INVESTIGATION OF NMR-BASED SURFACE AREA MEASUREMENT AS A QUALITY MONITOR FOR NANOPARTICLE SILICA ABRASIVES

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Good Control of Silica Particle Size and Contamination is Important for CMP

- Big nanoparticles permanently damage transistors during polishing
- Small nanoparticles don’t polish well and are harder to wash off in later stages
- Chemical contamination of slurries may damage transistors (for example, iron)
- Improper shipment and/or storage may alter slurries' properties and be undetected

Xigo Area Quant Has a Number of Benefits as a Quality Control Instrument

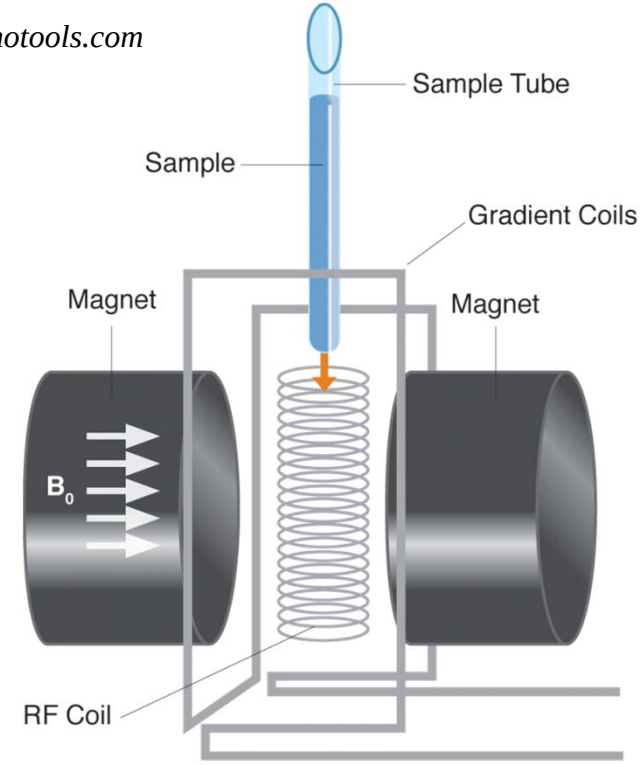
Benefits

- Uses wet samples with 1-60% concentration
- Measures relaxation rate that is directly proportional to surface area
- Able to perform fast (less than 1 min) and continuous measurements

Picture (xigonanotools.com)

NMR Equipment

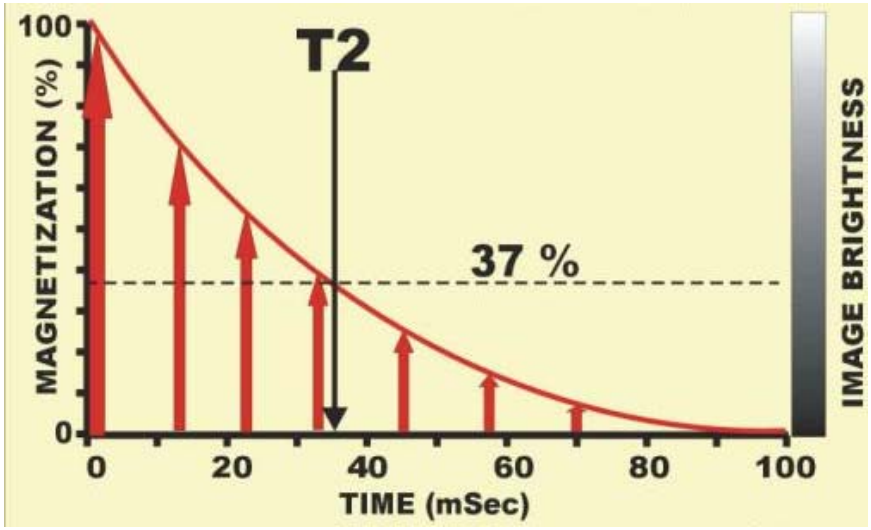
xigonanotools.com



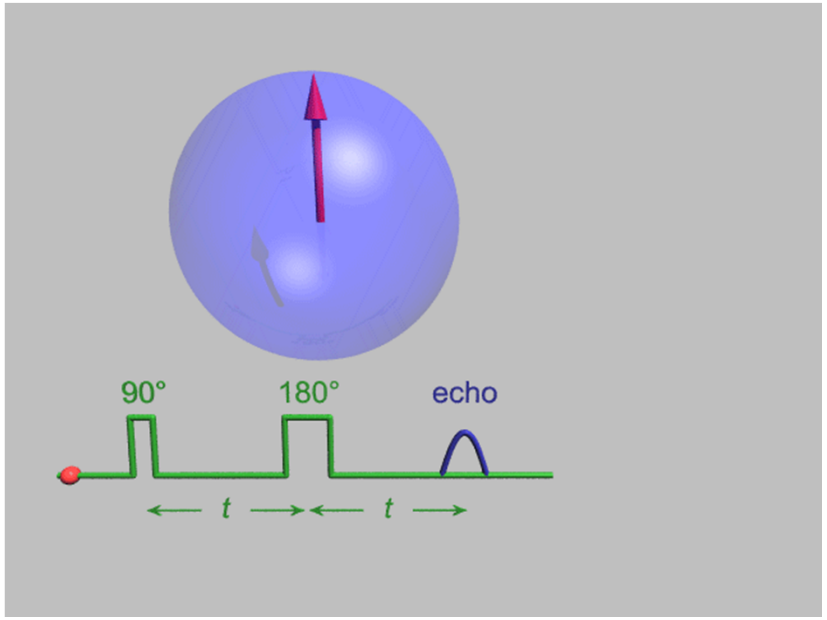
1. Short radio frequency pulse excited the coil at ~14 MHz.
2. Produced magnetic field changes the orientation of protons' spins.
3. As the spins relax and realign with static magnetic field B_0, a decaying voltage is produced in the coil – "free induction decay".

Sample T_2 (transverse) Graph

4. A combination of specific pulse sequences allows to determine sample's T_1 or T_2 relaxation times.



http://www.sprawls.org/mripmt/MRI04/index.html



Wikipedia.org

NMR Relaxation Time of H Near Particle Surface is Very Short

Due to constrained mobility H in water molecules around nanoparticles relax at faster rate compared to H in free water

Data Analysis:

Relaxation rate: $R = 1/T$

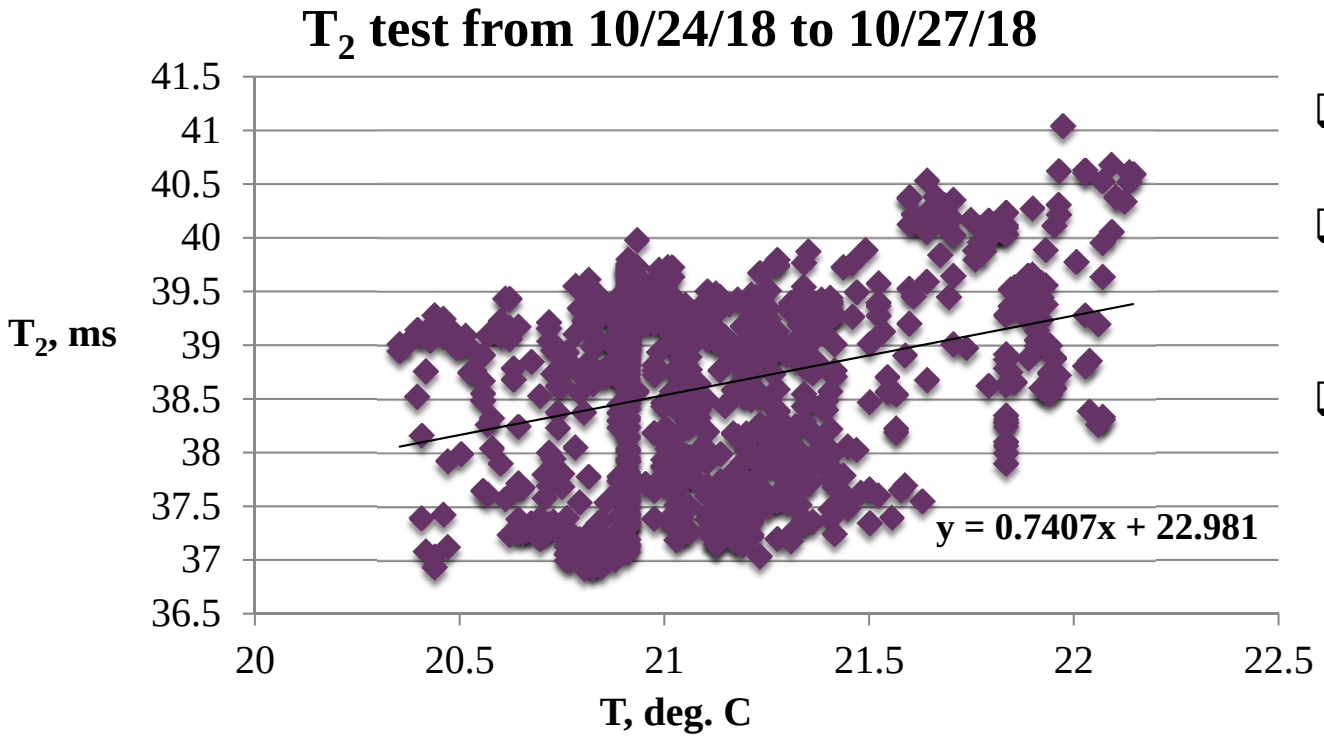
$R_{av} = k_a S \psi_p + R_b$

- R_{av} – average relaxation rate (the reading)
- R_b – bulk relaxation rate
- k_a – specific surface relaxivity
- S – total surface area of particles per unit weight
- ψ_p – volume fraction of particles

Research Questions

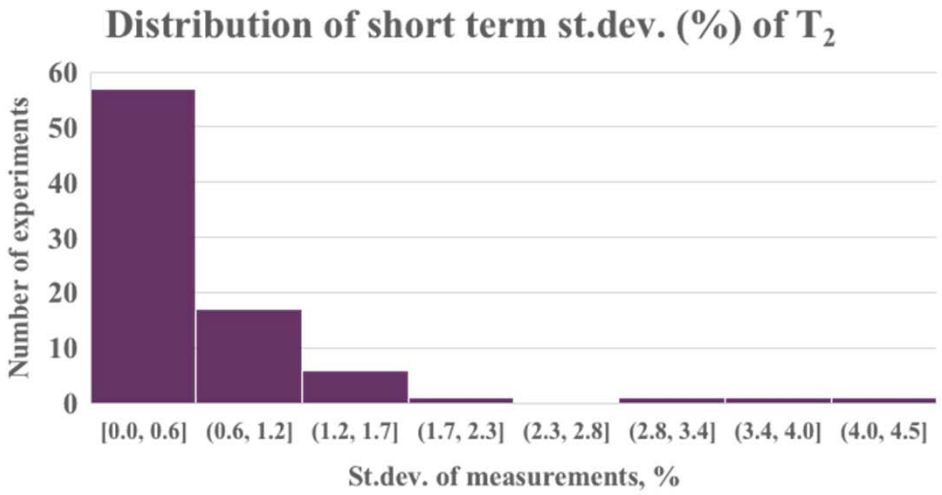
- Does temperature affect the measurements?
- How reliable and stable are the measurements?
- Does the signal depend on the chemistry of the solution? Is k_a affected by background electrolyte concentration?
- What is the lowest Fe detectability limit? Does it depend on the type iron compound and phase?

1. Temperature Dependence of T_2



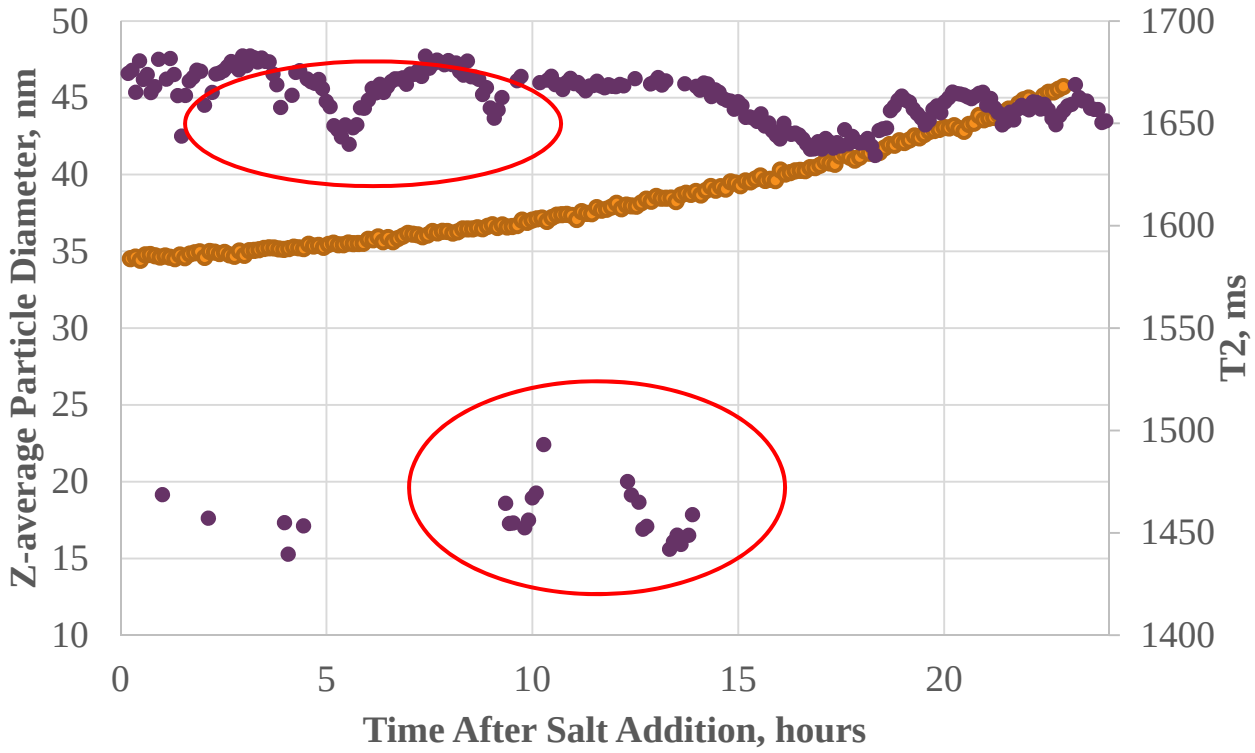
- For every degree C, T_2 changes by 2%
- Temperature controlled cell is needed for better measurements
- Inline metrology may not be feasible if significant temperature swings are present

2. Precision of “Fast” Measurements



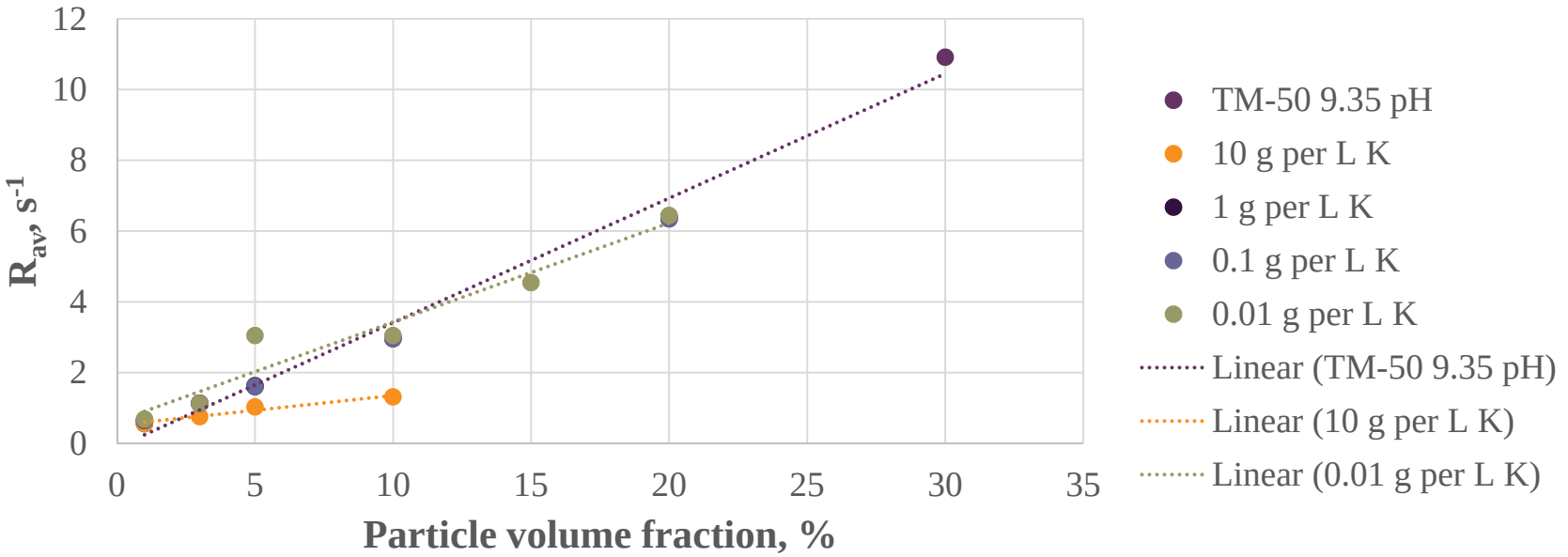
Small deviations in T_2 signal when the measurements are taken within minutes apart

2. Stability of T_2 Measurements Over Time



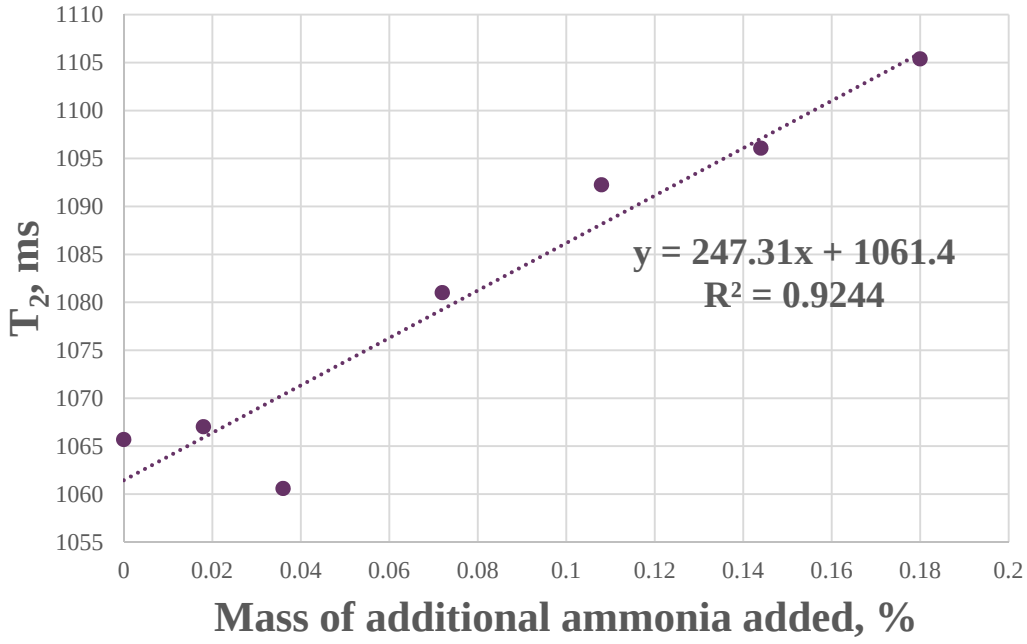
- For slow aggregation induced by low salt, T_2 does not show a systematic change when the size increases by a few nanometers
- Large fluctuations in T_2 signal are seen
- Presence of significant outliers is detected over timescale of several hours

3. Chemistry: effect on k_a



- For TM-50, k_a varied by about 1% as electrolyte (KNO_3) was increased.
- At 10 g per L K^+, gelation occurred, and k_a is not meaningful

3. Chemistry: effect on calculated area

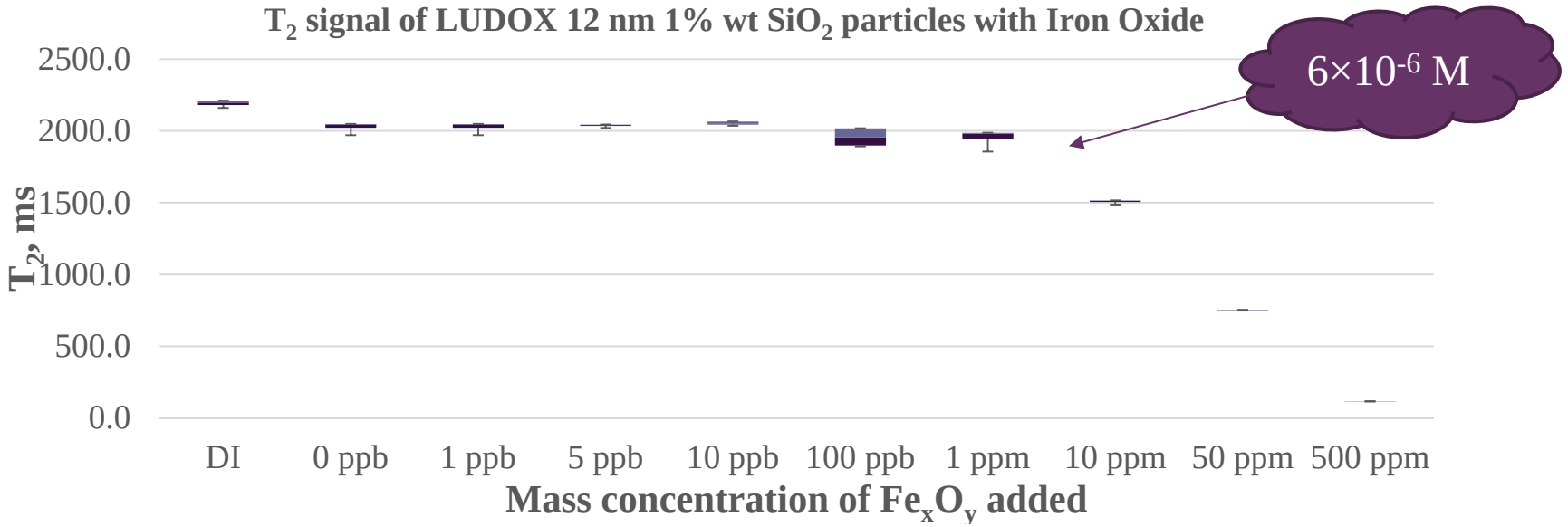


For given nanoparticles for every 0.1 wt% [NH_3/NH_4^+] added

- T_2 goes up by 24 ms
- **Calculated** surface area of the particles appears to be smaller by 1.3 m^2/g

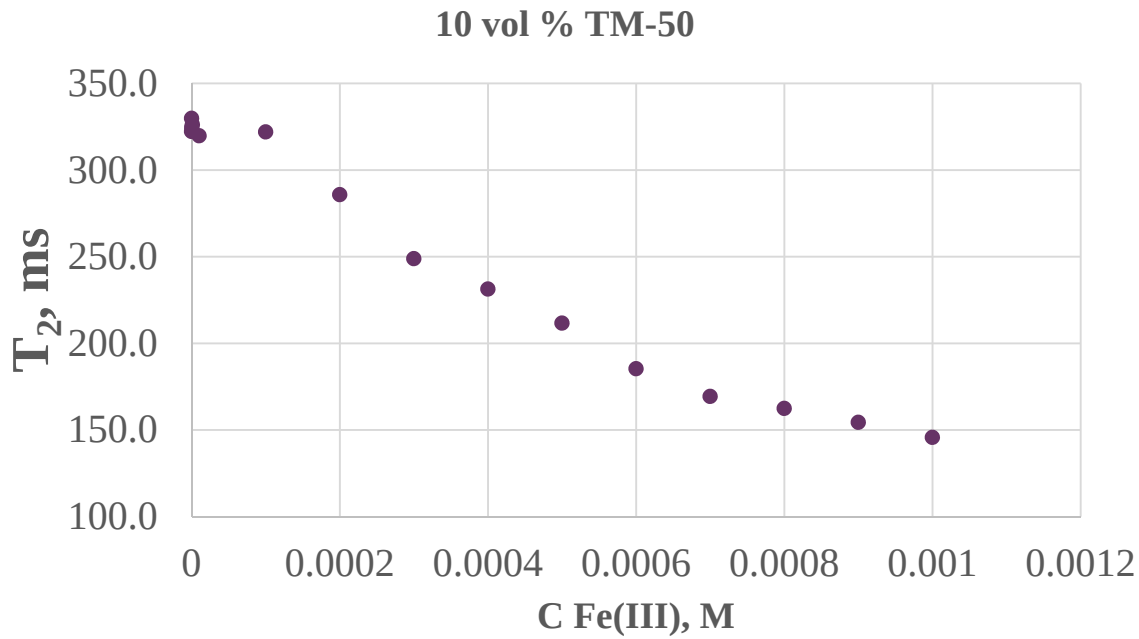
The effect of ammonia on T_2 and indicated surface area may be substantial depending on the specs

4. Detection of Insoluble Iron (Fe_xO_y) at ~10^{-5} M



Insoluble iron oxide can be detected at low concentrations of ~10^{-5} M

4. Detection of Soluble Iron ($FeCl_3$) at ~10^{-4} M



- Soluble iron salts can be detected at low concentrations of ~10^{-4} M
- Detectability limit may depend on silica solids loading

Summary

- Reliable measurements require temperature control
- Effects of chemistry on relaxation rate and indicated surface area can be small but significant depending on product specifications
- NMR equipment is very good at quickly detecting iron contamination at levels of 10-100 ppm
- More investigation is needed of precision and deviations in T_2 signal

Bottom line: the technique is promising but more work is needed to reduce measurement variation

Thank you for your attention!

Questions?