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.

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.

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.

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

Test with 9 alcoholic beverages
Comparison with conventional method 3
- Good qualitative agreement
- CPMG method faster than IR

References
3. Method 9.2.6 of the European Brewery Convention

Introduction of Experimental Data

- Figure 1: Relaxation of nuclear magnetization after a 90° radiofrequency pulse (Wikipedia)
- Figure 2: Inner sphere relaxation mechanism
- Figure 3: Longitudinal and transverse relaxation in water-ethanol Gd$^{3+}$ solution
- Figure 4: Biexponential transverse relaxation of a vodka sample containing a small amount of Gd$^{3+}$
- Figure 5: Comparison of ethanol content obtained with NMR and measured by the alcolyzer 4.

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

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

Figure 5: Comparison of ethanol content obtained with NMR and measured by the alcolyzer 4.