# Cryogenic probes
## Practical tips and tricks

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Strong Points

Weak Points

Future Developments

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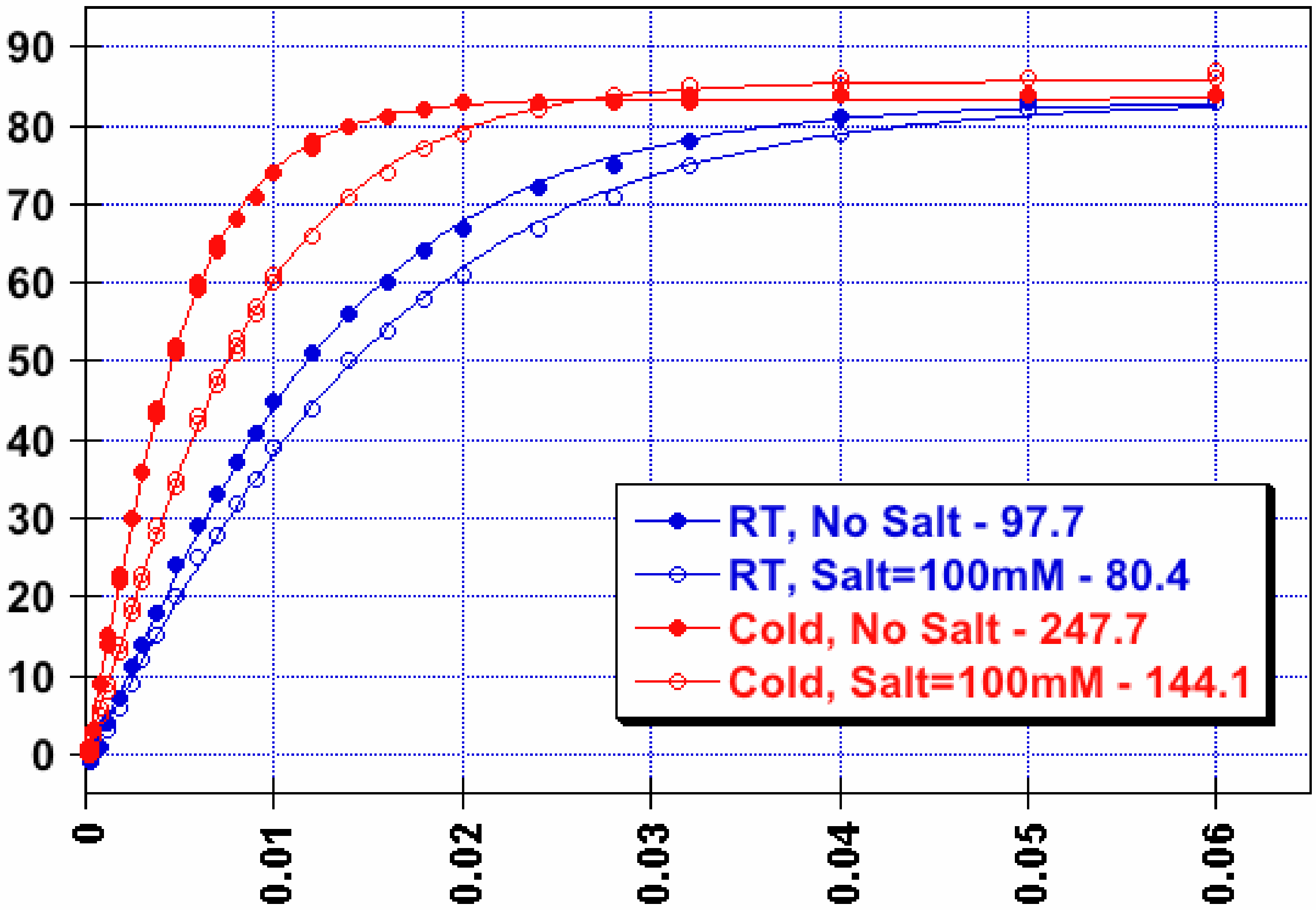
# Sensitivity of cryogenic probes

| | |
|---|---|
| 600 MHz : ETB 5000 :1 | Sucrose 700 to 750 :1 |
| 800 MHz : ETB 7000 : 1 | Sucrose 820 to 1100 : 1 |
| 900 MHz : ETB 8500 : 1 | Sucrose 1150 : 1 |

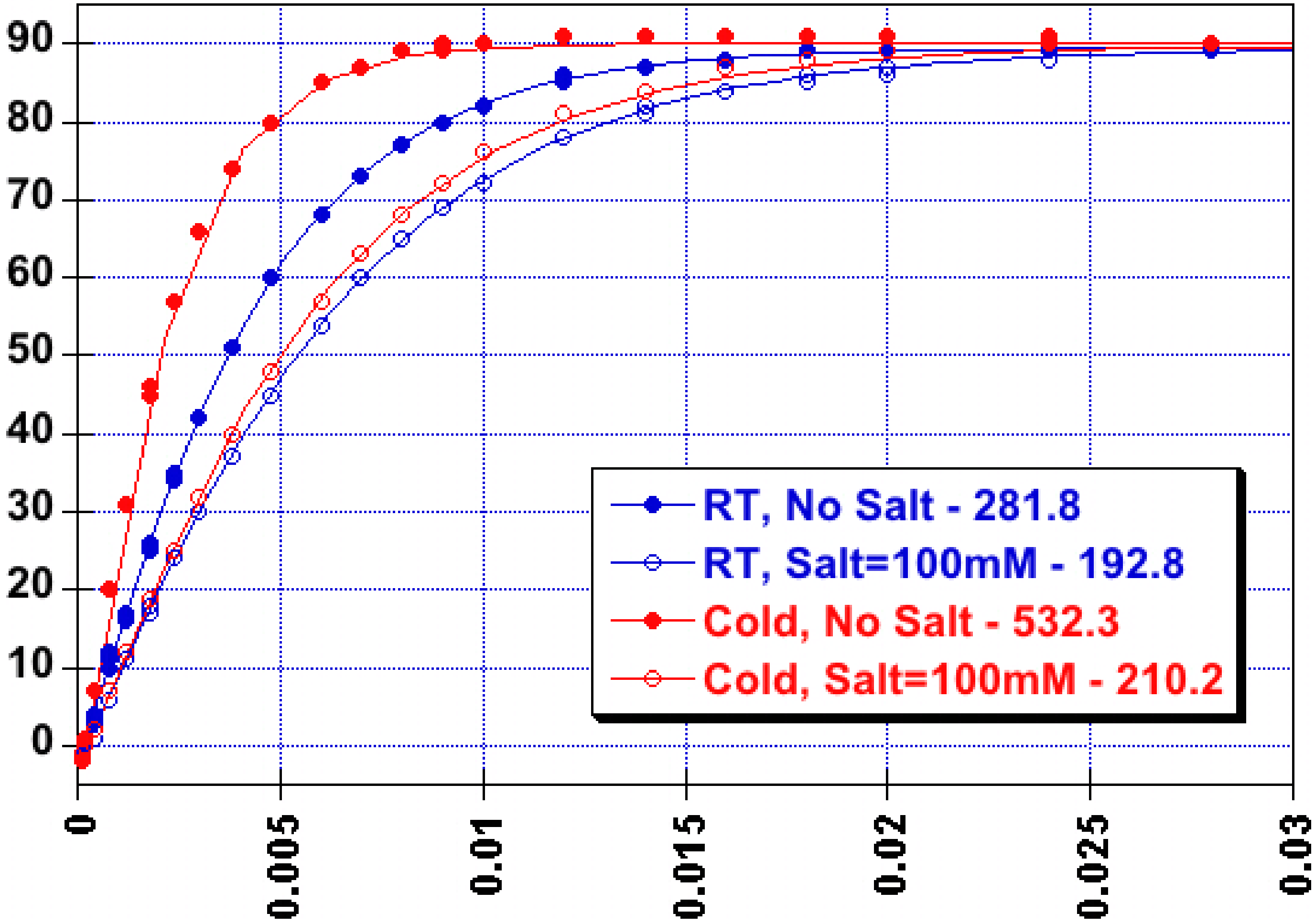
# Weak points

More frequent breakdowns
Longer repair turn-around times
More difficult to exchange
Strong radiation Damping
Longer gradient recovery times
High Maintenance

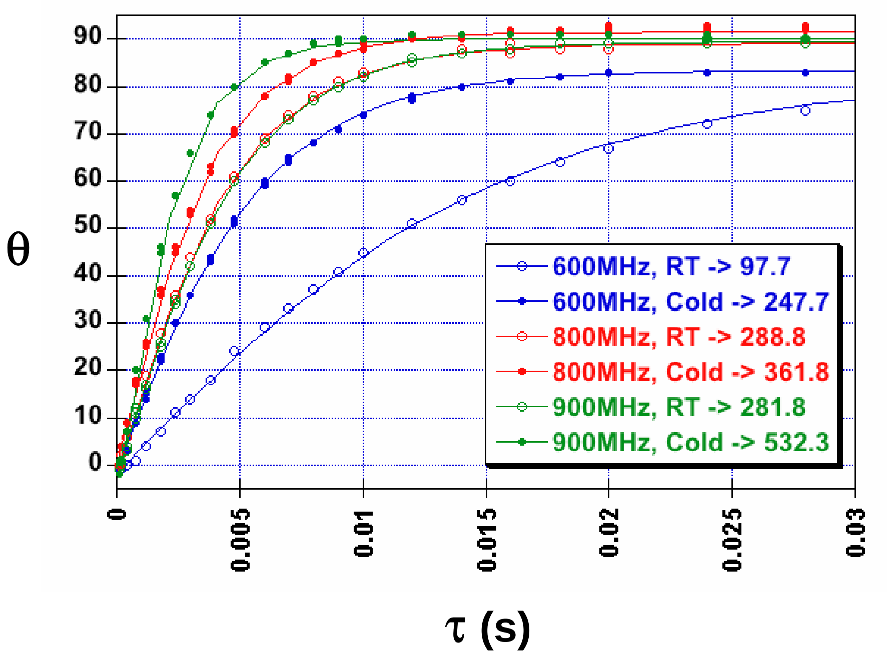
$H_2O$ $M_{xy}$ recovery to $M_z$ by radiation damping followed by the angle $\Theta$ (t in s.) made with the xy plane at 600 MHz for cold and RT probe

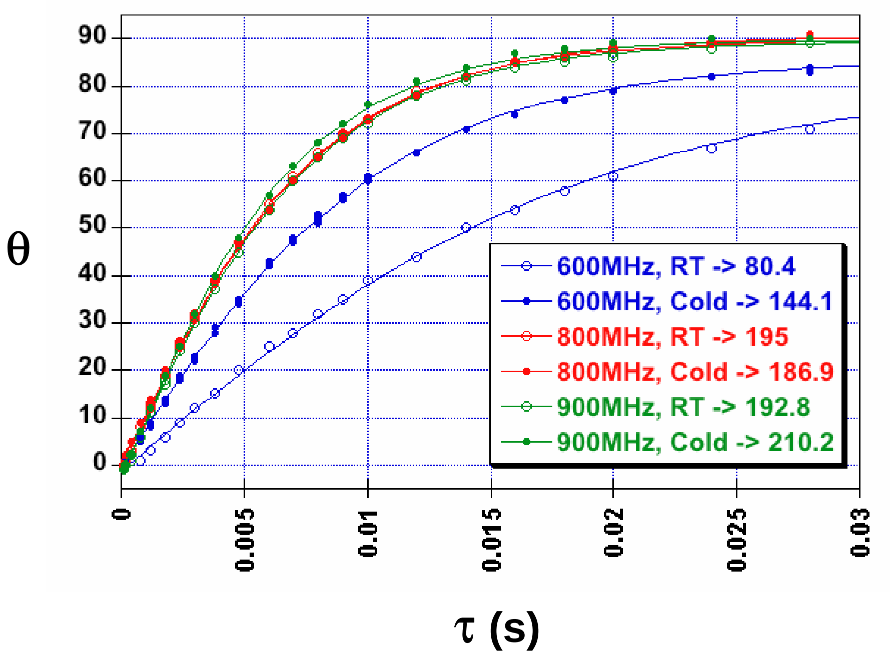


$H_2O$ $M_{xy}$ recovery to $M_z$ by radiation damping followed by the angle Θ (t in s.) made with the xy plane at 900 MHz for cold and RT probe

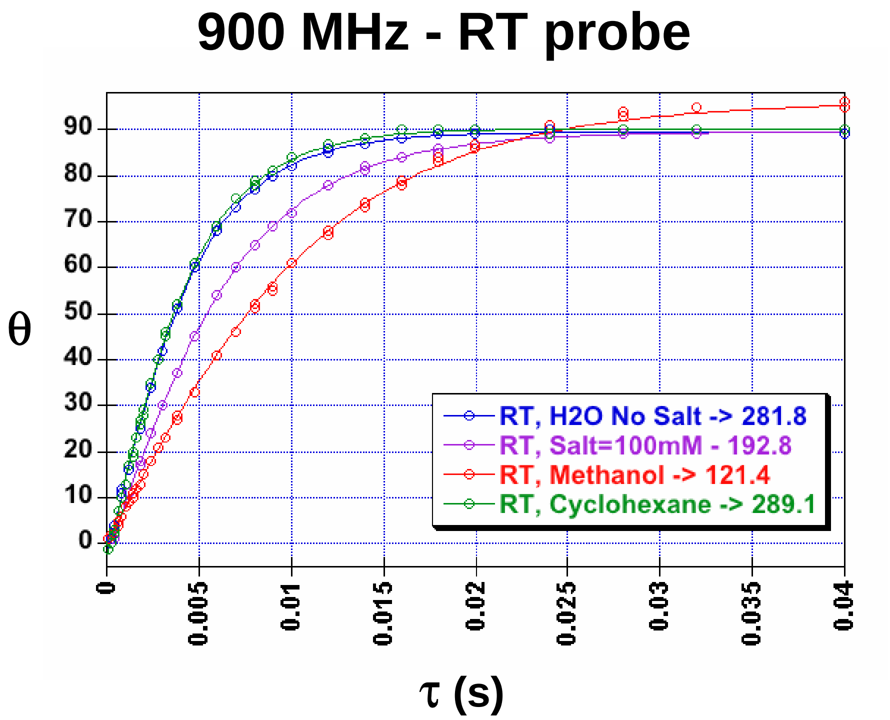


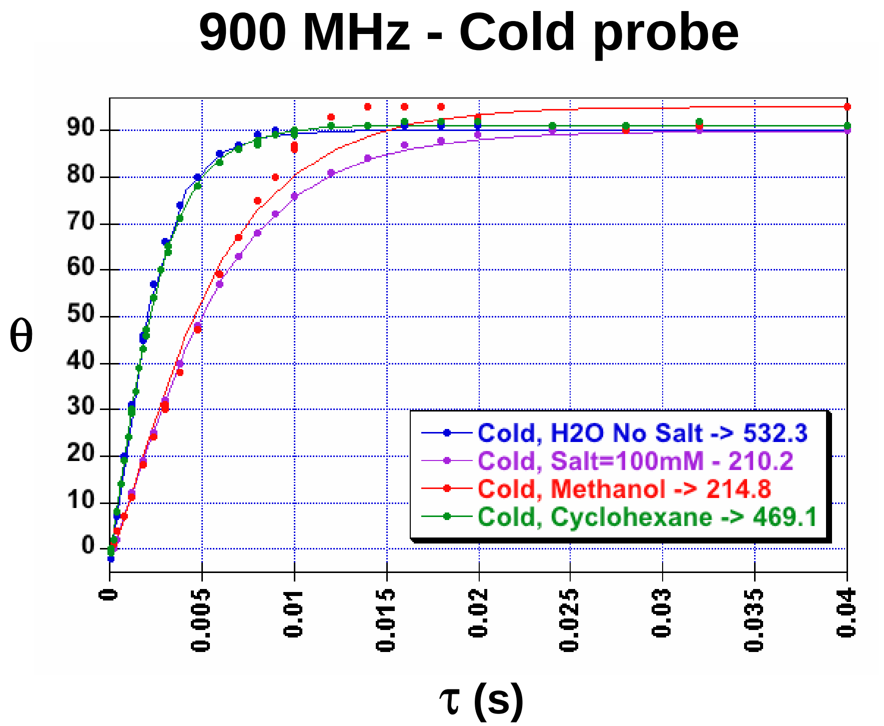
# Direct comparison of radiation damping on cold and RT probes at different magnetic fields for samples with and without salt.


**No Salt**


**Salt = 100mM**

# Influence of solvent polarity as compared to influence of salt


900 MHz - RT probe


900 MHz - Cold probe

# Results of curve fitting for $\Theta(t)$ to $R_{RD}$, $\Theta_0$(nominal 90º) and F(nominal 2)

| $\theta = \theta_{equil} - F \bullet \arctan\{\exp(-\tau \bullet R_{RD})\}$ | | | $R_{RD}$ | $\theta_0$ | F | R |
|---|---|---|---|---|---|---|
| 600MHz | R.T. | No Salt | **97.7** | 83.0 | 1.88 | 0.99969 |
| | | 100mM Salt | **80.4** | 83.3 | 1.87 | 0.99972 |
| | Cold | No Salt | **247.7** | 83.4 | 1.88 | 0.99983 |
| | | 100mM Salt | **144.1** | 85.7 | 1.91 | 0.99984 |
| 800MHz | R.T. | No Salt | **288.8** | 89.1 | 2.00 | 0.99974 |
| | | 100mM Salt | **195** | 89.9 | 2.02 | 0.99984 |
| | Cold | No Salt | **361.8** | 91.5 | 2.03 | 0.99943 |
| | | 100mM Salt | **186.9** | 90.7 | 2.01 | 0.99983 |
| 900MHz | R.T. | No Salt | **281.8** | 89.4 | 2.05 | 0.99992 |
| | | 100mM Salt | **192.8** | 89.5 | 2.04 | 0.99993 |
| | Cold | No Salt | **532.3** | 90.1 | 2.12 | 0.99975 |
| | | 100mM Salt | **210.2** | 89.8 | 2.06 | 0.99984 |

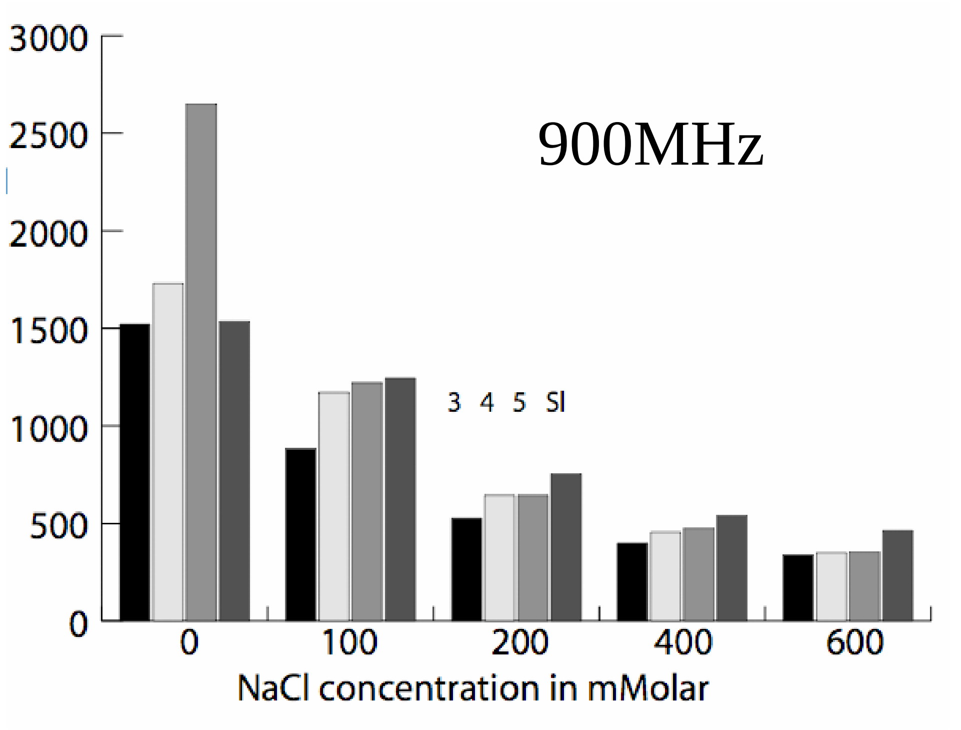
## Sample Volume for the Shigemi tubes

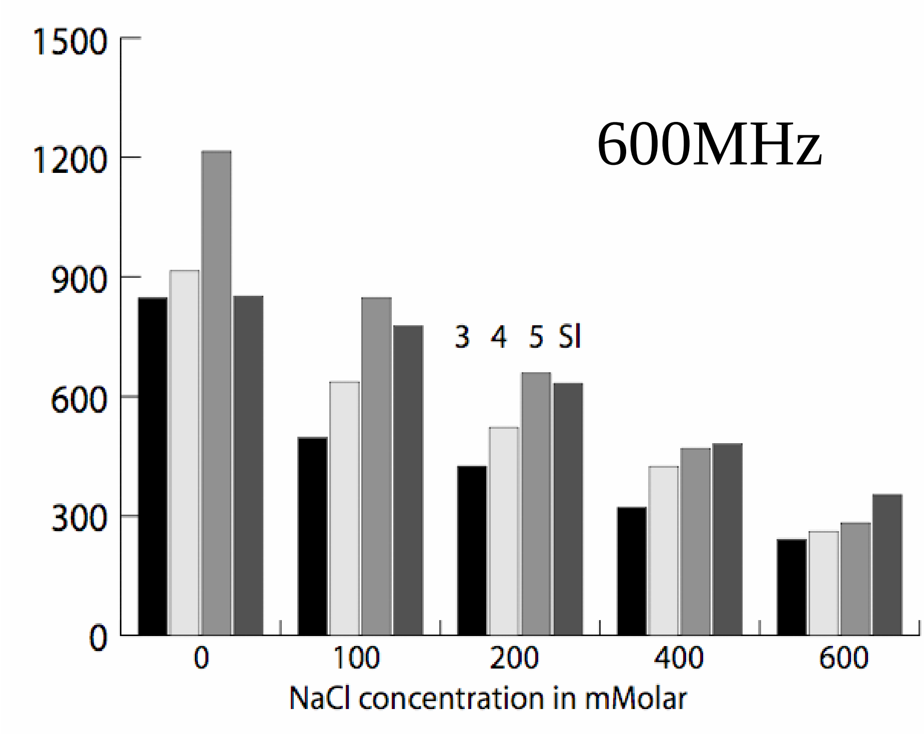
| Sample Height | 3 mm | 4 mm | 5mm | Slotted tube |
|---|---|---|---|---|
| 16 mm | 100 | 164 | 282 | 140 |
| 18 mm | 113 | 184 | 318 | 140 |

## Relative volume for 16 mm high samples

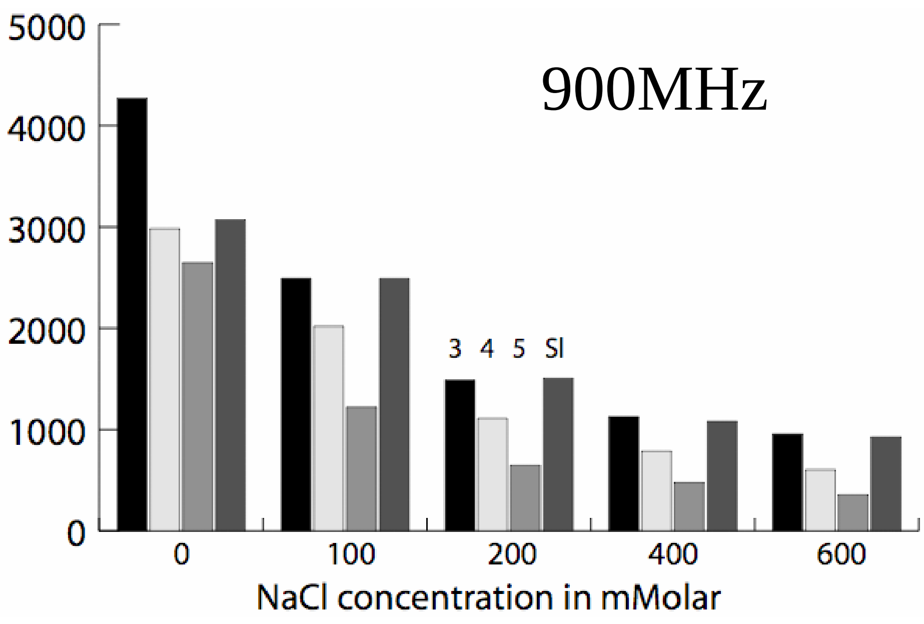
| Tube type | Relative Volume In % |
|---|---|
| 3 mm | 35.4 |
| 4 mm | 58 |
| 5 mm | 100 |
| Slotted | 50 |

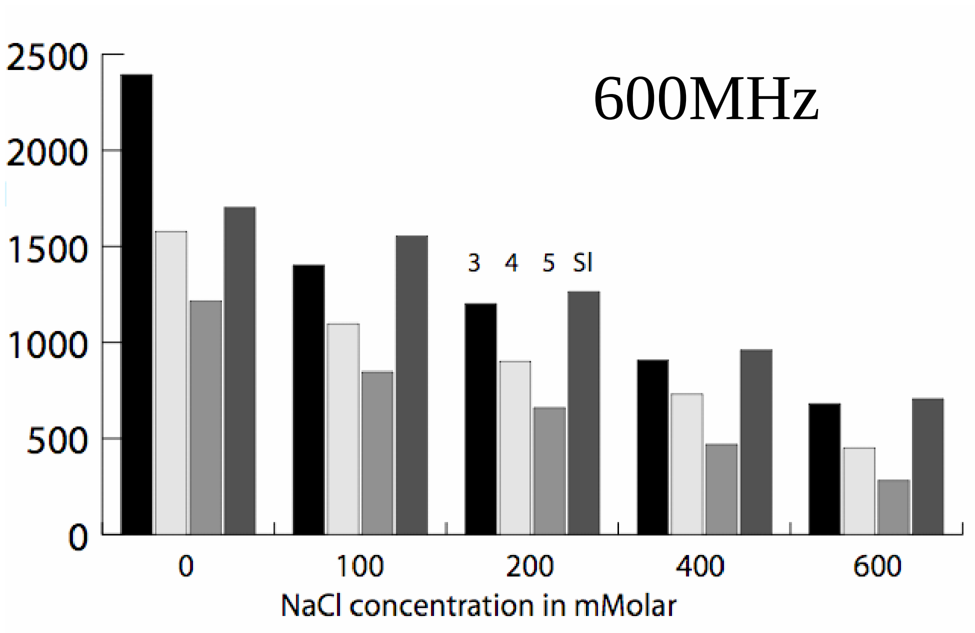
# Signal to Noise of the HOD signal at 900 and 600 MHz for 3,4,5 and Sl tubes



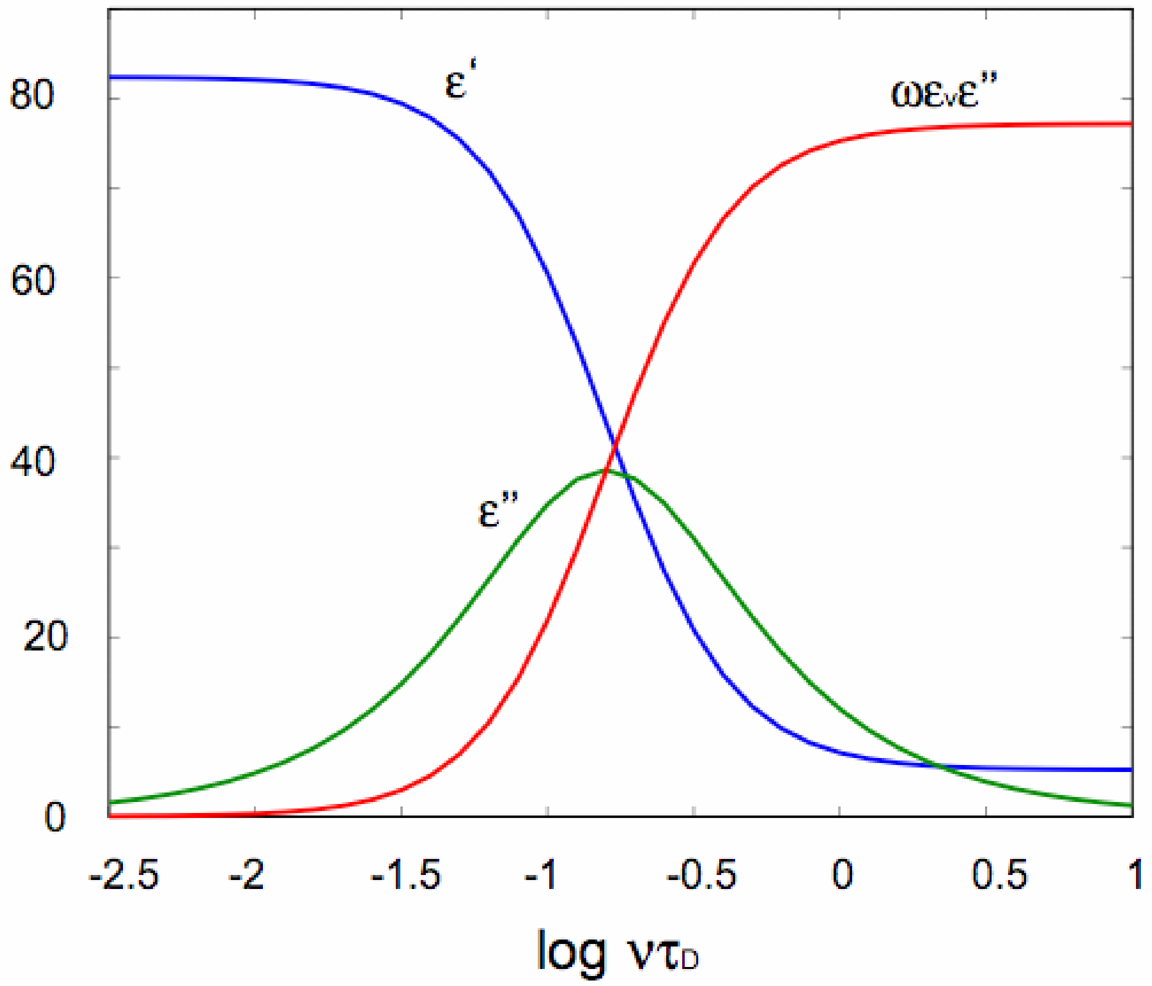


# Signal to Noise per unit concentration of the HOD signal at 900 and 600 MHz for 3,4,5 and Sl tubes





Real and imaginary part of dielectric permittivity of $H_2O$ at 25 ºC as a function of frequency. The conductivity $\omega\varepsilon_v\varepsilon''$ is also shown in dielectric units



The frequency ν is in GHz while the dielectric reorientation time $\tau_D$ is in picoseconds

In order to calculate dielectric losses the imaginary part of the dielectric permittivity must be compared to conductivity as caused by ions in solution (Maxwell):

$$\sigma_{\text{total}}(\omega) = \sigma\,(\text{ion}) + \sigma\,(\varepsilon) = \sigma_i + \omega\varepsilon\,''$$

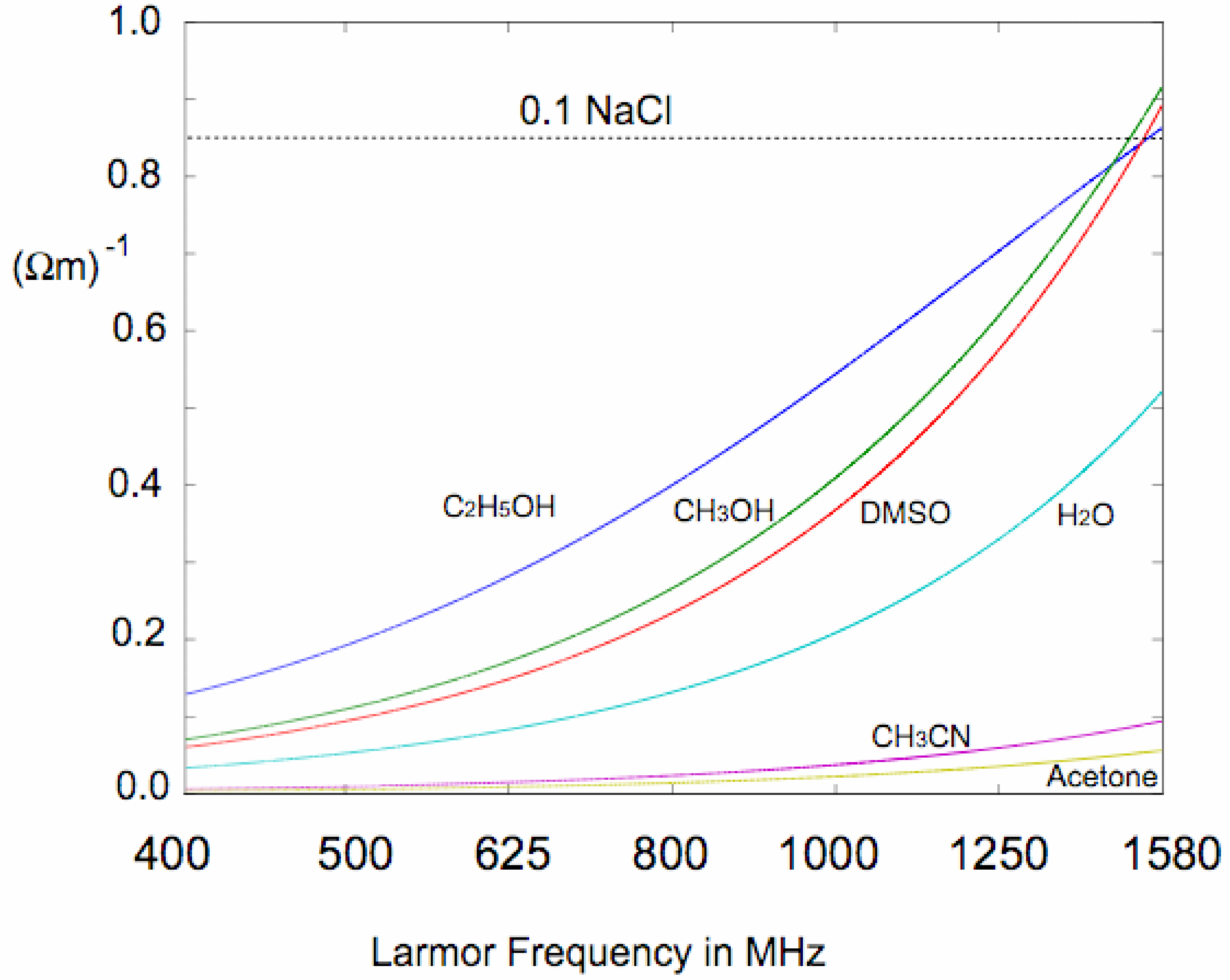
This leads to:

$$\sigma_{\text{total}}(\omega) = \sigma_i + \omega^2\tau\,(\varepsilon_0 - \varepsilon_\infty)/\{1 + (\omega\tau)^2\}$$

As a consequence:

- for $\omega\tau << 1$ , J($\varepsilon$) increases proportional to $\omega^2$
- for aqueous solutions at low temperature the dielectric losses become equivalent to that of 50 mM NaCl at 1000 MHz.
- for DMSO, methanol and ethanol the $\sigma(\varepsilon)$ values are significantly larger than that of $H_2O$ at any temperature.
- for polar liquids and aqueous solutions dielectric losses increase with $\omega^4$

# Dielectric loss at 25 ºC of various NMR solvents vs. .1M acq. NaCl in units of specific conductivity



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# Conclusions

- Avoid high salt conditions and certain solvents if possible
- Use regular wall thickness Shigemi tubes
- If possible concentrate all your material into a 3 mm tube
- Use a slotted Shigemi tube
- Acquire a salt and solvent tolerant probe
- More research needs to be done on the effect of the dielectric permittivity on NMR sensitivity, in particular at the highest frequencies.

# References

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2 J-H Chen, B. Cutting and G. Bodenhausen: *J. Chem. Phys.* **112**, 6511-6514 (2000).

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