

Nuclear Magnetic Resonance: Determination of T1 and T2 values for Oil, Methanol, and Water

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Abstract

Nuclear magnetic resonance (NMR) is a phenomenon that results from the interactions of nuclei with magnetic fields. The nuclei of atoms in compounds behave uniquely in response to extrinsic magnetic fields and intrinsic magnetic fields in their surrounding chemical environment. In this lab, the behavior of ^1H atoms of oil, methanol, and water, in response to magnetic fields, were quantitatively measured and qualitatively observed. T1 and T2 for oil, methanol, and water, were experimentally determined by applying radio frequency pulses to a sample in the presence of a constant external magnetic field with a TeachSpin PS1-A (a pulsed NMR spectrometer) and measuring the response of the magnetization. Additionally, the magnetic field gradient of the inhomogeneous magnetic field and the diffusion coefficient of ethanol were determined.

Theory

^1H atoms contain a nucleus which is solely composed of a single proton which characterizes it as paramagnetic (odd number of protons). Paramagnetic nuclei are essential for NMR since paramagnetic substances are susceptible to magnetization. The atom consists of an angular momentum, J , and a magnetic moment, μ , which are related through the following equation

$$\mu = \gamma J = \gamma \hbar l \quad (1)$$

where γ is the gyromagnetic ratio ($\gamma_{\text{proton}} = 4.2596 \times 10^3 \text{ s}^{-1} \text{ Gauss}^{-1}$). Magnetic nuclei act like a small spinning bar magnet due to its spin, l , which produces the magnetic moment of the atom. For the proton, the value of the spin is $1/2$. Without an applied magnetic field, the magnetic moments are randomly oriented in space. However, when an external magnetic field is applied, the magnetic moments will align parallel or anti-parallel to the field (figure 1).

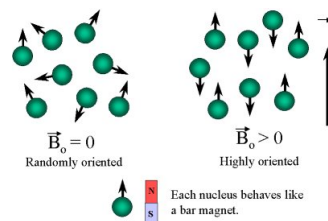


Figure 1. Magnetic moment of nuclei in the absence (left) and presence (right) of a magnetic field B_0

In the presence of an external magnetic field (B_0), the magnetic moments have an associated magnetic energy U .

$$U = -\boldsymbol{\mu} \cdot \mathbf{B}_0 \quad (2)$$

In our experiment, the external magnetic field is aligned along the z-axis so

$$U = -\mu_z B_0 = -\gamma \hbar l_z B_0 \quad (3)$$

For the proton, the allowed values of l_z are $m_l = \pm \frac{1}{2}$ which correspond to the two possible spin-states. If the magnetic moment aligns parallel to the magnetic field, the spin state of the proton will be $m_l = 1/2$ and a magnetic moment antiparallel to the magnetic field will have a spin state of $m_l = -1/2$ as shown in Figure 2.

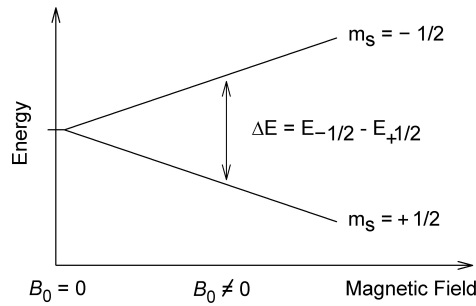


Figure 2. Energy separation of magnetic moments in the presence of a magnetic field

The transition energy between the two spin states is

$$\Delta E = U_{-\frac{1}{2}} - U_{\frac{1}{2}} = \gamma \hbar B_0 \quad (4)$$

which is proportional to the applied magnetic field. In the presence of a magnetic field, the magnetic moment precesses about the applied field as shown in Figure 3.

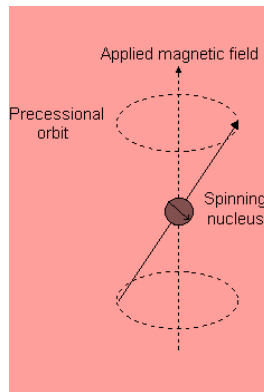


Figure 3. Precession of a magnetic moment about the applied magnetic field B_0

The energy separation between the two states can be expressed in terms of the angular frequency

$$\Delta E = \gamma \hbar B_0 = \hbar \omega_0 \quad (5)$$

The proton's magnetic moment precesses about the magnetic field at the angular frequency ($\omega_0 = \gamma B_0$) which is also known as the Larmor frequency, due to a torque exerted on the magnetic moment by the field

$$\tau = \mu \times B \quad (6)$$

There are a certain number of spins per unit volume in the first spin state (N_1) and a certain number of spins in the second spin state (N_2). If there is an unequal amount of the two possible spin states ($N_1 \neq N_2$), a magnetization will be established in the z-direction. Based on the alignment of the nuclei, there will be a resulting net sum magnetization along the z-axis which is modeled after the equation

$$M_z = (N_1 - N_2)\mu_z \quad (7)$$

By summing the vector components of the magnetic moments, the magnetization in the x-y plane cancels out to zero due to a phase relationship between the spins. After being exposed to a magnetic field, the magnetization along the z-axis will reach a thermal equilibrium magnetization value of

$$M_0 = N\mu \tanh \frac{\mu B}{k_B T} \quad (8)$$

where T is the temperature and k_B is the Boltzmann constant. At thermal equilibrium, there are more protons in the lower energy spin state than the higher energy spin state. In order to reach the thermal equilibrium magnetization, the magnetization will increase in the z-direction parallel to the magnetic field at a rate of

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1} \quad (9)$$

During the recovery of the magnetization, energy flows from the excited proton to the lattice in order to return to the lower energy spin state and reestablish thermal equilibrium. The proton in the excited spin state is surrounded by other protons with a magnetic moment at different distances. In order for a transfer of energy to occur between two spins states, there needs to be a lattice field of a nucleus at a specific distance away in a lower energy state that can interact with the nuclei in a higher energy state. The spin-lattice relaxation time, T_1 , is the decay constant associated with the recovery of the z-component of magnetization back to thermal equilibrium. If the initial condition for the magnetization at $t=0$ is $M_z = -M_0$, then the behavior of the recovery of the magnetization to thermal equilibrium can be modeled by

$$M_z(t) = M_0(1 - 2e^{-\frac{t}{T_1}}) \quad (10)$$

For varying samples such as oil, methanol, and water, they will each have a characteristic T_1 value which produces a unique rate at which the magnetization approaches thermal equilibrium.

In the case of having a transverse (x-y plane) magnetization, the magnetization decays exponentially at the rate

$$\frac{dM_{x,y}}{dt} = -\frac{M_{x,y}}{T_2} \quad (11)$$

A magnetization in the transverse plane will exponentially decay over time due to the decoherence of spins due to spin-spin interactions. Each of the individual spins produces a localized magnetic field which creates a distribution of local fields. The random fluctuations of magnetic field strengths experienced by each individual spin may cause the spin to experience a stronger or weaker magnetic field than the applied magnetic field of B_0 . If the localized magnetic field increases the strength of the magnetic field experienced by a spin, the spin will precess faster than the Larmor frequency and vice versa. Therefore, there is a distribution of precessional frequencies which causes the spins to become out of phase with one another. If the initial magnetization at time $t=0$ is $M_{x,y}=M_0$, the exponential decay of the magnetization can be modeled by

$$M_{x,y}(t) = M_0 e^{-t/T_2} \quad (12)$$

The spin-spin relaxation time, T_2 , is the decay constant associated with exponential decay of the transverse component of the magnetization. Also, $t=2\tau$ where τ is the delay time.

The behavior of the transverse magnetization does not always follow this exponential decay model. For example in the case of water and ethanol due to self-diffusion, the behavior of the magnetization is modeled after the equation

$$M_{x,y}(t) = M_0 e^{\left[-\frac{t}{T_2} - \frac{\gamma^2 G^2 D t^3}{12 n^2} \right]} \quad (13)$$

as shown in Carr and Purcell. The decay of the transverse magnetization at time t is dependent on the magnetic field gradient ($G = \frac{\partial B}{\partial z}$), the diffusion coefficient (D) of the compound, the number of 180° pulses applied, and the decay constant T_2 .

Materials and Methods

In this experiment, we utilized a TeachSpin PS1-A pulse NMR spectrometer which consists of: 1) a magnet with a magnetic field strength of ~ 3640 Gauss, 2) a pulse programmer that creates the pulse stream that gates the synthesized oscillator into radio frequency (RF) pulse bursts, 3) coils that accept the RF pulse bursts and produce a 12 Gauss rotating magnetic field at the sample, 4) a pickup/receiver coil in the transverse plane which detects the precessing nuclear magnetization, 5) an RF amplitude detector produces a signal on the oscilloscope and allows us to read the free induction decay signal and the spin echo signals, 6) a mixer which multiplies the precessional signal from the sample's magnetization and the master oscillator to determine the proper frequency of the oscillator (zero-beat output signal of mixer on oscilloscope). A diagram of the experimental set up of the TeachSpin PS1-A is shown in figure 4.

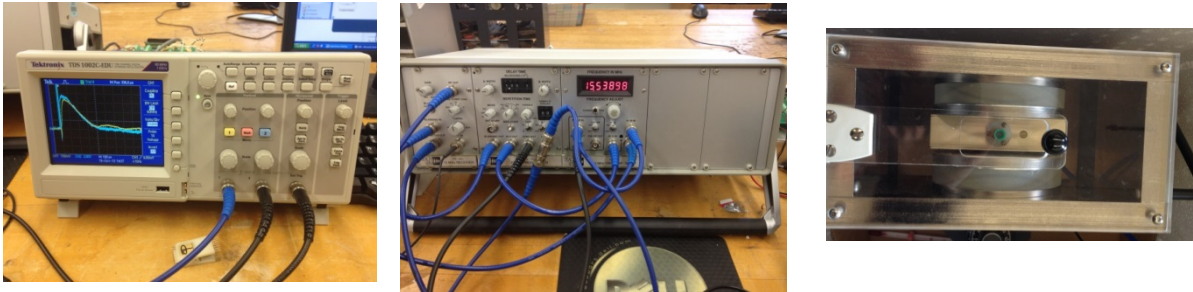
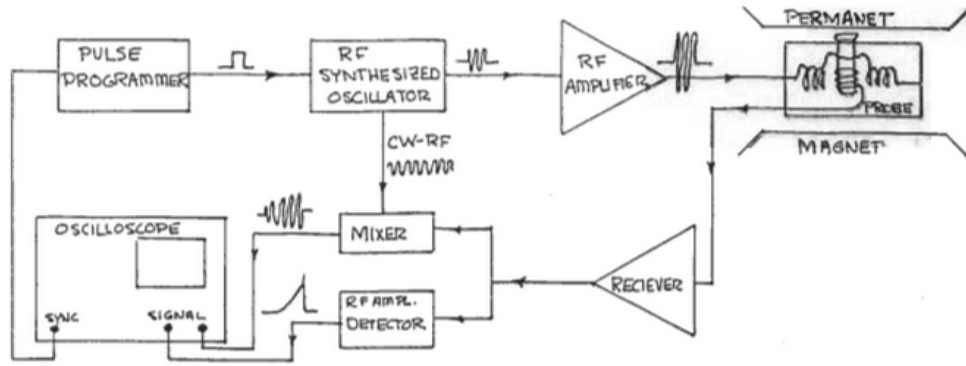


Figure 4. Components of the experimental set up

We are able to control the width of the RF pulse bursts by adjusting the A-width and B-width, the time between pulses by adjusting the delay time, the time between a set of pulses with the repetition time, the number of B pulses, the frequency of the RF pulse, and several other controls which are shown in the TeachSpin Instrument manual.

Set Resonant Frequency

In our experiment, radio frequency current bursts produce a 12 Gauss rotating magnetic field at the sample. The magnetic field experienced by the sample is

$$B(t) = B_1 \cos \omega t \hat{i} + B_1 \sin \omega t \hat{j} + B_0 \hat{k} \quad (14)$$

To simplify the analysis of magnetization, we switch into the rotating frame of reference, which rotates at the angular frequency of our RF pulse. By rotating at the same frequency of the RF pulse, the B_1 magnetic field will appear to be stationary in the new rotating frame. The new effective magnetic field in the rotating frame of reference is

$$B_{eff}^* = B_1 \hat{i}^* + (B_0 - \frac{\omega}{\gamma}) \hat{k}^* \quad (15)$$

In this frame of reference, we want the magnetization to appear stationary in the absence of our applied B_1 magnetic field. In order for the magnetization to be stationary, the torque must be zero

$$\tau = \frac{dM}{dt} = \gamma M \times B = 0 \quad (16)$$

In order for the torque to be zero, the value for B must be zero. By applying an RF pulse at the Larmor frequency of ω_0 , the magnetic field in the \hat{k}^* direction cancels out to zero (since $B_0 = \omega_0 \gamma$) and results in a $B_{eff}^* = B_1 \hat{i}$. Therefore when an RF pulse of the same frequency as the precessional frequency is applied, the magnetization will rotate in the plane perpendicular to the applied B_1 field in the rotating frame due to a torque

$$\frac{dM}{dt} = \gamma M \times B_{eff}^* \quad (17)$$

as shown in Figure 5.

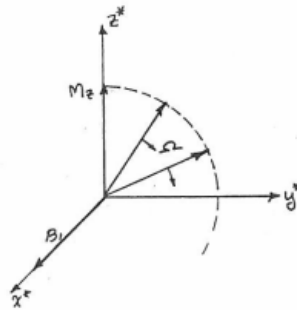


Figure 5. rotation of the magnetization due to a RF pulse

At resonance, the oscilloscope will produce a free induction decay signal that has a zero beat with the signal produced by the master oscillator as shown in Figure 6.

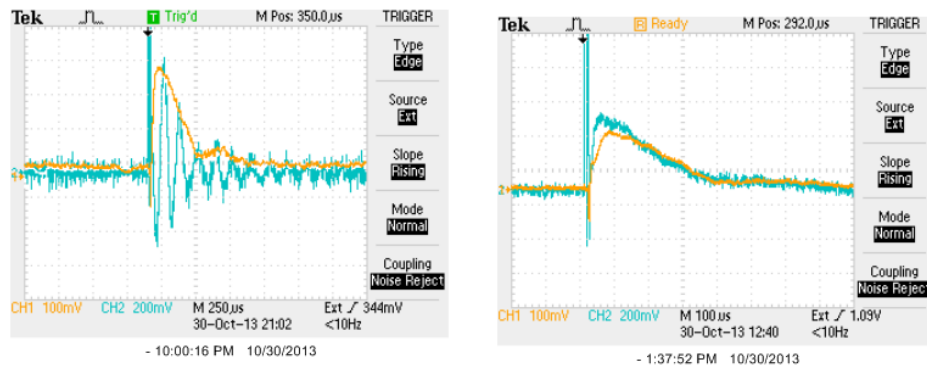


Figure 6. Beats are produced when the frequency of the RF pulse is not equal to the magnetization precessional frequency (left). Zero beat signal produced at resonant frequency (right).

T₁ Measurement: inversion recovery

The value of T₁ is experimentally determined by utilizing a two pulse sequence: 180° pulse followed by a 90° pulse after a delay time τ as shown in figure 7.

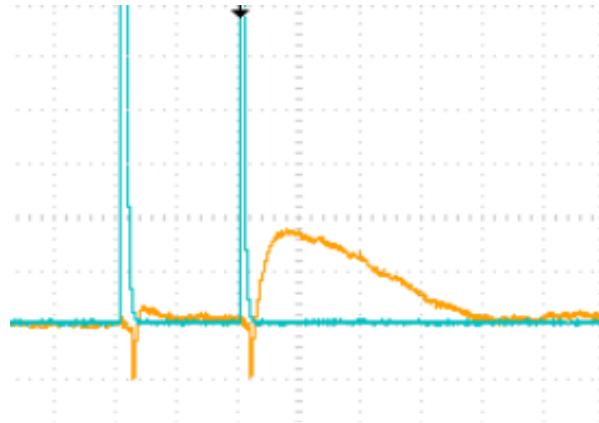


Figure 7. FID signal response on the oscilloscope resulting from a 180° pulse followed by a 90° pulse

On the pulse programmer, the A-width and B-width knobs were adjusted to create a 180° pulse and then a 90° pulse. By applying an 180° pulse, the magnetization is rotated and aligned in the $-z^*$ direction so that the FID signal produced is approximately zero. After the 180° pulse is applied, the magnetization grows exponentially towards its thermal equilibrium value. The spectrometer can't detect magnetization along the z-axis since it only measures the net magnetization in the x-y plane. In order to measure the magnetization in the z-axis, a 90° degree pulse was applied to rotate any net magnetization in the $-z$ direction into the x-y plane to produce a maximum FID signal. The amplitude of the FID signal following the 90° pulse is proportional to the net magnetization along the z-axis just before the 90° pulse. By varying the delay time and measuring the peak of the FID signal response, the plot of FID signal vs. delay time can be made which is modeled after equation 10. The plot was fitted with Mathematica to determine the value of T_1 .

T_2 Measurement: method A

The value of T_2 is experimentally determined by utilizing a two pulse sequence: a 90° pulse followed by a 180° pulse which corresponds to a maximum spin-echo signal as shown in figure 8.

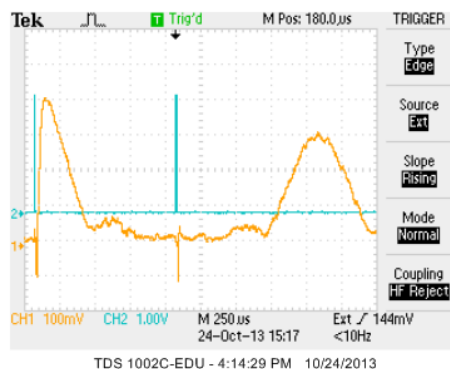


Figure 8. Spin-echo signal produced on the oscilloscope by a 90° pulse followed by a 180° pulse

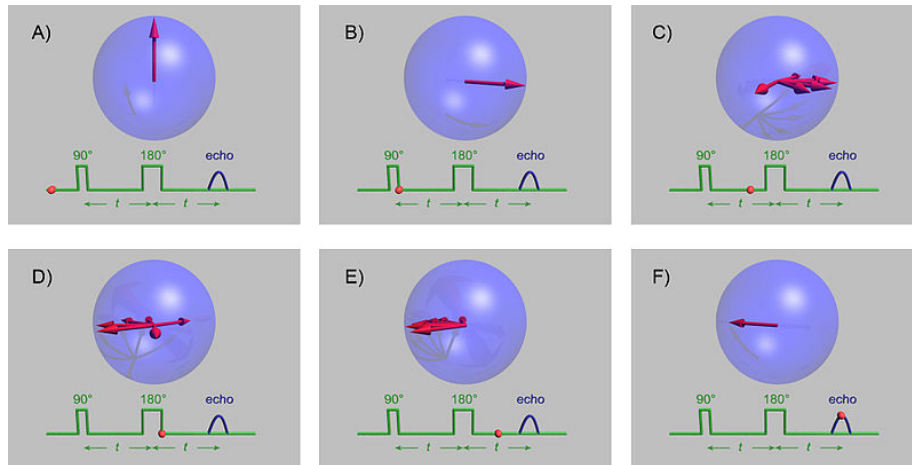


Figure 9. Various stages of the T_2 measurement for method A

After a 90° pulse is applied, the magnetization is picked up by detector coil in the transverse plane and a maximum FID signal is produced on the oscilloscope (figure 8 and 9A). Some delay time, τ , is allowed to go by and the spins become out of phase due to magnetic field inhomogeneities from the magnet as well as spin-spin interactions (figure 9C). A 180° pulse is then applied which allows the x-y magnetization to rephase and refocus the diffused spins to generate the spin-echo signal (figure 8 and 9D-F). The spins that are able to become in phase again are the spins that were dephased solely due to the inhomogeneous magnetic field. Therefore, despite the 180° pulse, there is a loss of magnetization in the transverse plane which is the decay directly caused by spin-spin interactions (figure 8). The amplitude of the spin-echo signal was measured for varying delay times. A plot of spin-echo signal vs. t was made and modeled after equation 12. The plot was fitted with Mathematica to determine the value of T_2 .

T_2 Measurement: method B

In the cases of methanol and water, method A does not result in an exponential decay that can be modeled after equation 12. Instead, the relationship can be modeled after equation 13 due to significant diffusion effects in methanol and water. However if the T_2 value is desired, method B can be implemented to acquire an exponential decay of the magnetization. By increasing the number of 180° pulses, n , the diffusion effects in methanol and water are minimized so the transverse magnetization can be modeled after equation 12. The pulse sequence will be $90^\circ \rightarrow \tau/2 \rightarrow 180^\circ \rightarrow \tau \rightarrow 180^\circ \rightarrow \tau \rightarrow 180^\circ \rightarrow \tau \rightarrow 180^\circ$, etc. which is displayed in figure 10.

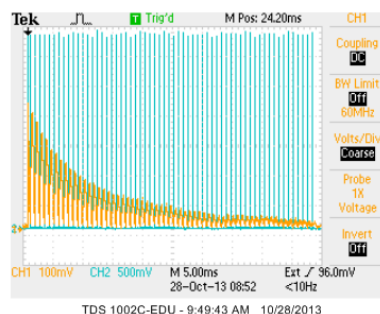


Figure 10. Method B pulse sequence to determine T_2

The FID signal was plotted against time and the data was modeled after equation 12 and fitted with Mathematica to determine T_2 .

T_2 Measurement: method B with Meiboom-Gill pulse

The application of successive 180° pulses when utilizing method B results in an accumulation of error over time since it is extremely hard to implement a pulse that rotates the magnetization exactly 180° with the provided instrumentation. If the applied pulse is less than 180° or more than 180° , a weaker signal will be produced since the magnetization will not be perfectly rotated to the x-y plane. The effect of this constant error is a magnetization that decays faster than expected. The Meiboom-Gill pulse fixes this issue by providing an additional 90° phase shift to the initial 90° pulse with respect to the 180° degree pulse as shown in figure 11.

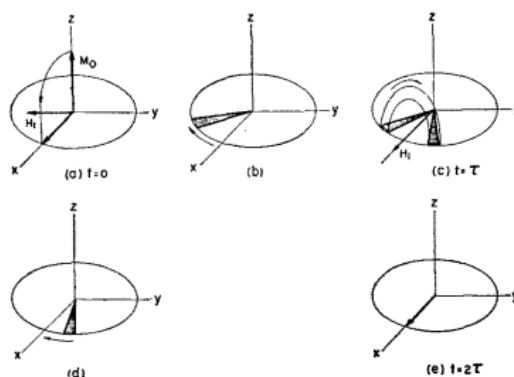


Figure 11. Meiboom-Gill pulse allows the spins to rephase along the x axis each time an 180° pulse is applied

Time Delay between Pulses for Water and Methanol

In the lab manual, it is recommended that the time between the applied RF pulses for compounds is approximately $6-10 T_1$ values. Therefore, for water and methanol the time between pulses would be approximately 30 seconds. However, for the measurements of water and methanol, the automatic RF pulse was utilized with a repetition time of 10 seconds. The 10 second repetition time was justified because the T_1 determination for both compounds indicates that the time it takes for the magnetization to approach the thermal equilibrium is approximately 10 seconds or less.

Magnetic Field Gradient Determination

In the case water, the plot of the spin-echo signal vs. t produces a data set that can be modeled after equation 13 due to the diffusion effects. Rearranging equation 13 to

$$\ln\left(\frac{M_{x,y}(t)}{M_0}\right) + \frac{t}{T_2} = -\frac{\gamma^2 G^2 D t^3}{12 n^2} \quad (18)$$

produces a linear equation where the slope is equal to $-\frac{\gamma^2 G^2 D}{12n^2}$ for the plot of $\ln\left(\frac{M_{x,y}(t)}{M_0}\right) + \frac{t}{T_2}$ vs t^3 .

Using method A for the T_2 determination for water, the values of $M_{x,y}(t)$ were acquired for various times and the linear relationship between $\ln\left(\frac{M_{x,y}(t)}{M_0}\right) + \frac{t}{T_2}$ and t^3 was plotted. A linear fit was applied with Excel and the slope was determined. With the known diffusion coefficient for water, $D_{\text{water}}=2 \times 10^{-5}$ cm^2/sec , the magnetic field gradient (G) was calculated.

Diffusion Coefficient of Methanol

Similarly for methanol, the plot of the spin-echo signal vs. t produced a data set that can be modeled after equation 13 due to the diffusion effects. The same analysis as the magnetic field gradient determination is performed. Using method A for the T_2 determination for methanol, the values of $M_{x,y}(t)$ were acquired for various times and the linear relationship between $\ln\left(\frac{M_{x,y}(t)}{M_0}\right) + \frac{t}{T_2}$ and t^3 was plotted. A linear fit was applied to the data plot and the slope was determined. Setting the slope equal to $-\frac{\gamma^2 G^2 D}{12n^2}$, the diffusion coefficient (D) for methanol was calculated.

Results and Conclusion

T_1 values

Utilizing the inversion recovery method, the T_1 values for oil, methanol, and water were 27.51 ms, 2.51 seconds, and 2.33 seconds respectively. The plots acquired for each of the compounds are shown below in figure 12.

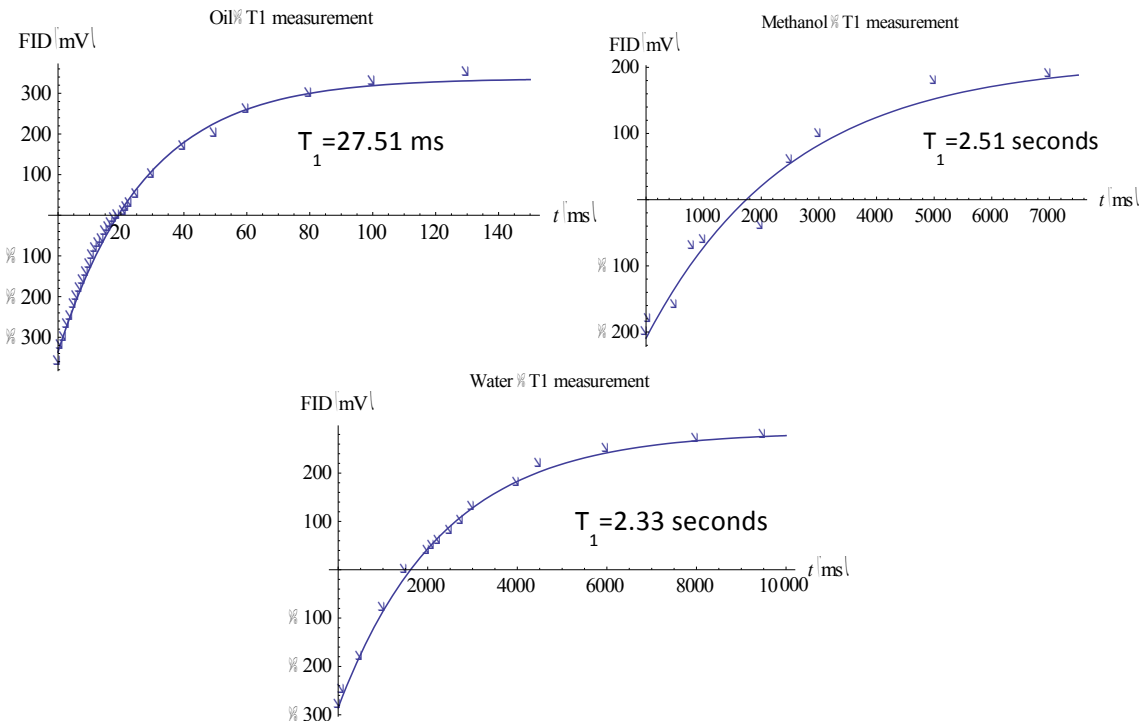


Figure 12. Recovery of longitudinal magnetization for oil, methanol, and water. The plots were fitted with Mathematica, modeled after equation 10

T₂ values: Method A

The first method for the determination of T₂ values for oil, methanol, and water produced the graphs depicted in figure 13.

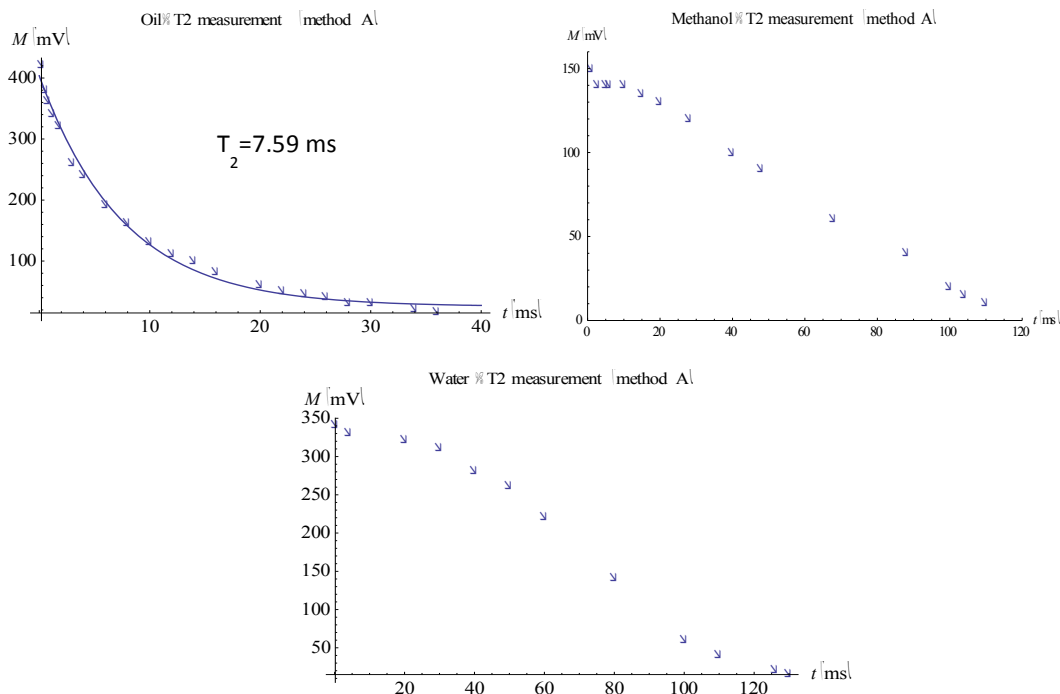


Figure 13. Exponential decay of the transverse magnetization of oil, methanol, and water acquired through method A

Oil was the only compound that had a transverse magnetization which exponentially decayed based on the model of equation 12. The data was fitted with Mathematica and oil was experimentally determined to have a T₂ value of 7.59 ms. Methanol and water, on the other hand, exhibited an exponential decay behavior that was dominated by the diffusion term and modeled after equation 13.

T₂ values: Method B with Meigill-Boom pulse

Using method B with a Meigill-Boom pulse, the T₂ values for oil, methanol, and water were 8.39 ms, 5.58 seconds, and 6.26 seconds respectively. The plots of the exponential decay for the transverse magnetization can be seen in figure 14.

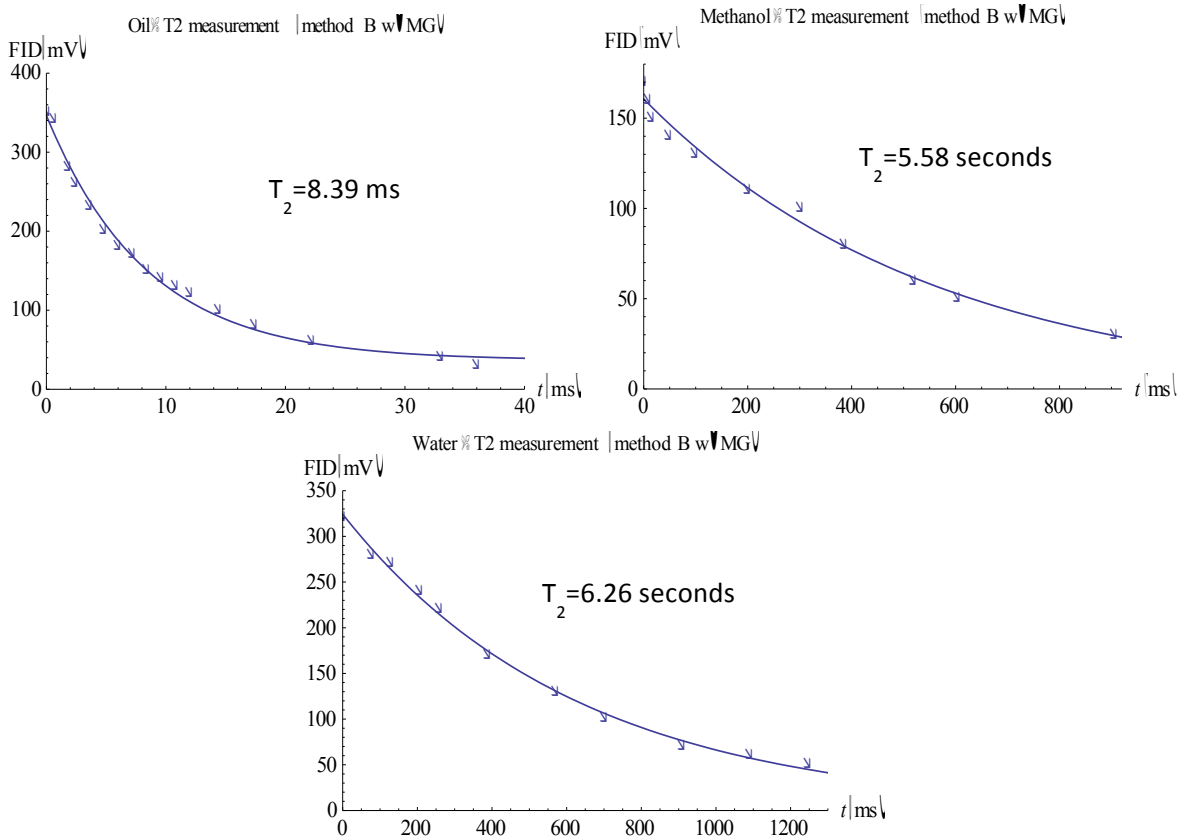


Figure 14. Exponential decay of the transverse magnetization for oil, methanol, and water obtained through method B

Without the Meigill-Boom pulse, the transverse magnetization decayed at a faster rate which resulted in shorter T_2 times. For oil, the T_2 time was 7.80 ms and for water, the T_2 time was 3.21 seconds.

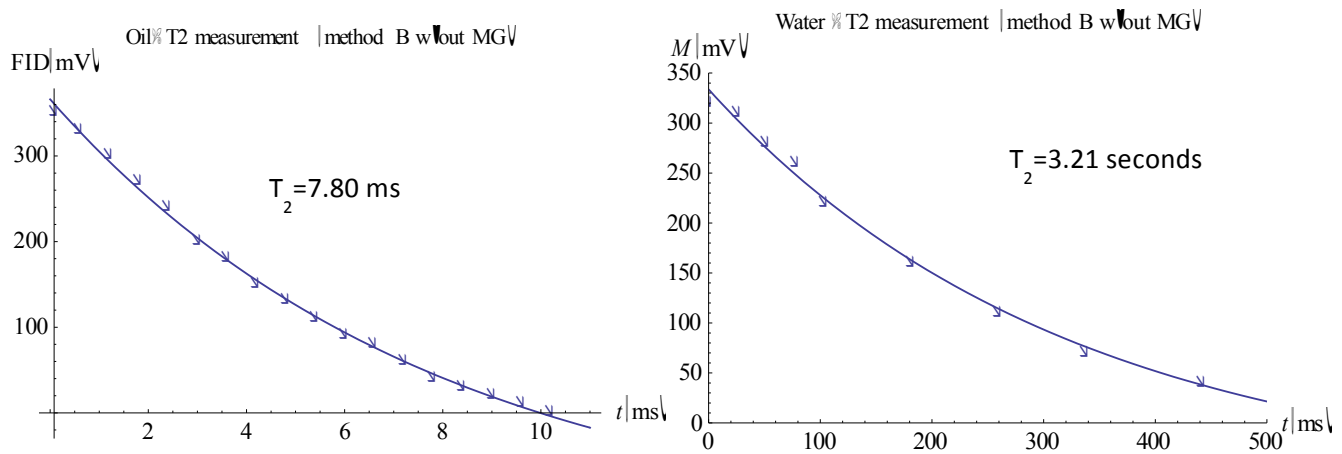


Figure 15. Exponential decay of the transverse magnetization produced with method B without the Meigill-Boom pulse

Magnetic Field Gradient and Diffusion Coefficient for Methanol

The plot of $\ln\left(\frac{M_{x,y}(t)}{M_0}\right) + \frac{t}{T_2}$ vs t^3 was produced with the times and corresponding magnetization values acquired for water with the T_2 measurement (method A). The slope of the linear fit was -1.341×10^{-6} . Using the known diffusion coefficient of water ($2 \times 10^{-5} \text{ cm}^2/\text{sec}$), the magnetic field gradient was calculated to be $G = 2.1 \times 10^{-4} \text{ G/cm}$.

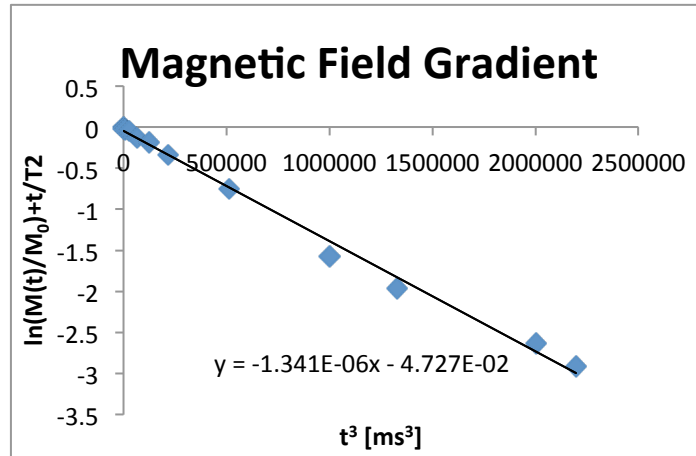


Figure 16. Plot of the linear relationship between $\ln\left(\frac{M_{x,y}(t)}{M_0}\right) + \frac{t}{T_2}$ and t^3 for water

The same type of analysis was performed to determine the diffusion coefficient of methanol. The slope of the linear fit was -1.780×10^{-6} . With the experimentally determined magnetic field gradient, the diffusion coefficient of methanol was experimentally determined to be $D_{\text{methanol}} = 2.67 \times 10^{-5} \text{ cm}^2/\text{sec}$.

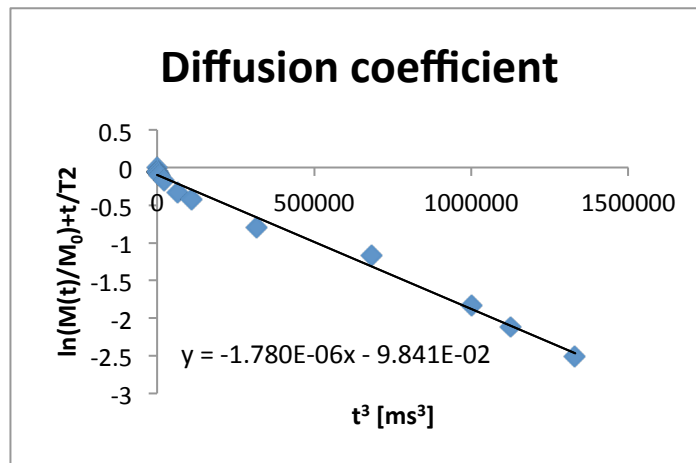


Figure 17. Plot of the linear relationship between $\ln\left(\frac{M_{x,y}(t)}{M_0}\right) + \frac{t}{T_2}$ and t^3 for methanol

Conclusion

In this lab, we were successfully able to measure the T_1 and T_2 values of oil, methanol, and water. The inversion recovery method produced T_1 values of 27.51 ms, 2.51 seconds, and 2.33 seconds for oil, methanol, and oil respectively. The behavior of the longitudinal magnetization during the recovery to thermal equilibrium was exactly what we expected to see. For the measurements of T_2 , the first method

proved to be only suitable for oil since the diffusion coefficient of oil was small enough to make the diffusion term of equation 13 negligible. It appears that there is a relationship between the viscosity and the diffusion coefficient of a compound: more viscous compounds have a smaller diffusion coefficient. The plots in figure 13 for methanol and water were similar to the results found in Carr and Purcell for the “method A” decay associated with water. These results signify that the diffusion coefficient is significant in both cases and must be modeled after equation 13. Since we were able to modify equation 13 as in Carr and Purcell (IV. Measurement of a Diffusion Constant), the magnetic field gradient and the diffusion coefficient of methanol were determined. The linear relationship formed in both cases was sufficient enough to produce a linear fit to acquire a magnetic field gradient of 2.1×10^{-4} G/cm and a diffusion coefficient of 2.67×10^{-5} cm²/sec. Method B was successful in determining the T₂ values of oil, methanol, and water which were 8.39 ms, 5.58 seconds, and 6.26 seconds respectively. The exponential decay of the magnetization was observed as expected. Additionally, the Meiboom-Gill pulse increased the T₂ values which can be seen by comparing figures 14 and 15. Each of the results was expected for all experiments performed. Further experiments can be performed for more complex samples.

References

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