Nuclear Magnetic Resonance (NMR) relaxometry for the determination of ethanol content in alcoholic beverages: a tool for NMR education?

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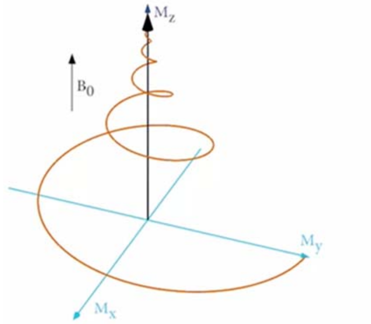
In this work, we propose a funny experiment to illustrate the phenomenon of Nuclear Magnetic Resonance (NMR) relaxation and to introduce two of the most important NMR sequences, namely the Carr-Purcell-Meiboom-Gill (CPMG) and Inversion Recovery (IR) sequences.

1. Nuclear Magnetic Resonance relaxation

- NMR = resonance of nuclear spins when put in a B_0 magnetic field and excited by a suited RF field,
- Relaxation = return to equilibrium of nuclear magnetization after an RF excitation,
- Two kinds of magnetization : longitudinal (along B_0 field) and transverse (in the plane $\perp$ to B_0),
- Major influence of relaxation on the detected NMR signal,
- Must be understood before introducing Magnetic Resonance Imaging (MRI) and NMR spectroscopy,
- Measurement of longitudinal relaxation time (T_1) with the inversion recovery (IR) sequence[1],
- Measurement of transverse relaxation time (T_2) with the Carr-Purcell-Meiboom-Gill (CPMG) sequence[2].

***Figure 1:** Relaxation of nuclear magnetization after a 90° radiofrequency pulse (Wikipedia)*



2. Relaxation in water-ethanol solutions

- T_1 and T_2 of water protons spins decrease in the presence paramagnetic Gd^{3+} ions,
- Relaxation due to dipolar interaction of proton spin with Gd^{3+} spin, inside the hydration sphere of Gd^{3+} + exchange with bulk water protons = inner sphere relaxation mechanism,

⇒ Importance of the accessibility of the hydration sphere for hydrogen protons,

- In water-ethanol Gd^{3+} solutions, only water protons have access to the hydration sphere,

⇒ faster relaxation for "OH protons" of water and "OH proton" of ethanol than for "CH protons" of ethanol => biexponential relaxation.

***Figure 2:** Inner sphere relaxation mechanism*

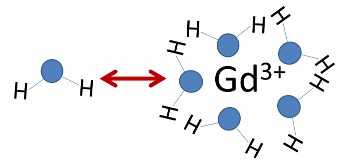
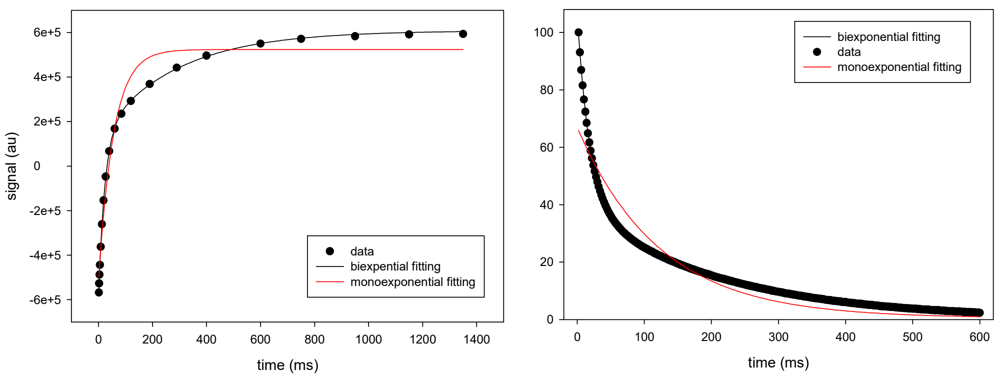
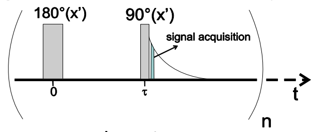


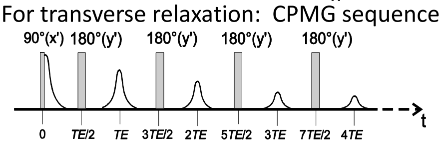
***Figure 3:** Longitudinal and transverse relaxation in water-ethanol Gd^{3+} solution*



- For longitudinal relaxation: IR sequence



- For transverse relaxation: CPMG sequence



- Two fractions of the biexponential fitting = fractions of OH (fast) and CH (slow) protons
- Fitting equation for CPMG experiment:

$$signal = A_1 \exp\left(-t / T_{21}\right) + A_2 \exp\left(-t / T_{22}\right)$$

3. NMR relaxometry to measure ethanol content in alcoholic beverages

Same behavior for alcoholic beverages in which a small amount of Gd^{3+} has been added,

⇒ Biexponential T_1 and T_2 relaxation during the IR and CPMG sequences,

⇒ From the biexponential fractions, one obtains OH and CH fractions,

⇒ The volume fraction of ethanol of the beverage can be estimated.

Test with 9 alcoholic beverages

Comparison with conventional method[3]

✓ Good qualitative agreement

✓ CPMG method faster than IR

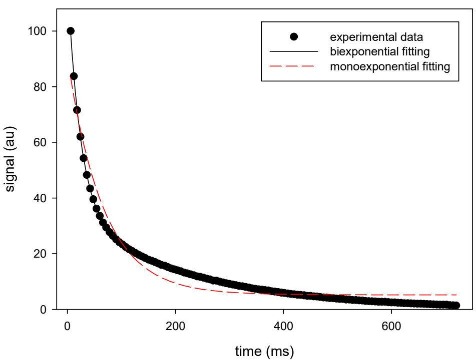


***Figure 4:** Biexponential transverse relaxation of a vodka sample containing a small amount of Gd^{3+}*

4. Conclusions

Simple experiments to illustrate:

- Relaxation,
- IR and CPMG sequences,
- Proton exchange between water and ethanol OH
- Effect of Gd^{3+} on water relaxation

You need:

-vodka, Gd^{3+} and a benchtop relaxometer

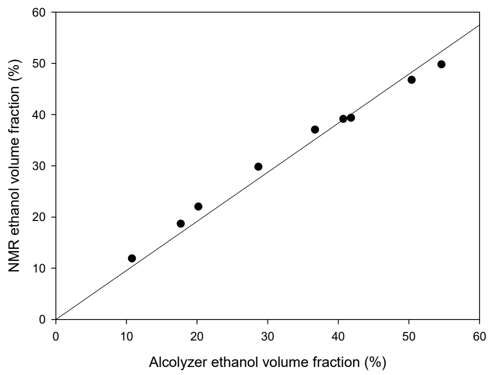


***Figure 5:** Comparison of ethanol content obtained with NMR and measured by the alcolyzer[3]*

References

1. Vold, R. L. et al. Chem. Phys. 1968, 48 (8), 3831–3832.
2. Meiboom, S. et al. Rev. Sci. Instrum. 1958, 29 (8), 688–691.
3. Method 9.2.6 of the European Brewery Convention