

# Nuclear Magnetic Resonance: $T_1$ and $T_2$ relaxation times of $^1\text{H}$ nuclei in Mineral Oil, Ethanol, and Water



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## ABSTRACT

Nuclear Magnetic Resonance is a physical phenomenon resulting from the interactions of nuclei exposed to a magnetic field. We studied the behavior of  $^1\text{H}$  nuclei (protons) of mineral oil, ethanol, and water. We used a TeachSpin PS1-A pulsed NMR spectrometer to measure the relaxation times  $T_1$  and  $T_2$  for each of the substances by various methods. We also determined the diffusion constant of ethanol and measured the magnetic field gradient.

## THEORY

### Proton spin and precession

All nucleons have an intrinsic quantum property called spin ( $l$ ), which is a form of angular momentum. We studied the lone protons in the nuclei of Hydrogen-1 ( $^1\text{H}$ ) atoms in mineral oil, ethanol, and water.  $^1\text{H}$  atoms have two possible spin states,  $m_l = \pm \frac{1}{2}$ . Charged particles with spin, such as protons, have a magnetic moment ( $\vec{\mu}$ ):

$$\vec{\mu} = \gamma \hbar \vec{l} \quad (1)$$

where  $\gamma$  is the gyromagnetic ratio ( $\gamma = 4.26 \times 10^3 \text{ s}^{-1} \text{ G}^{-1}$ ) and  $\hbar$  is Planck's constant.

When there is no external magnetic field, the spins of the protons are randomly oriented. However, in the presence of a uniform magnetic field, the spins align either parallel ( $m_l = +\frac{1}{2}$ ) or antiparallel ( $m_l = -\frac{1}{2}$ ) to the field. In our experiment, protons placed in an external magnetic field ( $\vec{B} = B_0 \hat{z}$ ) and have the following potential energy ( $U$ ):

$$U = -\vec{\mu} \cdot \vec{B} = \gamma \hbar m_l B_0 \quad (2)$$

The transition energy ( $\Delta E$ ) between the two spin states is:

$$\Delta E = \gamma \hbar B_0 \quad (3)$$

So, when provided with enough energy, the orientation of the magnetic moments of the protons will precess relative to the applied field. This energy is electromagnetic, generally at a radio frequency (RF) in the MHz range. This resonant frequency ( $f$ ) can be calculated by equating equation 3 to  $E = hf$ , the energy of a photon:

$$f = \frac{\gamma B_0}{2\pi} \quad (4)$$

This frequency can also be expressed as an angular frequency,  $\omega = \gamma B_0$ , also known as the Larmor frequency.

### $T_1$ – Longitudinal relaxation time

If there is an unequal number of spins in the two spin states, a magnetization ( $M_z$ ) will be established in the direction of the applied magnetic field, in this case, the z-direction. After a substance is exposed to an external magnetic field, the magnetization will reach a thermal equilibrium value ( $M_0$ ), as the protons transition into the lower energy spin state, i.e. align parallel to the magnetic field. Magnetization will reach  $M_0$  at a rate described by the equation:

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1} \quad (5)$$

where  $T_1$  is the spin-lattice or longitudinal relaxation time. Integrating equation 5 under the condition  $M_z = -M_0$ , the behavior of the magnetization can be modelled by the following equation:

$$M_z(t) = M_0(1 - 2e^{-\frac{t}{T_1}}) \quad (6)$$

Essentially,  $T_1$  is the decay constant associated with the recovery of longitudinal magnetization to thermal equilibrium and its value will vary for each substance we study.

### **$T_2$ – Transverse relaxation time**

The behavior of the magnetization in the  $x$ - $y$  plane or transverse magnetization ( $M_{x,y}$ ) can be described by the equation:

$$\frac{dM_{x,y}}{dt} = -\frac{M_{x,y}}{T_2} \quad (7)$$

where  $T_2$  is the spin-spin or transverse relaxation time. Each spin has its own magnetic field and these localized magnetic fields interact with each other causing the strength of the magnetic field experienced by individual spins to vary from the applied magnetic field. If a spin experiences a stronger magnetic field than applied, the spin will precess at a frequency higher than the Larmor frequency, and conversely, at a lower frequency if it experiences a weaker field. All the spins will therefore be out of phase with each other because of these spin-spin interactions and inhomogeneity in the magnetic field, causing the transverse magnetization to decay exponentially, as is described by the following equation derived by Carr and Purcell:

$$M_{x,y}(t) = M_0 e^{\left[ -\frac{t}{T_2} - \frac{\gamma^2 G^2 D t^3}{12n^2} \right]} \quad (8)$$

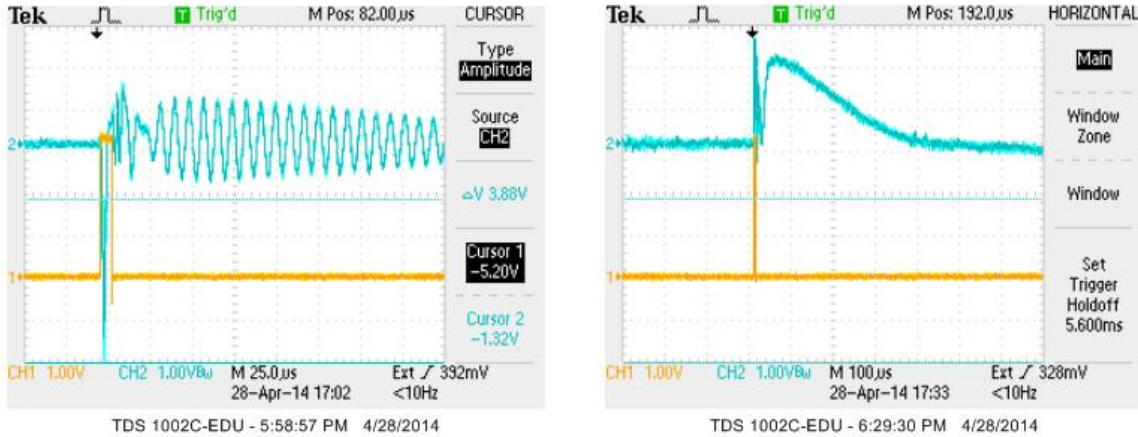
where  $G$  is the magnetic field gradient ( $G = \frac{\partial B}{\partial x}$ ),  $D$  is the diffusion constant, and  $n$  is the number of  $180^\circ$  pulses. The  $\frac{\gamma^2 G^2 D t^3}{12n^2}$  term in equation 7 is called the diffusion term. Carr and Purcell showed that inhomogeneity in the magnetic field causes self-diffusion of the magnetic moments and under these circumstances the diffusion term dominates. When the effects of diffusion are negligible, equation 7 simplifies to:

$$M_{x,y}(t) = M_0 e^{-\frac{t}{T_2}} \quad (9)$$

$T_2$  is the decay constant associated with the exponential decay of the transverse magnetization and every substance we study will have a characteristic value of  $T_2$ .

### **Beats**

In our experiment, the magnetization signal is picked up by a detector and mixed with a RF pulse at a user-tuned frequency. The frequencies of these two signals need to be equal. If the frequencies are not equal, the signals will interfere and create a beat pattern (figure 1). The frequency of the beat pattern is the difference between the magnetization frequency and the user-tuned frequency. The user-tuned frequency has to be adjusted to the resonant frequency, so that there are no beats and the RF pulse has an energy that corresponds to a spin flip.



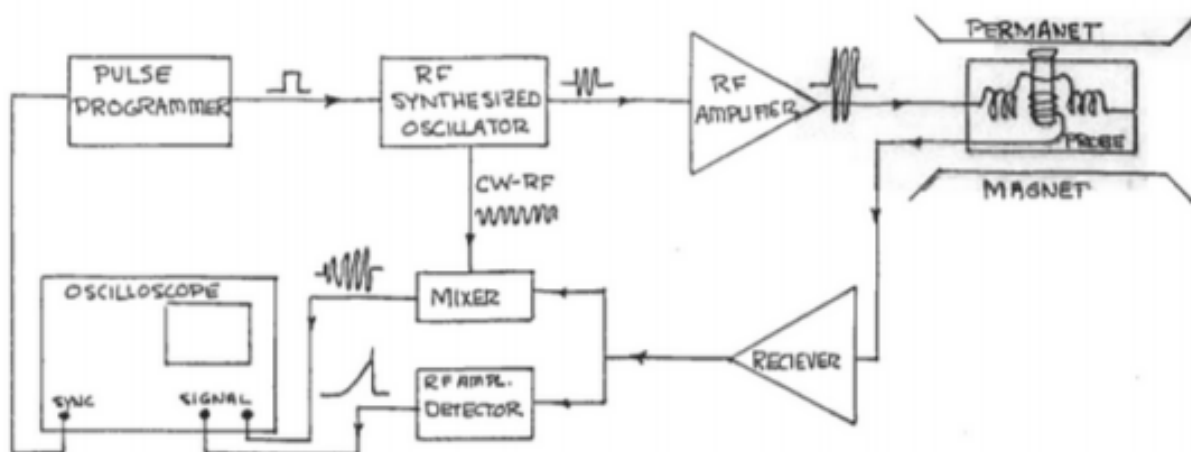
**Figure 1:** Beat pattern produced when RF pulse is not tuned to resonant frequency (left). Zero-beat signal at resonant frequency (right).

## APPARATUS & EXPERIMENTAL SETUP

In this experiment, we used TeachSpin's PS1-A pulsed NMR spectrometer. It consists of the following:

- A permanent magnet with a magnetic field strength of  $\sim 3640$  Gauss.
- A transmitter coil (radio frequency coil) which induces a rotating magnetic field strength of 12 Gauss at the sample. This field produces the precession of protons and its signals are referred to as the  $90^\circ$  and  $180^\circ$  pulses.
- A pulse programmer which controls the transmitter coil by controlling the oscillator. It is used to adjust the pulse width, the delay time between pulses, the repetition time of the pulses, and the number of pulses. It also triggers the oscilloscope on the appropriate pulse.
- An oscillator which creates the radio frequency pulse bursts that induce a current in the transmitter coil.
- An EMF is induced in the receiver coil (another radio frequency coil) by magnetization in the  $x$ - $y$  plane. This signal is detected by two detectors.
- A radio frequency amplitude detector picks up the magnetization signal from the receiver coil and outputs a proportional signal, which is displayed on the oscilloscope.
- The other detector is a mixer that multiplies the magnetization signal with the oscillator signal (at user-tuned frequency) and its output frequency is proportional to the difference between the frequencies of the two signals. This allows us to determine the frequency of the oscillator, which can then be tuned to the right precessional / resonant frequency of the magnetization in order to produce a zero beat signal.
- An oscilloscope (Tektronix TDS-1002) displays the output from the receiver coil.

**Figure 1: Block diagram of experimental setup from TeachSpin Instrument Manual**



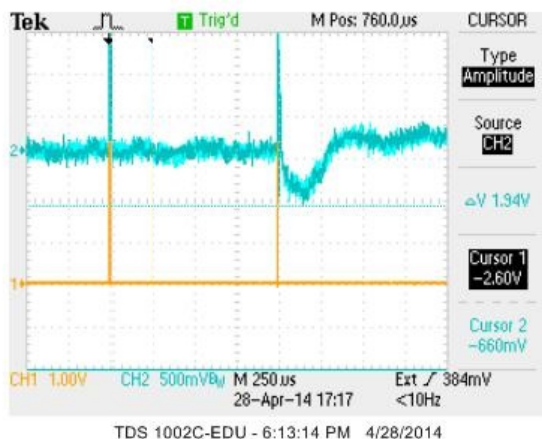
## PROCEDURE

### Applying $90^\circ$ and $180^\circ$ pulses

In this experiment, the equilibrium condition of a sample placed in a magnetic field is disturbed by applying a RF pulse at the Larmor frequency. Two kinds of pulses were used:  $90^\circ$  and  $180^\circ$ . The signal produced by applying a single  $90^\circ$  pulse is called a Free Induction Decay (FID) signal and its amplitude is at a maximum. The  $180^\circ$  pulse, as the name suggests, is used to rotate the magnetization vector by  $180^\circ$ . The resulting signal corresponds to an FID signal of zero.

### Measuring $T_1$

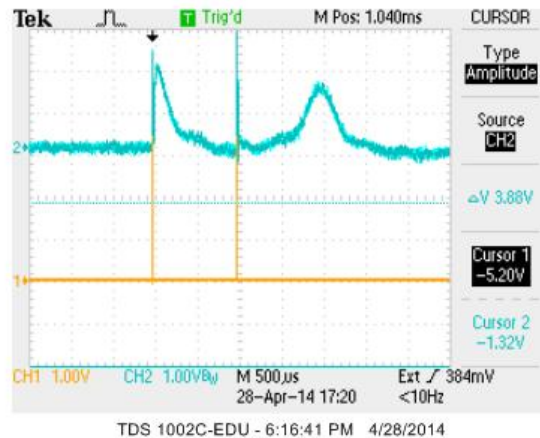
A two pulse sequence is used in order to measure  $T_1$ : a  $180^\circ$  pulse followed by a  $90^\circ$  pulse (figure 2). The  $180^\circ$  rotates the magnetization, which then decays according to equation 6, and approaches its thermal equilibrium value. Our setup is such that only magnetization in the  $x$ - $y$  plane is measured and magnetization along the  $z$ -axis is not detected. The  $90^\circ$  pulse is then applied to rotate any magnetization along the  $z$ -axis into the  $x$ - $y$  plane. A maximum FID signal is produced and that signal is proportional to the magnetization along the  $z$ -axis just before the  $90^\circ$  pulse. The experiment was performed at various delay times (time between pulses) and the FID signal was recorded for each case. Equation 6 was fit to the data in order to find  $T_1$ .



**Figure 2: FID signal produced after applying a  $180^\circ$  pulse followed by a  $90^\circ$  pulse – Pulse sequence for measuring  $T_1$**

### Measuring $T_2$ : method A

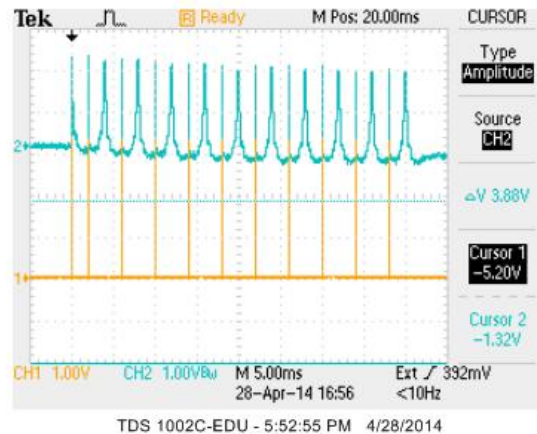
One method for measuring  $T_2$  involves applying a  $90^\circ$  pulse followed by a  $180^\circ$  pulse (figure 3). A maximum FID signal is produced after the  $90^\circ$  pulse but eventually, spin-spin interactions and inhomogeneity in the magnetic field cause the spins to become out of phase. The  $180^\circ$  pulse follows, bringing all the spins back in phase in the  $x$ - $y$  plane, which results in a spin-echo signal (figure 3). Only spins that were dephased by inhomogeneity in the magnetic field become in phase again but the spins that dephased due to spin-spin interactions don't rephase. This is a loss in transverse magnetization and hence the spin-echo signal is smaller in amplitude than the FID signal. A plot of the spin-echo signal versus delay time was made and the decay in transverse magnetization was modelled by equation 9, in order to obtain a value for  $T_2$ .



**Figure 3:** Spin-echo signal produced after applying a  $90^\circ$  pulse followed by a  $180^\circ$  pulse – method A for measuring  $T_2$

### Measuring $T_2$ : method B

With method A, the diffusion effects in methanol and water are significant and the relationship between spin echo and delay time is modelled by equation 8. So, a second method for measuring  $T_2$  involves applying the  $90^\circ$  followed by multiple  $180^\circ$  pulses (figure 4). Increasing the number of  $180^\circ$  pulses reduces the effects of diffusion (increasing  $n$  in equation 8 causes the diffusion term to no longer dominate).



**Figure 4:**  $90^\circ$  pulse followed by multiple  $180^\circ$  pulse – method B for measuring  $T_2$

### Measuring $T_2$ : method B with Meiboom-Gill pulse

The  $180^\circ$  pulse corresponds to a zero FID signal but it's difficult to identify a  $180^\circ$  pulse because of background noise, making it difficult to distinguish a pulse very close to  $180^\circ$  from an actual  $180^\circ$  pulse. This means we are generally off by a small angle and applying multiple pulses, as in Method B, compounds the error. This accumulation of error results in a decay in magnetization that is faster than expected. The NMR spectrometer has a Meiboom-Gill (MG) modification which reduces this accumulated error by adding a  $90^\circ$  phase shift to the  $90^\circ$  pulse with respect to the  $180^\circ$  pulse.

### Magnetic field gradient & diffusion constant of Ethanol

Using the data for water from Method A for measuring  $T_2$  and the known diffusion constant for water ( $D = 2.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ), we can calculate the magnetic field gradient ( $G$ ). Rearranging equation 8 to

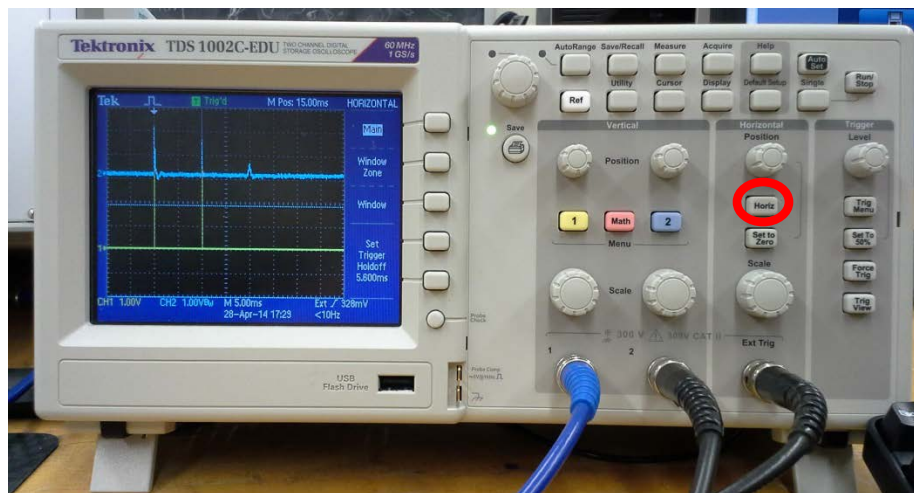
$$\ln\left(\frac{M_{x,y}(t)}{M_0}\right) + \frac{t}{T_2} = -\frac{\gamma^2 G^2 D t^3}{12n^2} \quad (10)$$

gives us a linear relationship between  $\ln\left(\frac{M_{x,y}(t)}{M_0}\right) + \frac{t}{T_2}$  and  $t^3$ , with a slope  $-\frac{\gamma^2 G^2 D}{12n^2}$ . A linear fit is applied to the data and the slope was determined and was used to calculate  $G$ .

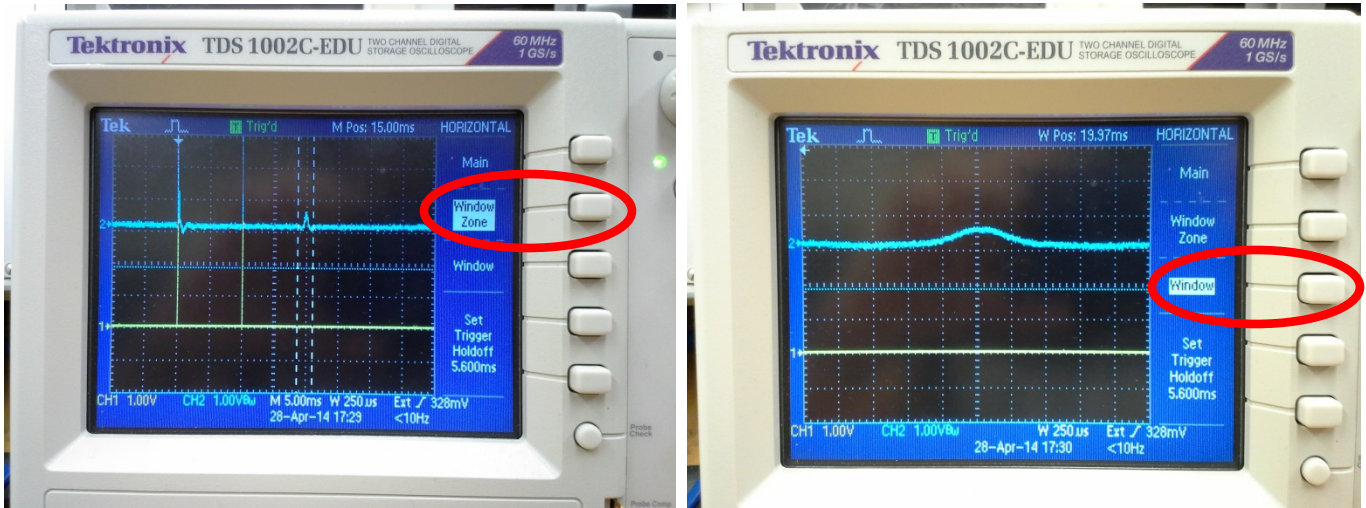
Using the calculated value of  $G$ , a similar analysis was done on the Method A data for ethanol and was used to calculate the diffusion constant.

### Window zone

For some measurements (generally  $T_2$  measurements for ethanol and water), it is hard to see detail on a specific portion of the waveform displayed on the oscilloscope. There is a built in Window function which makes taking data easier by allowing the user to select a specific portion of the waveform and expand it in the window zone (figure 5, 6).



**Figure 5:** Window function accessible by pressing HORIZ button (circled in red) on the oscilloscope

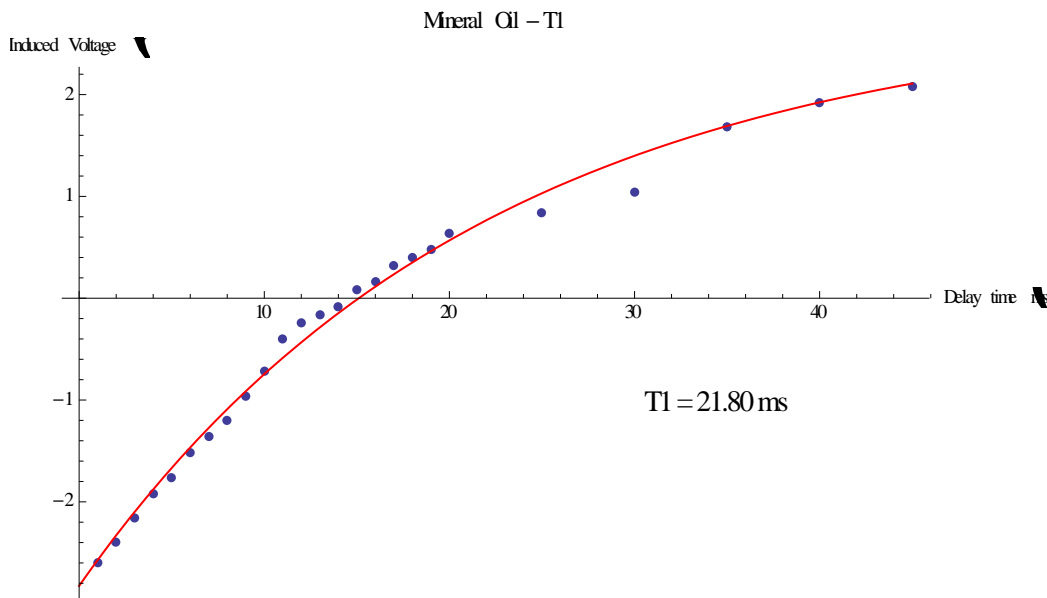


**Figure 6:** Window zone button (circled in red on the left), opens the window, displayed as two white dashed, vertical lines (left). The HORIZONTAL POSITION knob allows the user to position the window around the portion of the waveform that needs to be expanded and the SEC/DIV knob controls the how much that portion will be expanded. Window button (circled in red on the right), displays the expanded view of the selected portion of the waveform.

## RESULTS

### Mineral Oil

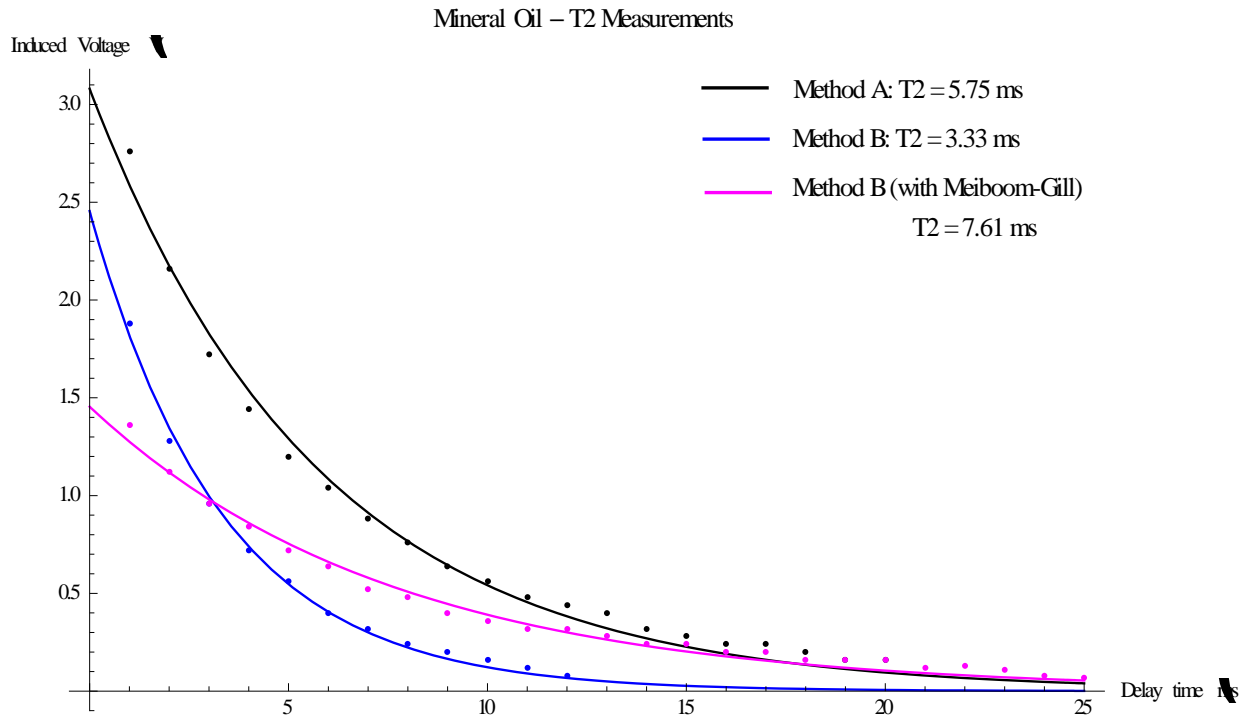
Figure 7 shows the recovery of longitudinal relaxation of mineral oil. Mathematica was used to fit the data with equation 6 and the value of  $T_1$  for mineral oil was found to be 21.80 ms.



**Figure 7:** Recovery of longitudinal relaxation of mineral oil modelled by equation 6



The decay of transverse magnetization / measurement of  $T_2$  of mineral oil by various methods is shown in figure 8. The data was fitted with equation 9 and the various values of  $T_2$  for mineral oil are displayed in table 1.



**Figure 8:** Measurements of  $T_2$  for mineral oil by method A, method B with MG on and MG off, modelled by equation 9.

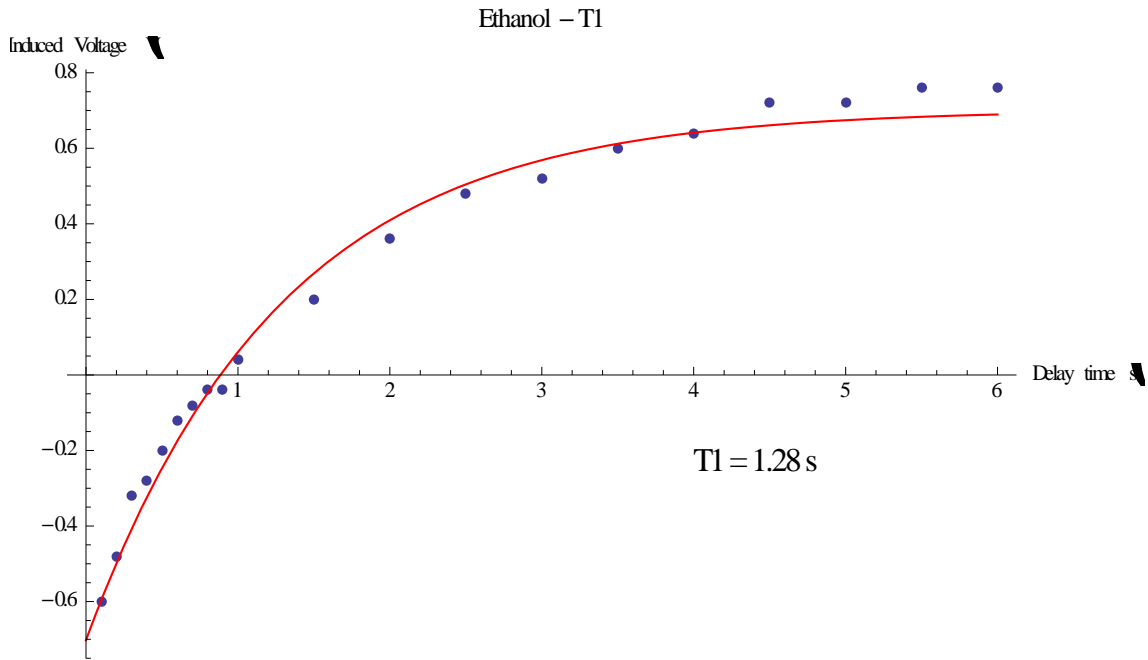
	T1	T2		
		Method A	Method B	Method B w/ MG
Mineral oil	21.80 ms	5.75 ms	3.33 ms	7.61 ms

**Table 1:** Summary of values of  $T_1$  and  $T_2$  for mineral oil

Both  $T_1$  and  $T_2$  values for mineral oil are on the order of milliseconds. While the values for  $T_2$  aren't exactly the same, they are in the same order of magnitude. In both, the measurement of  $T_1$  and  $T_2$ , the models fit the data very well.

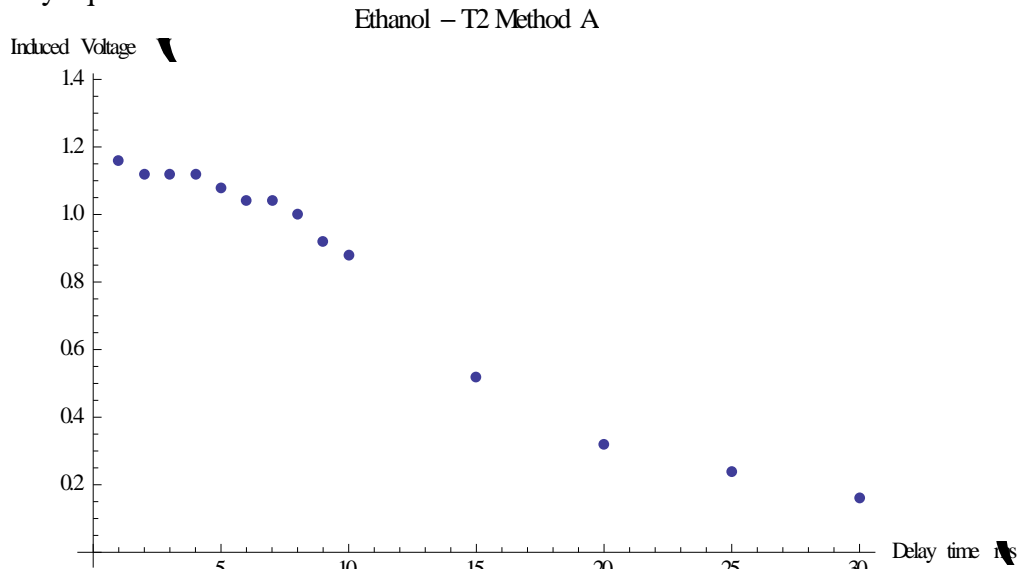
### Ethanol

Figure 9 shows the recovery of longitudinal relaxation of ethanol. The data was fit with equation 6 and the value of  $T_1$  for ethanol was found to be 1.28 s.



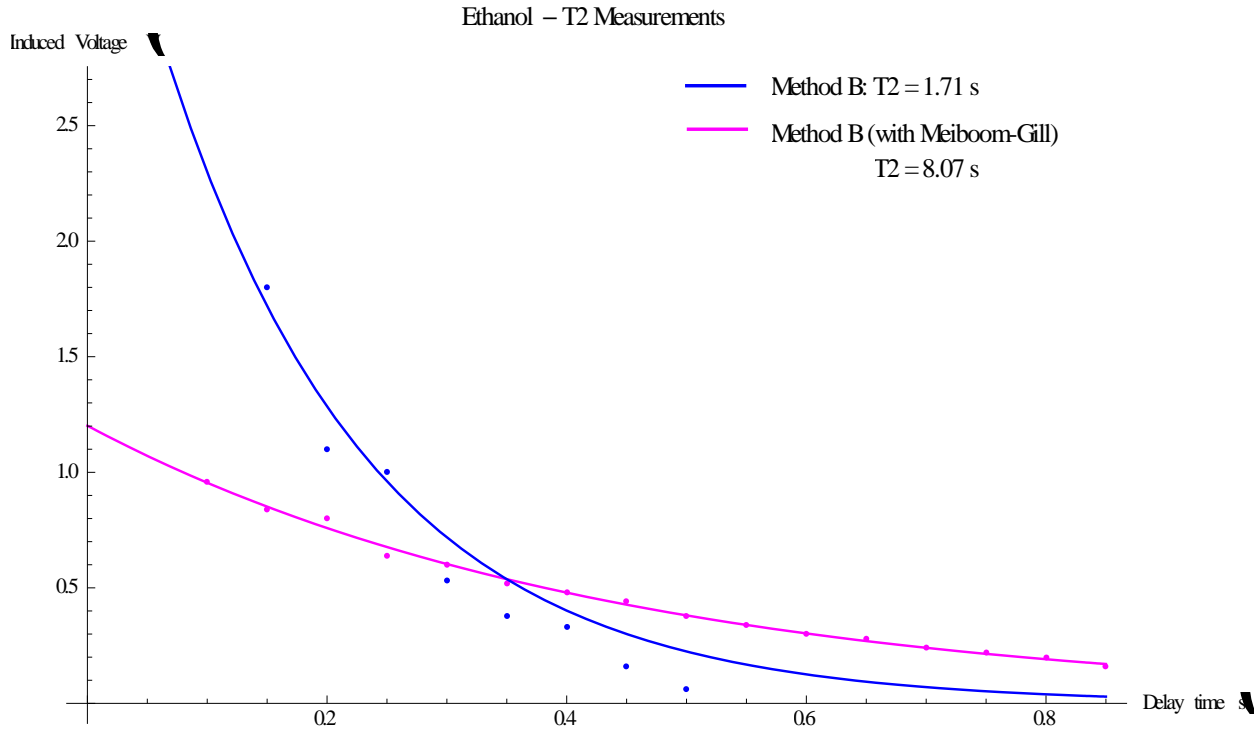
**Figure 9:** Recovery of longitudinal relaxation of ethanol modelled by equation 6

Figure 10 shows the data from method A for measuring  $T_2$  of ethanol. The exponential decay of the transverse magnetization of ethanol was dominated by the diffusion term and hence can be modelled by equation 8.



**Figure 10:** Decay of transverse relaxation of ethanol as measured by Method A for measuring  $T_2$ . Modelled by equation 8 as diffusion term dominates.

The decay of transverse magnetization / measurement of  $T_2$  of ethanol by method B with MG on and MG off is shown in figure 11. The data was fitted with equation 9 and the various values of  $T_2$  for ethanol are displayed in table 2.



**Figure 11:** Measurements of  $T_2$  for ethanol by method B with MG on and MG off, modelled by equation 9.

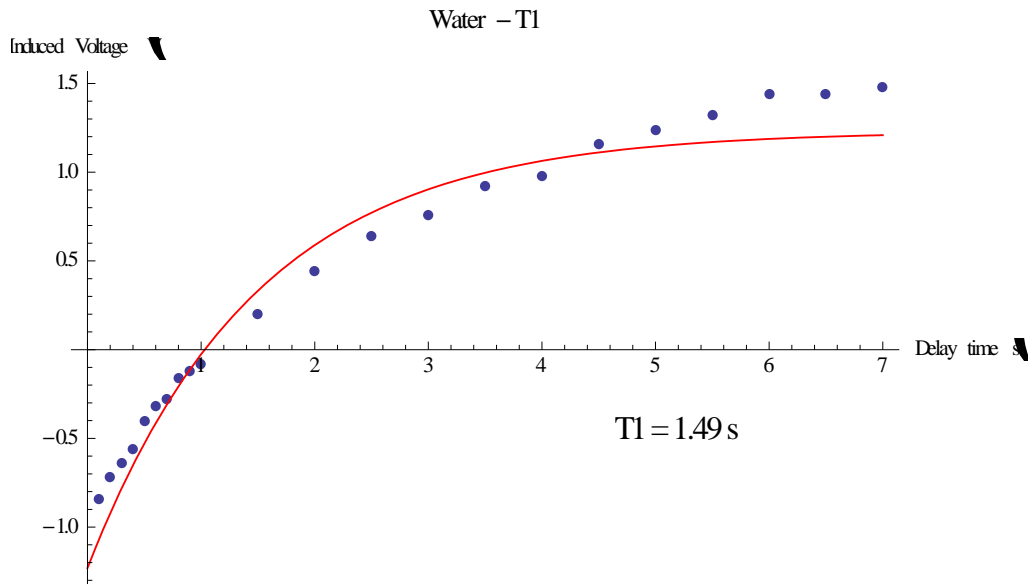
	T1	T2		
		Method A	Method B	Method B w/ MG
<b>Ethanol</b>	1.28 s	-	1.71 s	8.07 s

**Table 2:** Summary of values of  $T_1$  and  $T_2$  for ethanol

Both  $T_1$  and  $T_2$  values for ethanol are on the order of seconds. While the values for  $T_2$  aren't exactly the same, they are in the same order of magnitude. In both, the measurement of  $T_1$  and  $T_2$ , the models fit the data very well.

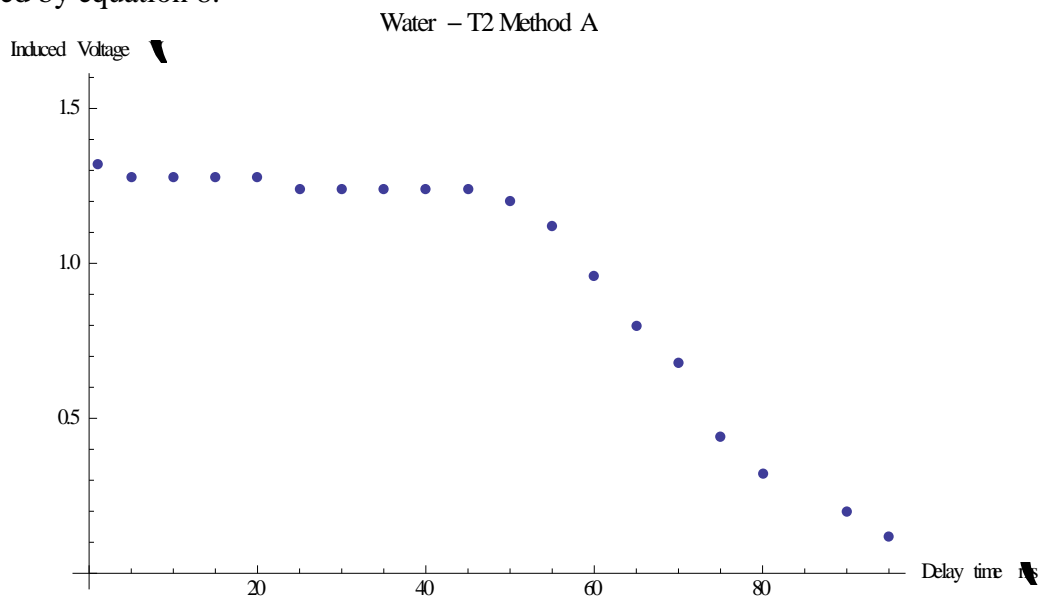
### Water

Figure 12 shows the recovery of longitudinal relaxation of water. The data was fit with equation 6 and the value of  $T_1$  for water was found to be 1.49 s.



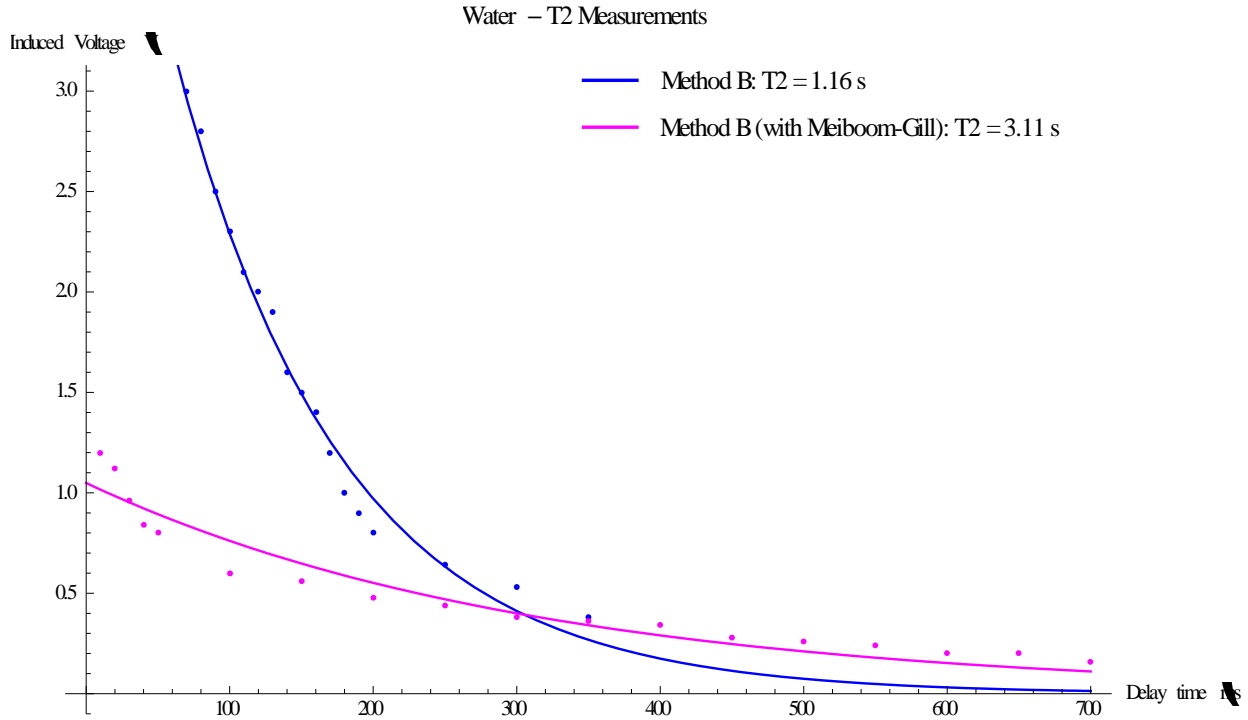
**Figure 12:** Recovery of longitudinal relaxation of water modelled by equation 6

Figure 13 shows the data from method A for measuring  $T_2$  of water. The exponential decay of the transverse magnetization of water was dominated by the diffusion term and hence can be modelled by equation 8.



**Figure 13:** Decay of transverse relaxation of water as measured by Method A for measuring  $T_2$ . Modelled by equation 8 as diffusion term dominates.

The decay of transverse magnetization / measurement of  $T_2$  of water by method B with MG on and MG off is shown in figure 14. The data was fitted with equation 9 and the various values of  $T_2$  for water are displayed in table 3.



**Figure 14:** Measurements of  $T_2$  for water by method B with MG on and MG off, modelled by equation 9.

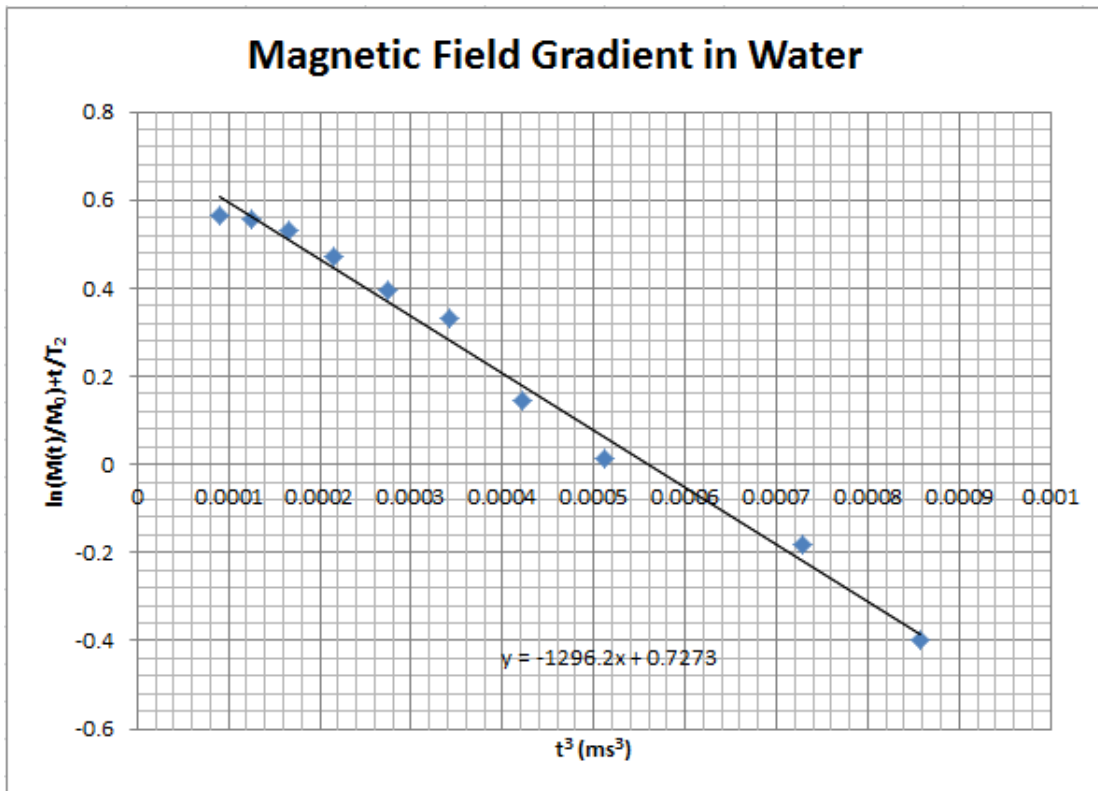
	T1	T2		
		Method A	Method B	Method B w/ MG
<b>Water</b>	1.49 s	-	1.16 s	3.11 s

**Table 3:** Summary of values of  $T_1$  and  $T_2$  for water

Both  $T_1$  and  $T_2$  values for water are on the order of seconds. While the values for  $T_2$  aren't exactly the same, they are in the same order of magnitude. In both, the measurement of  $T_1$  and  $T_2$ , the models fit the data very well.

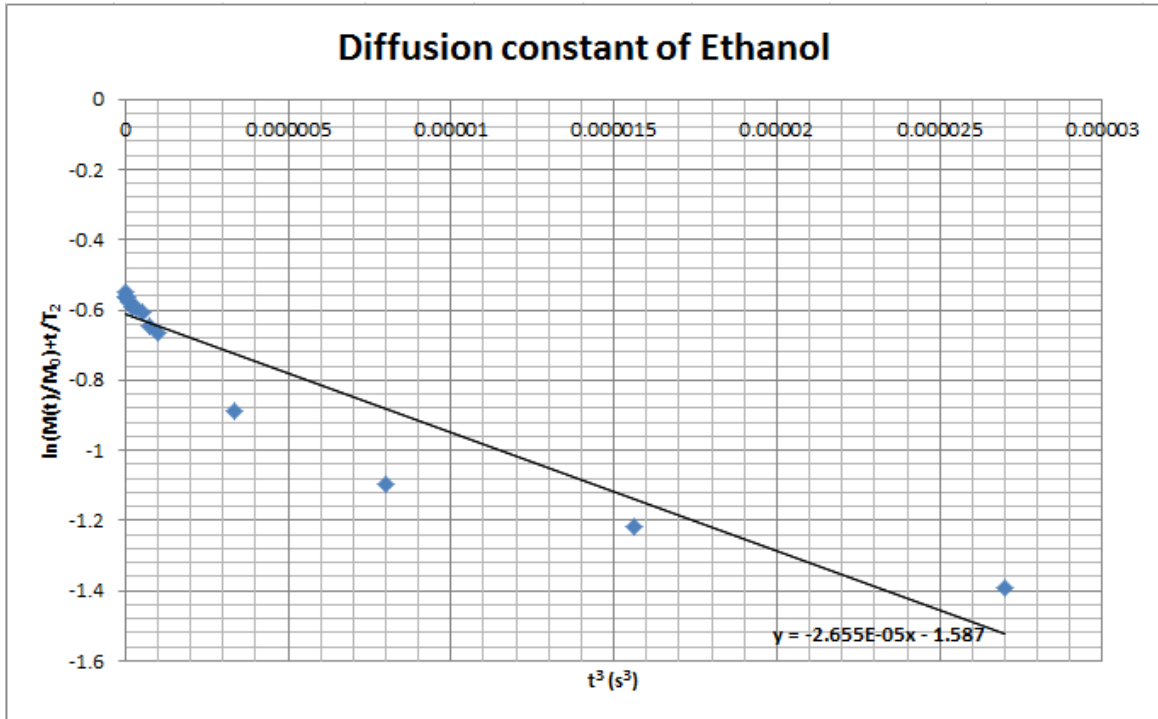
### Magnetic field gradient & diffusion constant of Ethanol

The plot of  $\ln\left(\frac{M_{x,y}(t)}{M_0}\right) + \frac{t}{T_2}$  and  $t^3$  for data for method A for measurement of  $T_2$  for water is shown in figure 15. The slope of the linear fit was found to be -1296.159. Given that we know the slope is equal to  $-\frac{\gamma^2 G^2 D}{12n^2}$  and the diffusion constant of water is  $2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , the magnetic field gradient was calculated to be  $6.56 \text{ G cm}^{-1}$ .



**Figure 15:** Plot of  $\ln\left(\frac{M_{x,y}(t)}{M_0}\right) + \frac{t}{T_2}$  and  $t^3$  for data for method A for measurement of  $T_2$  for water

Similar analysis was done to data for method A for measurement of  $T_2$  for ethanol to measure its diffusion constant. The plot of  $\ln\left(\frac{M_{x,y}(t)}{M_0}\right) + \frac{t}{T_2}$  and  $t^3$  for data for method A for measurement of  $T_2$  for ethanol is shown in figure 16. The slope of the linear fit was found to be  $-2.655 \times 10^{-5}$ . Given that we know the slope is equal to  $-\frac{\gamma^2 G^2 D}{12n^2}$ , the calculated value of magnetic field gradient,  $6.56 \text{ G cm}^{-1}$ , the diffusion constant of ethanol was found to be  $4.10 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ . This value does not seem to be very accurate because literature values for the diffusion constant of ethanol are generally in the  $10^{-5}$  to  $10^{-6}$  range. The plot of  $\ln\left(\frac{M_{x,y}(t)}{M_0}\right) + \frac{t}{T_2}$  and  $t^3$  for ethanol also doesn't seem to display a linear relationship.



**Figure 16:** Plot of  $\ln\left(\frac{M_{x,y}(t)}{M_0}\right) + \frac{t}{T_2}$  and  $t^3$  for data for method A for measurement of  $T_2$  for ethanol

## CONCLUSION

**Table 4: Summary of values of values of  $T_1$  and  $T_2$  for mineral oil, ethanol, and water**

	T1	T2		
		Method A	Method B	Method B w/ MB
<b>Mineral oil</b>	21.80 ms	5.75 ms	3.33 ms	7.61 ms
<b>Ethanol</b>	1.28 s	-	1.71 s	8.07 s
<b>Water</b>	1.49 s	-	1.16 s	3.11 s

All the values for  $T_1$  and  $T_2$  for mineral oil, ethanol and water seem to agree with each other. The self-diffusion effect for ethanol and water while measuring  $T_2$  by method A was found to be significant and has to be modelled by equation 8. In fact, the diffusion effect was significant even for method B but this problem was fixed by moving the sample from the middle of the magnetic field (where the magnetic field gradient is zero) to a ‘sweet spot’ in the magnetic field, where the gradient wasn’t zero.



The magnetic field gradient was found to be  $G = 6.56 \text{ G cm}^{-1}$  (before sample was adjusted to the ‘sweet’ spot). The diffusion constant for ethanol,  $D_{ethanol}$ , was found to be  $4.10 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ . This value does not seem to be very accurate because literature values for the diffusion

constant of ethanol are generally in the  $10^{-5}$  to  $10^{-6}$  range. Again, this measurement was done before adjusting to the 'sweet' spot so the data may be skewed as a result of that. But otherwise, the data collected for the measurement of  $T_1$  and  $T_2$  seems to agree with known values from previous experiments.

#### **REFERENCES**

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2. H. Y. Carr and E. M. Purcell, Physical Review 94, 630 (1954)
3. TeachSpin PS1-A pulsed NMR spectrometer manual