Nuclear Magnetic Resonance

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(Dated: February 27, 2016)

I. INTRODUCTION

Nuclear magnetic resonance (NMR) aligns the spin states of atoms in an external magnetic field using systematic RF pulses. Purcell and Bloch independently discovered this response of frequency caused magnetism in 1946, which led to the now widely utilized principle of NMR. NMR is inherent to the analytic techniques of spectroscopy and magnetic resonance imaging (MRI). Resonant signals yield important information about the spin-lattice structure of the material being analyzed. Many nuclei have intrinsic magnetic moments (non zero spin) and therefore can be characterized through NMR. However, certain nuclides have equal protons and neutrons and therefore lack a magnetic (including dipole and quadrupole) moment necessary to detect NMR absorption.

In this experiment, we used NMR to measure the T1 and T2 times of various materials. We first optimized the experimental set up, calibrating the NMR instrument by minimizing beats in the FID curve. We measured the spin lattice relaxation time (T1) and spin-spin relaxation time (T2) of heavy mineral oil (HMO), water, and ethanol by placing these compounds in a magnetic field and systematically hitting them with RF pulses. The RF pulses have phases of π and $\pi/2$ (180 and 90 degrees). The series of applied π and $\pi/2$ pulses are specified by the Hahn, Purcell and Meiboom-Gill methods.

II. BACKGROUND THOERY

The change in energy experienced by a hydrogen atom is

$$E = \hbar\omega \qquad (1)$$

. This change in energy is proportional to the magnetic moment and B field

$$\Delta E = \gamma\hbar B = \mu_z B \qquad (2)$$

where $\gamma = g/2\mu_p$ particular to protons where g = gyromagnetic ratio. The gamma factor scales the Larmor (precessional) frequency proportional to the magnetic torque on the dipole.

$$\tau = \vec{\mu}x\vec{B} = |\mu B sin\theta| \qquad (3)$$

The proton loses this energy to the external environment and its magnetic moment decays, precessing about the z-axis. This return to equilibrium is measured by exponentially decaying voltage signals. The peaks of these
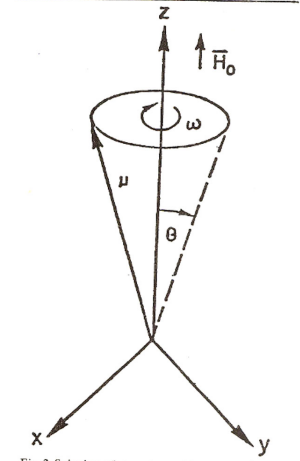

Fig. 2. Spinning of a proton with a magnetic moment, μ, At an angular velocity, ω at an angle θ, with the external Field H_0 z.

FIG. 1. Larmor frequency

signals are characteristic to the spin lattice relaxation time (T1) and spin-spin relaxation time (T2). As the spins return to a low energy state, the recovery rate T1 is given by the differential equation

$$dM_z/dt = (M_0 - M_z)/T_1 \qquad (4)$$

solved for $M_z(t = 0) = -M_0$:

$$M_z(t) = M_0(1 - 2e^{-t/T_1}) \qquad (5)$$

The transverse component of the magnetization x, y is given by

$$M_{x,y} = M_0 e^{-t/T_2} \qquad (6)$$

where T2 is the spin-spin relaxation time that stems from the spins interacting magnetic fields that alter the spin precessing. The phase change depends on both the diffusion constant of the sample and the inhomogeneity of the external magnetic field

$$M_{x,y} = M_0 e^{t/T_2 + \gamma^2(\partial B/\partial z)^2(Dt^3)/(12n^2)} \qquad (7)$$

To measure T2, the proton must be hit with a series of π and $\pi/2$ pulses. $\pi/2$ pulses excite the system to the high energy level while π pulses excite the particles from $\tau/2$ and then de-excite to the lower energy state as t goes from $\tau/2$ to τ. The Hahn method measures the decaying signal as a function of time as the τ increases. The Spin-Echo method (described in Carr Purcell [1]) hits the original magnetic moment aligned in z with a
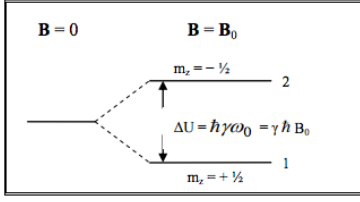
FIG. 2. Zeeman Splitting

FIG. 3. Behavior of the nuclear polarization if a 90° phase shift is introduced in the rf of the first pulse.

FIG. 4. Meiboom Gill pulse sequence

90 degree pulse. The magnetic field now exists in the x-y plane. Next, a 180 degree pulse flips the system, and the spins rephrase. This repetitive process maximizes the signal at $t = 2 * \tau * n$. The maximum signal (echo)

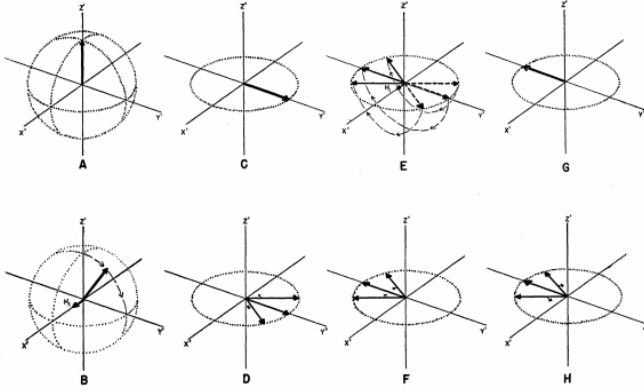decays as the vectors again fan out and the system loses energy through interactions [1]

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The oscilloscope feeds into the computer to capture the signal.

FIG. 3. The formation of an echo. Initially the net magnetic moment vector is in its equilibrium position (A) parallel to the direction of the strong external field. The rf field H_1 is then applied. As viewed from the rotating frame of reference the net magnetic moment appears (B) to rotate quickly about H_1. At the end of a 90° pulse the net magnetic moment is in the equatorial plane (C). During the relatively long period of time following the removal of H_1, the incremental moment vectors begin to fan out slowly (D). This is caused by the variations in H_z over the sample. At time $t=\tau$, the rf field H_1 is again applied. Again the moments (E) begin to rotate quickly about the direction of H_1. This time H_1 is applied just long enough to satisfy the 180° pulse condition. This implies that at the end of the pulse all the incremental vectors are again in the equatorial plane (F). In the relatively long period of time following the removal of the rf field, the incremental vectors begin to recluster slowly (F). Because of the inverted relative positions following the 180° pulse and because each incremental vector continues to precess with its former frequency, the incremental vectors will be perfectly reclustered (G) at $t=2\tau$. Thus maximum signal is induced in the pickup coil at $t=2\tau$. This maximum signal, or echo, then begins to decay as the incremental vectors again fan out (H).

FIG. 3. Spin Echo, from Carr Purcell

The modified Meiboom-Gill sequence minimizes accumulating errors by alternating between $\pi/2$ and π pulses. This way, error is not routinely propagated over the same plane as in the original spin-echo method.

III.   MATERIALS AND METHODS

We used a TeachSpin Pulsed/CW NMR Spectrometer (PS2-A/B/C). The set up consists of a control box and power system connected to the magnet. The control box modifies the user-inputted parameters, including A and B pulses, tau, frequency, and number of fired pulses. We inserted the samples (HMO, water, ethanol) into the magnetic field through a slot on the top of the magnet. The magnet connects to an oscilloscope that reads the voltage output as the protons magnetic moments decay.
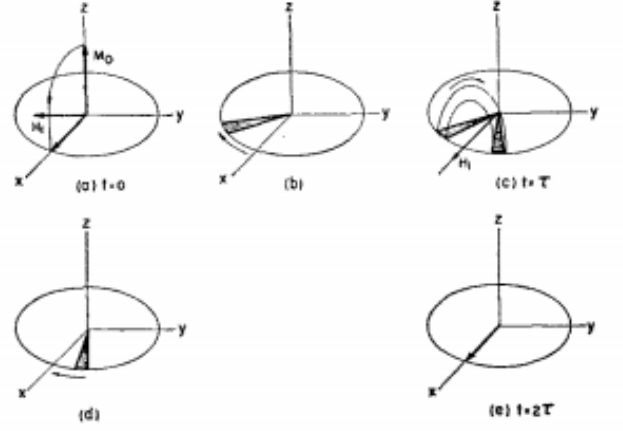

FIG. 5. Magnet setup

We first tuned the system by obtaining the free induction decay (FID) curve. We placed an RF probe into the magnet and tuned the system to the Larmor frequency. By tuning the frequency, we reduced the beats in the FID curve and effectively filtered out $\omega_r ef$ and $\omega_s pin$ by setting them equal to each other.

$$\sin(\omega_r t)\sin(\omega_s t) = (1/2)\cos(\omega_r - \omega_s)t - (1/2)\cos(\omega_r + \omega_s)t \tag{8}$$

where ω_r is the reference frequency and ω_s is the spin frequency. For this set up, the optimal frequency is 21.07 MHz. We systematically altered the A pulse to discover the π and $\pi/2$ pulses by searching for the period at which the signal reached a maximum amplitude. The π pulse occurs at 6.76 μs and $\pi/2$ at 3.38 μs. We then calculated T1 for HMO two ways. First we found the τ at which the FID amplitude is 0 and then used that τ to calculate T1. We also found T1 by fitting the data to (5). Next, we obtained voltage signals from the NMR using the Hahn, Carr Purcell, and Meiboom Gill methods for HMO, water, and ethanol. The signals and their characteristic T2 times are outlined in Results.
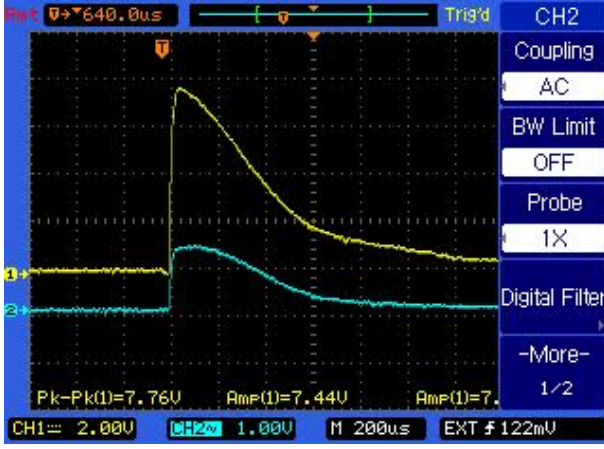
FIG. 6. FID Curve

FIG. 8. T2, Hahn, HMO

IV.   RESULTS

The amplitude of the FID curve for HMO goes to 0 when τ=0.0231 ± 0.0001 s. [1] [2] With $M_0 = 0.5$T, the calculated T1 time for HMO is 33±0.05 ms. The fitted
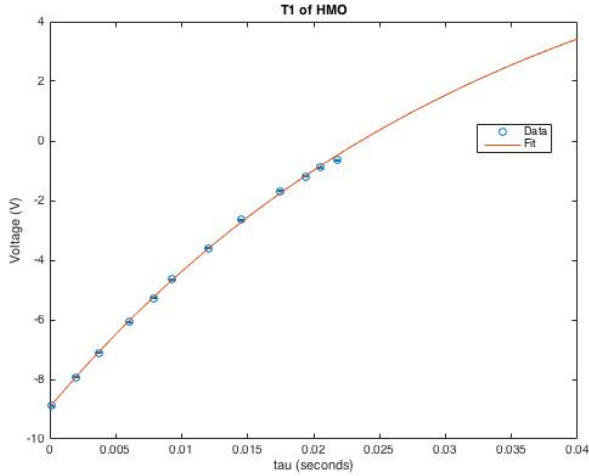

FIG. 7. T1 measurement for HMO

curve is shown in Fig 7. The fit ($R^2 = 0.94$) gives a T1 of 34±0.85 ms, which agrees with our expected value.

To find T2 of HMO, we obtained curves using the Hahn, Carr Purcell, and Meiboom Gill instructions. For the Hahn method, we used a single pulse at varying τ to observe the amplitude of the peaks as $\tau = 0.0001$s increased from τ to 6τ.
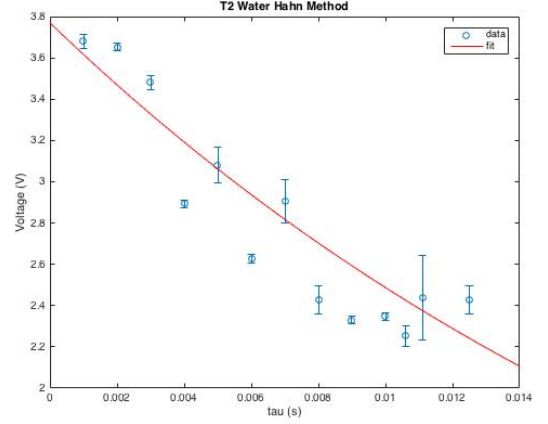
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[1] Data points in all Matlab plots are the peaks of the curves shown in oscilloscope captures

[2] For all fits, we used MatLab's fit function for our specific T1 and T2 equations. All curves take weights into account and are a Weighted Least Squares fit.
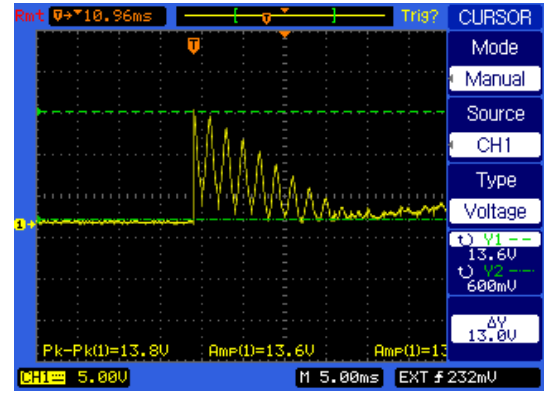

FIG. 9. T2, Spin Echo, HMO

This fit (R^2 =0.80) gave a T2 of 5.50±1.80 ms. However, of the three methods, this is the most error prone as the pulse becomes unreliable at higher τ. We then set the control box for the Carr Purcell (Spin Echo method). We observed the exponentially decaying peak curve in Fig 9. [3]

The curve of the peaks shown in 10 ($R^2 = 0.94$) from Spin Echo give a T2 of 6.98 ± 1.08 ms.

The final method, Meiboom Gill, propagates the least error by alternating between π and $\pi/2$ pulses. The control box has a built in Meiboom Gill switch to fire the pulses in the correct order. The fit for the curve shown in 11 ($R^2 = 0.99$) finds a T2 of 14.26±0.17 ms (the closest match for the value found in literature of the 3 methods for finding T2).

We repeated the Hahn, Spin Echo, and Meiboom Gill method for water.

The graphs are shown in Figures 12 through 14 and the results of these fits are shown in Table 1.

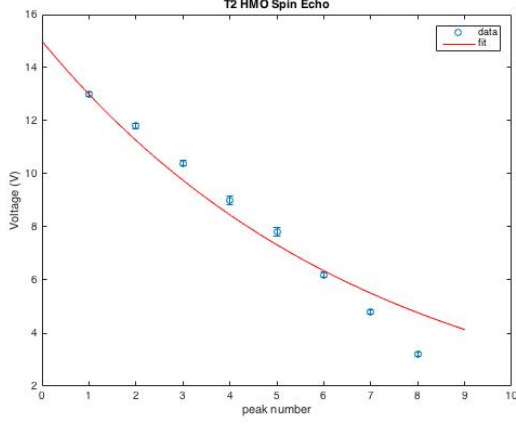[3] To see the oscilloscope captures of further materials and methods, please refer to the Appendix.

FIG. 10. T2, Spin Echo, HMO

FIG. 12. T2, Hahn, Water
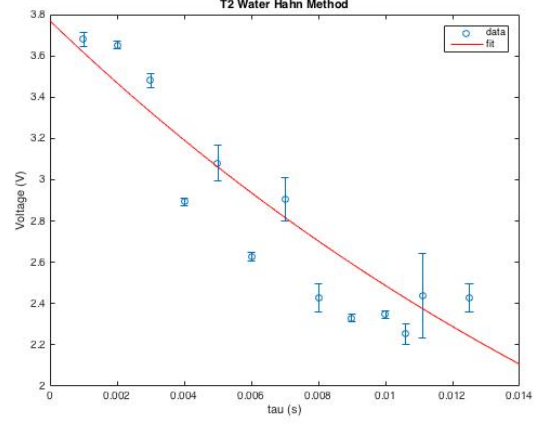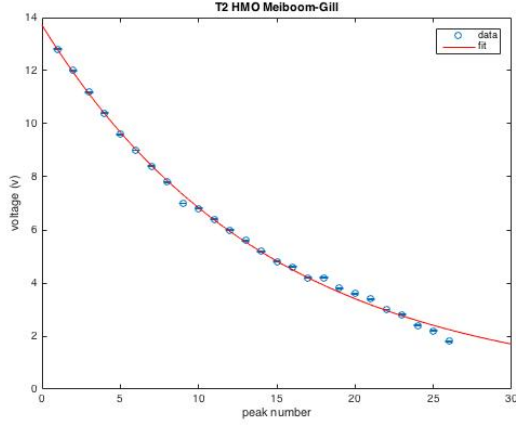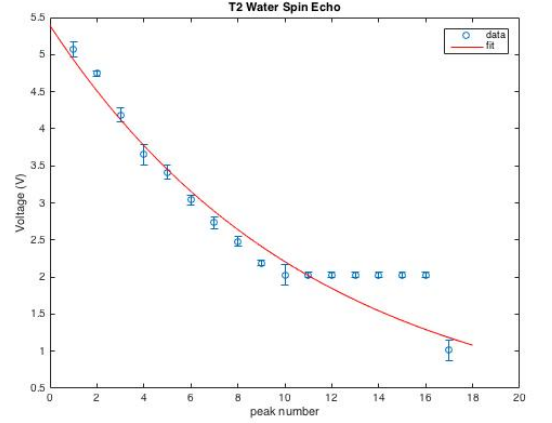

FIG. 11. T2, Meiboom Gill, HMO

FIG. 13. T2, Spin Echo, Water

Method	T2 (ms)	$\pm$ (ms)	R^2
Hahn	24.1	6.6	0.86
Spin Echo	11.2	1.55	0.96
Meiboom Gill	13.89	2.8	0.90

The voltage signal shown on the oscilloscope (Figure x in Appendix), shows the chaotic response of water to NMR. Water does not give a simple exponential decay. This is due to the diffusion coefficient that dominates at room temperature, referenced in (7) ($D_w = 2*10^{-9}m^2s^{-1}$. Knowing this diffusion constant, allows us to calculate $\partial B/\partial z$ for the NMR instrument by linearizing (7) and equating the slope to the exponential term. The calculated magnetic gradient is $2.76 \pm 0.20 \mu T/mm$.

Finally, we used the Meiboom Gill method to find T2 of ethanol. This curve ($R^2 = 0.885$) yields a T2 of 117.65 $\pm$ 29.3 ms. From $\partial B/\partial z$, we find that the diffusion of constant of ethanol equals $(4.56 \pm 0.41) * 10^{-7} m^2/s$.

V.   DISCUSSION

Using the NMR technique, we were able to measure the characteristic T1 time of HMO and T2 time of HMO, water, and ethanol. We tuned the resonance frequency with respect to the magnetic field and Larmor frequency. To calculate T1 we measured voltage as a function of the τ of the inputted pulse and used the derived formula shown in (5). The longer the τ time, the more likely the signal is to decrease as a function of time.

The three methods used to find T2 are the Hahn, Spin Echo (Carr Purcell), and Meiboom Gill. The Hahn method measured the voltage response of a single pulse as a function of τ. The Spin Echo method hit the system with a $\pi/2$ pulse followed by a series of π pulses. While this signal gives a decay, any error in angle is easily propagated as the system is routinely being rotated about the same axis. The Meiboom Gill method hits the system with an alternating series of π and $\pi/2$ pulses that minimize the propagation of error as the system is flipped. This curve is more clearly an exponential decay
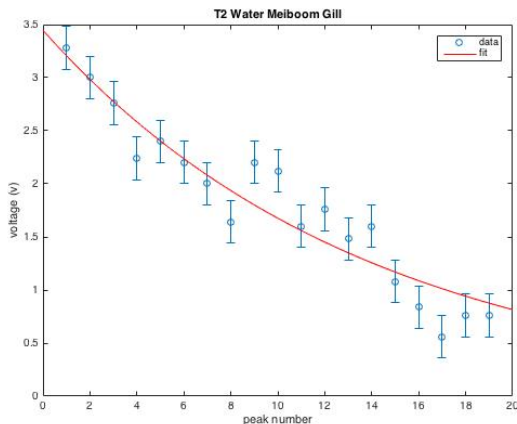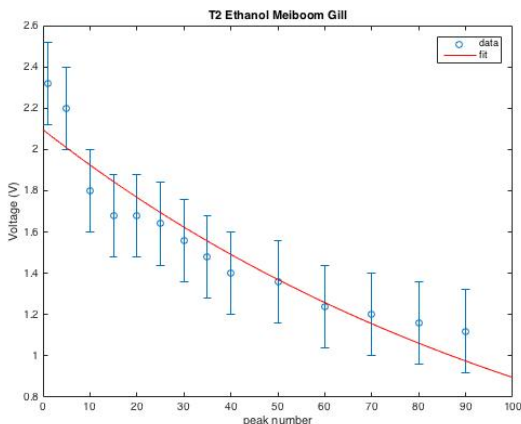
FIG. 14. T2, Meiboom Gill, Water

FIG. 15. T2, Meiboom Gill, Ethanol

than the signal obtained using spin echo when comparing 16 and 9. We performed all three methods on HMO and Water. The NMR analysis of water showed that the curve did not follow a simple decay as was the case for HMO, see 18.

In practice, other properties of materials, such a density, viscosity, and diffusion, affect the time it takes for the spins to relax into their lower energy states. For ethanol, we fitted the Meiboom Gill voltage curve to find T2. We considered the diffusion constant of ethanol in our calculated magnetic field gradient, finding the value to be $2.76 \pm 0.20 \mu T/mm$. Knowing this gradient allows us to examine the diffusion constant for ethanol, calculated to be $(4.56 \pm 0.41) * 10^{-7} m^2/s$.

The inhomogeneity of the magnetic field adds to the error in this experiment. This error is easily propagated in the Hahn and Spin Echo methods. The model for T1 and T2 could be improved by adding other features of the material into the analysis. In this experiment, we considered the diffusion constant of water and ethanol but did not include other properties such as viscosity.

VI.   CONCLUSION

We calculated the T1 time for HMO and the characteristic T2 times for HMO, water, and ethanol. The T1 of HMO was verified by calculating the number by finding the τ where the amplitude of the curve equals zero, used for solving (5), and then by fitting the full curve. The values are very close at 33 ± 0.05 ms and 34 ± 0.85 ms respectively. We confirmed that the Meiboom Gill method minimized the propagated error by alternating between π and $\pi/2$ pulses to give a more reliable measurement for T2 than the Hahn or Spin Echo methods. The Meiboom Gill T2 results of our experiment are summarized in Table 2.

Material	T2 (ms)	± (ms)	R^2
HMO	14.26	0.17	0.98
Water	13.89	2.80	0.90
Ethanol	117.65	29.30	0.89

ACKNOWLEDGMENTS

VII.   BIBLIOGRAPHY

[1] Effects of Diffusion on Free Precession in Nuclear Magnetic Resonance Experiements. Carr, Purcell. Physical Review. (1954).
[2] Modified Spin-Echo Method for Measuring Nuclear Relaxation Times. Meiboom, Gill. The Review of Scientific Instruments. (1958).
[3] NMR and MRI: Applications in Chemistry and Medicine. American Chemical Society National Historic Chemical Landmarks. (2011).
http://www.acs.org/content/acs/en/education/whatischemistry/landmarks/mri.html
[4] PS2 - A/B/C Instructor's Manual for Pulsed/CW NMR Spectroscopy. Teach Spin, Inc. Buffalo, NY. (2013).

VIII.   APPENDIX: FIGURES

VIII.1.   Oscilloscope Captures

IX.   APPENDIX: SAMPLE CODE

Sample code for fitting curves in MatLab
```
f = fittype('a*(1-2*exp(-x/T))');
lower=[0,0];
[F,G,H]=fit(tau, v,f, 'weights',err,'lower',lower);
```
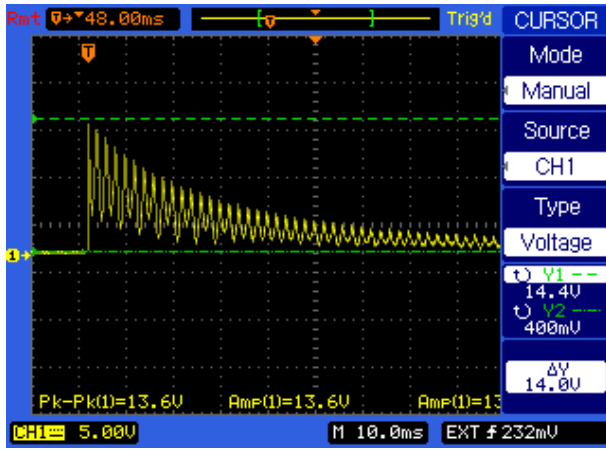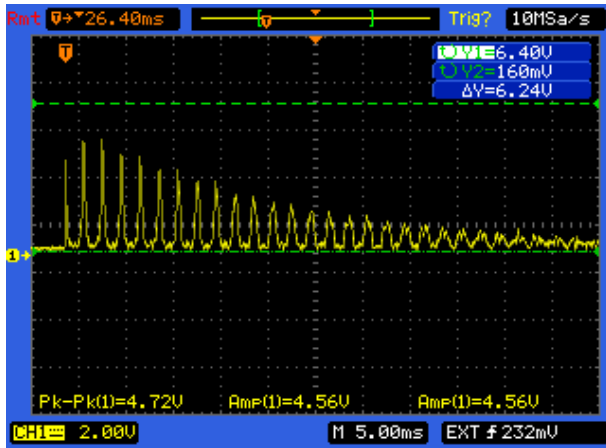
FIG. 16. T2, Meiboom Gill, HMO
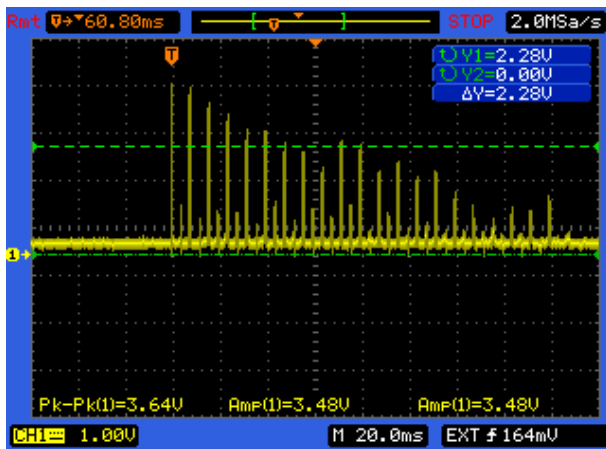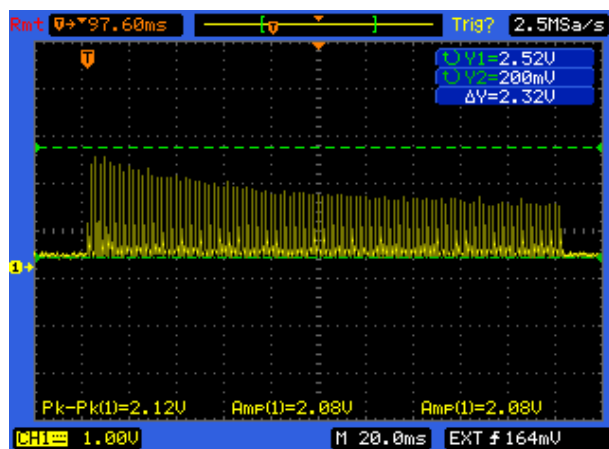

FIG. 17. T2, Spin Echo, Water

FIG. 18. T2, Meiboom Gill, Water

FIG. 19. T2, Meiboom Gill, Ethanol