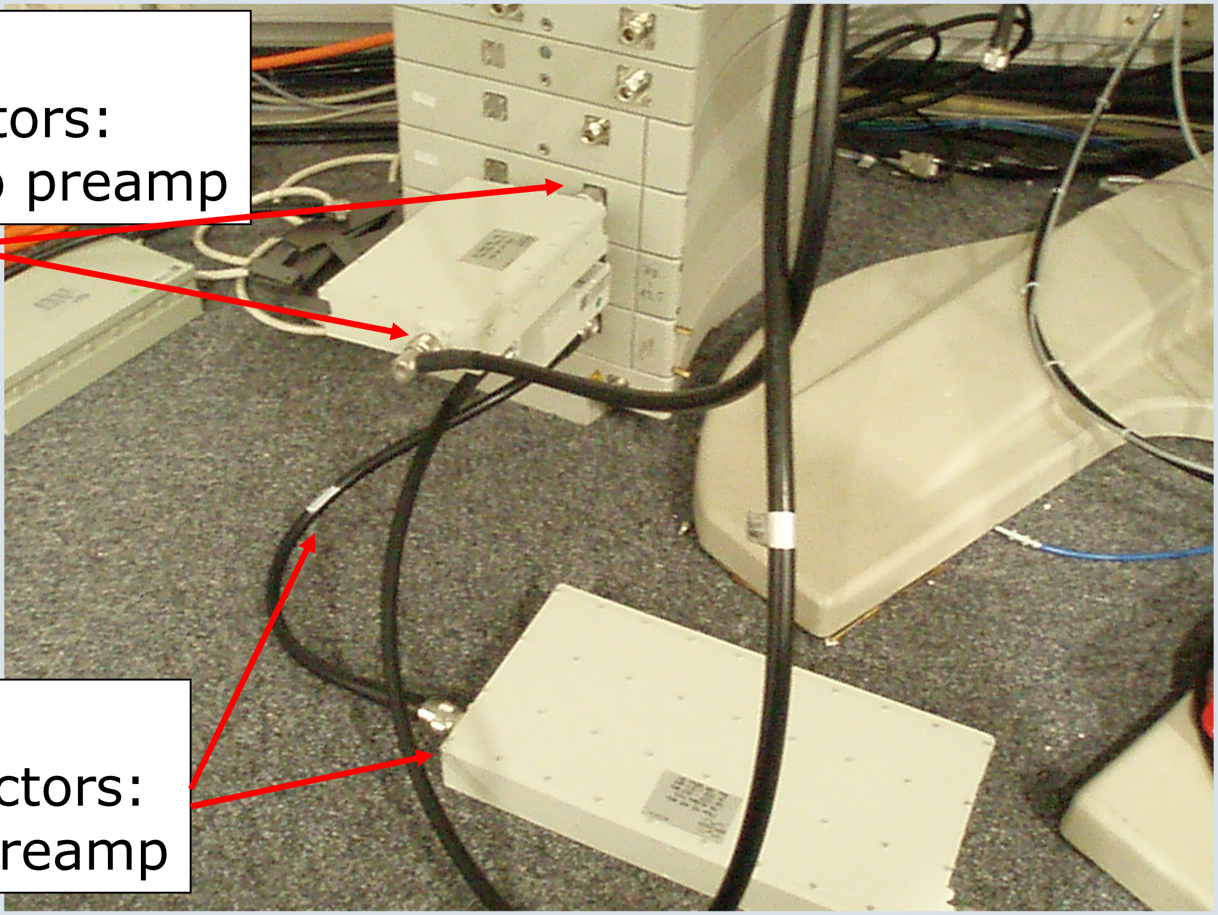
Band Pass Filters, Triple Resonance Experiments

band pass filter for a given pass band may come in several designs, depending on the stop frequency requirements



Positioning of RF Filters

smaller filters:
male/female connectors:
directly connected to preamp



larger filters:
female/female connectors:
cable connection to preamp

www.bruker-biospin.com