Pulsed Nuclear Magnetic Resonance

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ABSTRACT

Pulsed nuclear magnetic resonance (PNMR) is a powerful technique which can be employed to study numerous properties of materials. This document details work conducted using PNMR to measure the spin-lattice relaxation times, T_1, and the spin-spin relaxation times, T_2 of various materials. Spin-lattice relaxation times were measured using a two pulse technique. Spin-spin relaxation times were measured using two techniques, Carr-Purcell and two-pulse spin echo. The materials analyzed included mineral oil, glycerin, and petroleum jelly.

INTRODUCTION

The pulsed nuclear magnetic resonance (PNMR) technique employs the phenomenon of nuclear magnetic resonance (NMR) primarily for the purpose of spectroscopy. Developed in 1950 by Erwin Hahn at the University of Illinois[1], PNMR has become a vital tool in the study of condensed matter. The technique has even been employed for medical imaging, with MRI machines using the phenomenon for quick noninvasive diagnoses.

Consider the hydrogen nucleus, a single proton, submitted to a uniform, constant magnetic field B_0 in the $\hat{z}$ direction. The proton possesses both angular momentum in the form of spin and a magnetic moment μ. As a consequence of exposure to the magnetic field $B_0\hat{z}$, the magnetic moment of the proton will precess about an axis parallel to the applied magnetic field in the $\hat{z}$ direction. The precession of the magnetic moment is shown in Figure 1.

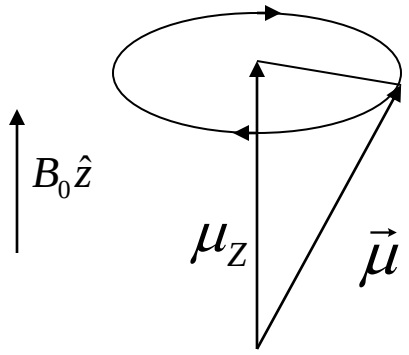

Fig. 1 The magnetic moment of the proton precesses about the applied magnetic field B_0. The PNMR technique takes advantage of the precession for the purpose of spectroscopy and imaging.

[1] Hahn, "Spin Echoes", Phys. Rev 80, 580-594 (1950).

The frequency at which this precession occurs is of the utmost importance for the deployment of the PNMR technique. The magnetic moment of the proton will be aligned either with or against the magnetic field $B_0\hat{z}$. The difference in energy between the two alignments is given by

$$\Delta U = \gamma\hbar B_0,$$

where γ is the gyromagnetic ratio of the proton equal to 2.675×10^4 radians/(Gauss-sec). The resonance frequency corresponding to this energy difference is then $\omega_0 = \gamma B_0$. All of the RF magnetic field pulses which the samples are submitted to operate at ω_0.

Pulsed nuclear magnetic resonance relies upon altering the direction of the magnetization of the protons in a sample. The magnetization is given by $\mathrm{M_Z} = (\mathrm{N_\uparrow} - \mathrm{N_\downarrow})\mu$, where $N_\uparrow$ is the number of proton magnetic moments aligned with the field B_0 and $N_\downarrow$ is the number of proton magnetic moments aligned against the field. In this experimental setup, using a constant field of $B_0\hat{z}$, the sample's magnetization can only be measured in the *x-y* plane. In order to measure any magnetization, the magnetization must be rotated into the *x-y* if it is not there already. It is the role of the pulses of rotating RF magnetic fields to rotate the magnetization for measurement.

In this experiment, the focus was placed on measurements of the spin-lattice relaxation time and the spin-spin relaxation time. The spin-lattice relaxation time, T_1, describes the amount of time necessary for an unmagnetized sample to align with an external magnetic field, in the $\hat{z}$ direction for this case. The spin-spin relaxation time, T_2, describes the decay of a magnetization present in the *x-y* plane in the presence of a constant magnetic field $B_0\hat{z}$. In this situation, the only field present in the *x-y* plane will be the magnetic fields produced by the protons themselves. The values of T_1 and T_2 were determined using PNMR techniques for mineral oil, glycerin, and petroleum jelly.

ELECTRONICS AND SETUP

The basic electronics for this experiment can be divided into three components: the pulse programmer, oscillator amplifier mixer and the receiver. The pulse programmer sets the lengths of the pulses sent to the sample, required for the redirection of the magnetization. The oscillator amplifier mixer was responsible for maintaining the correct resonance frequency of the precession, amplifying pulses from the pulse programmer, and mixing the resonance frequency with the output signal from the samples magnetization. The receiver picks up signals from the precession of the magnetic moments present in the sample.

The pulses sent from the pulse programmer were variable between lengths of 1 to 30 μs. The programmer was capable of delivering two different pulses with different lengths. The A pulse was the first pulse supplied, followed by a variable number of B pulses. The delay time on the pulse programmer corresponds to the length of time between the A pulse and the first B pulse. For multiple B pulses, the delay time was equal to half the time between consecutive B pulses. Also adjustable on the pulse programmer was the repetition time, which corresponded to the time between initiations

of the pulse sequence. Also present on the pulse programmer was a sync out used to trigger the oscilloscope for measurement of the magnetization of the sample.

The oscillator mixer amplifier had three primary responsibilities. Firstly, it was responsible for keeping the frequency of the rotating RF magnetic fields at the resonance frequency of the precession. The supplied frequency was adjustable, allowing for the user to counter temperature fluctuations resulting in changes in the constant magnetic field around the sample. The amplifier amplified the pulses from the pulse programmer into the 12 Gauss rotating RF magnetic fields responsible for redirecting the magnetization of the sample. Finally, the mixer multiplies the signal from the oscillator at the resonance frequency with the RF signal from the precessing magnetization in the sample.

Coils wrapped around the sample supplied the RF signal from the sample's magnetization to the receiver. The receiver picks up signals from the current induced in the coils from the precessing spins. The receiver is designed to operate at the resonance frequency of approximately 15 MHz. Also present in the receiver hardware is the detector. The detector sends an amplified precession signal to the oscilloscope. The signal out of the detector is used for the measurements of T_1 and T_2. A diagram of the electronics used is shown in Figure 2

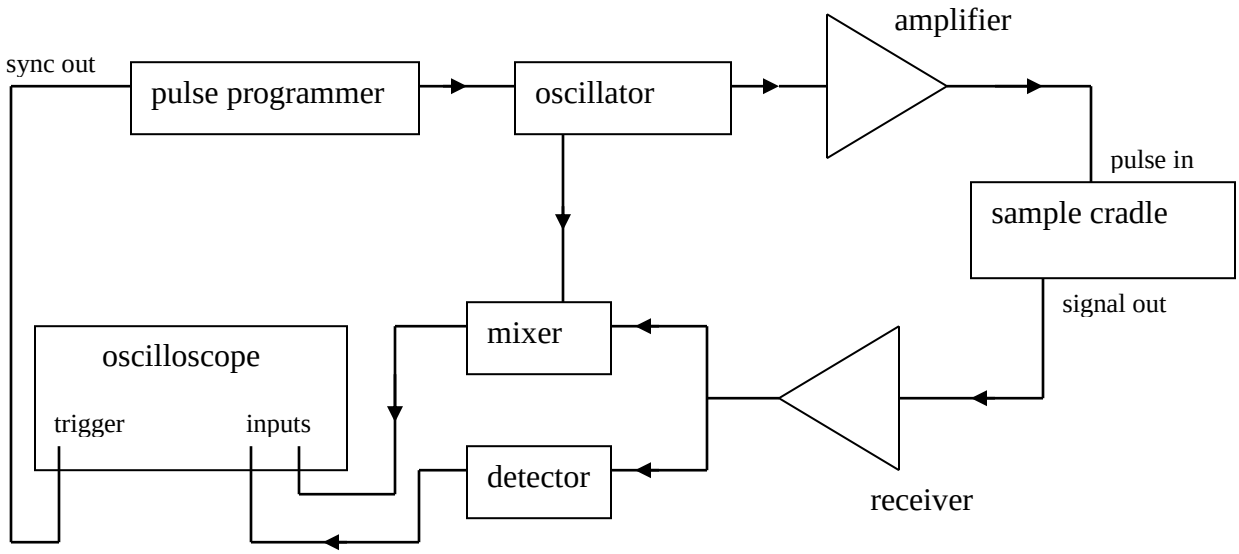

Fig 2. This circuit diagram depicts the electronics employed for the measurements of T_1 and T_2 using PNMR.

The samples were held in a cradle which supplied a constant magnetic field in the $\hat{z}$ direction at roughly 3.5 kG. Wrapped around the samples was a wire coil which picked up on precession signals in the *x*-*y* plane through induction. It is important to note that only magnetizations in the *x*-*y* plane can be detected. Helmholtz coils surrounding the sample supplied the RF magnetic field required for altering the magnetization of the samples. Figure 3 depicts the cradle used for taking measurements of the magnetization.

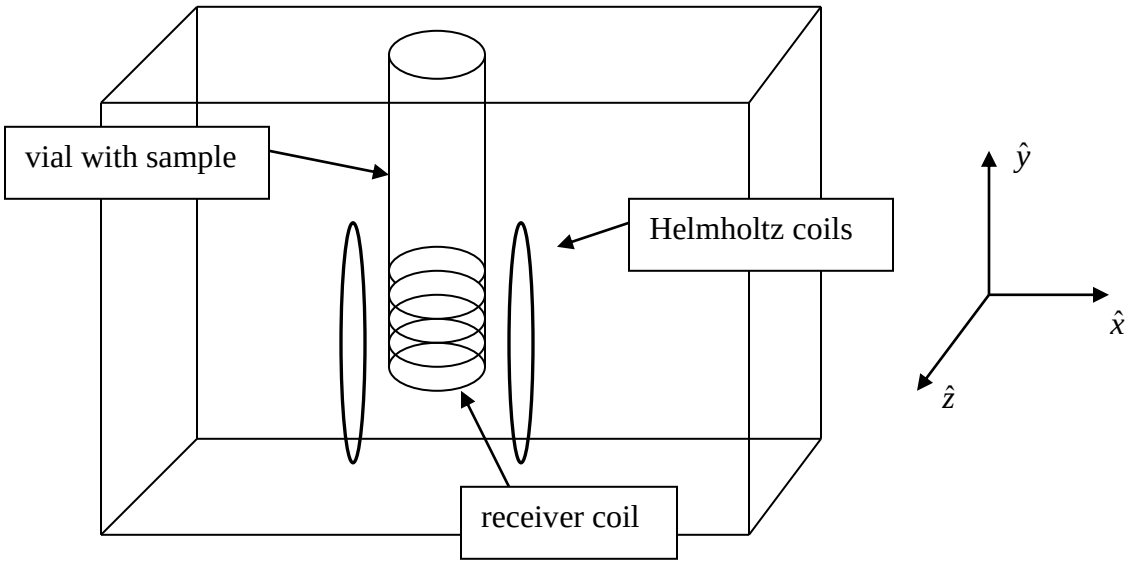

Fig 3. The cradle holds the sample in the constant magnetic field in the $\hat{z}$ direction. The receiver coils pick up the precession signal from the sample and relay it to the receiver. The Helmholtz coils supply the required pulses of magnetic fields for altering the orientation of the magnetization.

Due to temperature variations, the strength of the magnet supplying the constant magnetic field underwent fluctuations in strength. As a result, the field supplied by the permanent magnet changed, resulting in changes in the resonance frequency. When the field's strength changed, beats began appearing in the mixer signal since the oscillator no longer operated at the true resonance frequency of the spin precession. With a simple correction of the oscillator frequency, the beats were minimized and the oscillator would be once again operating at the resonance frequency.

PROCEDURE

The process of measuring T_1 and T_2 involved rotating the magnetization using the rotating RF magnetic field supplied by the Helmholtz coils around the sample. Two types of rotating magnetic fields were used, 90° and 180° pulses. When the rotating magnetic field is applied, the magnetic moments of the protons will precess about it. As the field rotates, the magnetization will be rotated from the $+\hat{z}$ direction to the $-\hat{z}$ direction. A 90° rotates the magnetization by 90° off of the $+\hat{z}$ direction and into the *x-y* plane. After a 90° pulse, a strong magnetization signal will be seen from the detector since the magnetization lies solely in the *x-y* plane.

A 180° pulse, which lasts twice as long as a 90° pulse, will rotate the magnetization by 180° into the $-\hat{z}$ direction. After a 180° pulse, no signal will be seen from the detector since the magnetization will lie solely in the $-\hat{z}$ direction and the detector cannot receive a signal if the magnetization is not in the *x-y* plane. Using these two pulses, the values of T_1 and T_2 can be measured.

The first measurement of T_1 involves varying the repetition time and is accurate to an order of magnitude. A 90° is first supplied to the sample, moving the magnetization into the *x*-*y* plane. The free induction decay (FID) curve appears on the oscilloscope from the detector output. The repetition time is the length of time before a new pulse sequence begins. Normally, the repetition time is set much longer than T_1, allowing the magnetization to return to its equilibrium value. If the repetition time is set to roughly T_1, the magnetization will not have the time required to return to equilibrium, zero in the case of being in the *x*-*y* plane. As a result, the largest value of the magnetization will be is 1/e its maximum value. By varying the repetition time, the value of T_1 can be determined to an order of magnitude. For all three samples, the value of T_1 was found to be on the order of 10 ms.

A better measurement of T_1 can be performed using a two pulse sequence. Initially, an A pulse of 180° pulse is applied, rotating the magnetization into the $-\hat{z}$ direction. After a delay time τ, a portion of the magnetization will have decayed back into the $+\hat{z}$ direction. A B pulse of 90° is then applied to rotate the magnetization into the *x*-*y* plane. Once in the *x*-*y* plane, the magnetization can be measured. The sequence of pulses used in the measurement is shown in Figure 4. In performing the measurement, the delay time τ is varied looking for a zero crossing. The magnetization in the $\hat{z}$ direction is given by

$$M_Z(\tau) = M_0(1-2e^{-\frac{\tau}{T_1}}).$$

Setting M_Z equal to zero and solving for T_1 gives $T_1 = \tau/\ln(2)$, where τ is the delay time at the zero crossing of the measured magnetization. A more precise measurement was carried out fitting the function above to a curve created by varying the delay time.

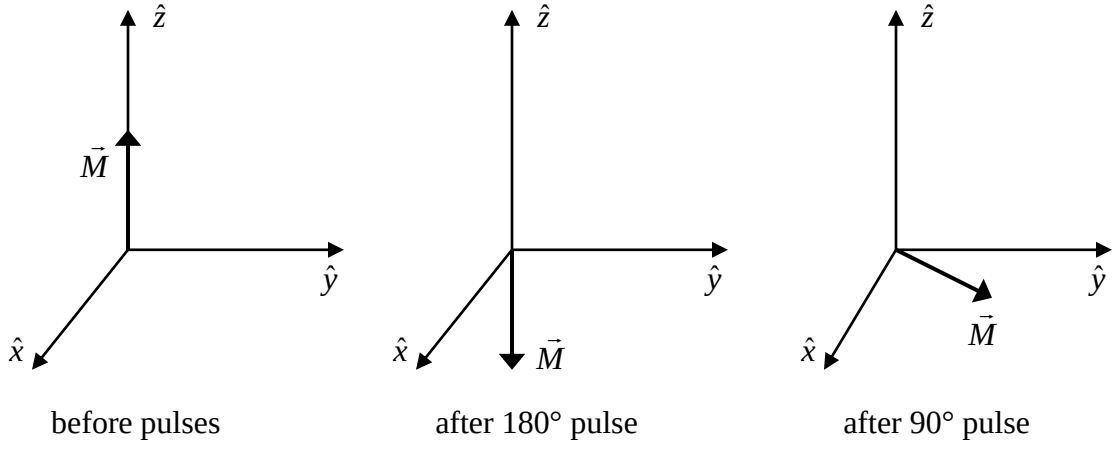

Fig. 4 The sequence of a 180° followed by a 90° pulse allows a measurement of T_1. The 180° pulse puts the magnetization into the $-\hat{z}$ direction. After letting the magnetization decay for a time τ, a 90° fires and rotates the magnetization into the *x*-*y* plane where it can be measured.

There are two primary methods for measuring T_2, two-pulse spin echo and the Carr-Purcell technique. In two-pulse spin echo, a 90° pulse is supplied followed by a 180° pulse. The 90° pulse puts the magnetization into the *x-y* plane. Once in the *x-y* plane, the magnetization begins to decay. After the delay time, the 180° pulse flips the magnetization by 180°. After the flip, the spins of the protons converge across the *x-y* plane again and an echo signal will be recorded by the detector. The strength of the echo pulse as a function of 2τ will follow an exponential decay with T_2 as the time constant. An oscilloscope image of an echo is shown in Figure 5.

The Carr-Purcell method makes use of multiple 180° pulses instead of one following the original pulse of 90°[2]. Much like the two-pulse spin technique, the magnetization in the *x-y* plane will decay exponentially as a function of the time between the first pulse and the echo. The time constant for a fit will also produce T_2 as the time constant.

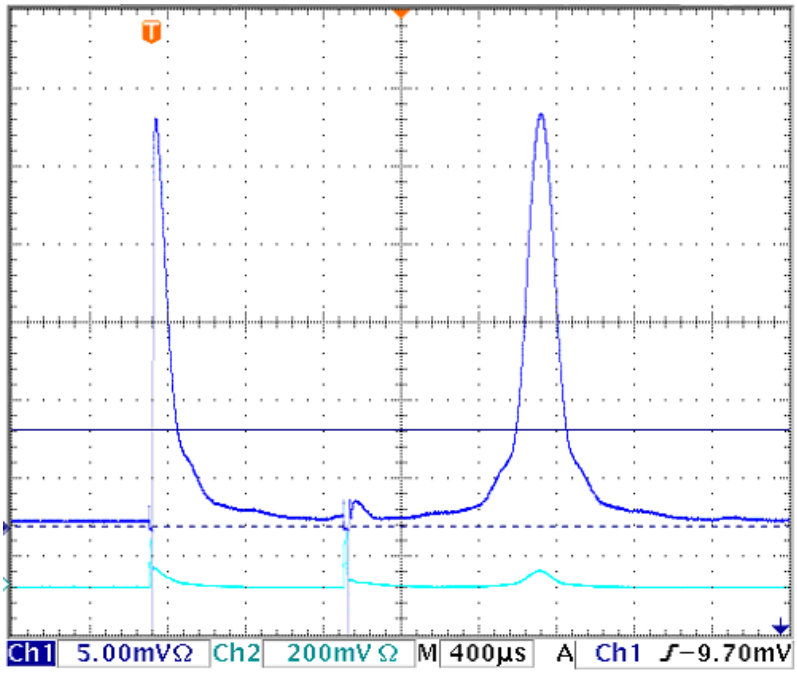

Fig. 5 The two-pulse spin echo and the Carr-Purcell techniques for measuring T_2 both make use of echoes following 90° and 180° pulses. The first spike corresponds to the FID following the 90° pulse. The middle hump corresponds to the 180° pulse. The last spike is the echo formed as the spins of the protons again converge on the *x-y* plane.

ANALYSIS AND RESULTS

The first measurement for each sample carried out was a precise determination of T_1. As described in the procedure, the magnetization will essentially follow an exponential as it transitions from pointing in the $-\hat{z}$ direction to the $+\hat{z}$ direction. The data for all three samples was fit with the following function,

[2] Meiboom and Gill, "Modified Spin-Echo Method for Measuring Nuclear Relaxation Times", Review of Science Instruments 29, 688-691 (1958).

$$M_Z(\tau) = M_0(1-2e^{-\frac{\tau}{T_1}}) + B,$$

with background term *B*. A fit of the data for the petroleum jelly sample appears in Figure 6. The T_1 values measured for all samples are shown in Table 1.

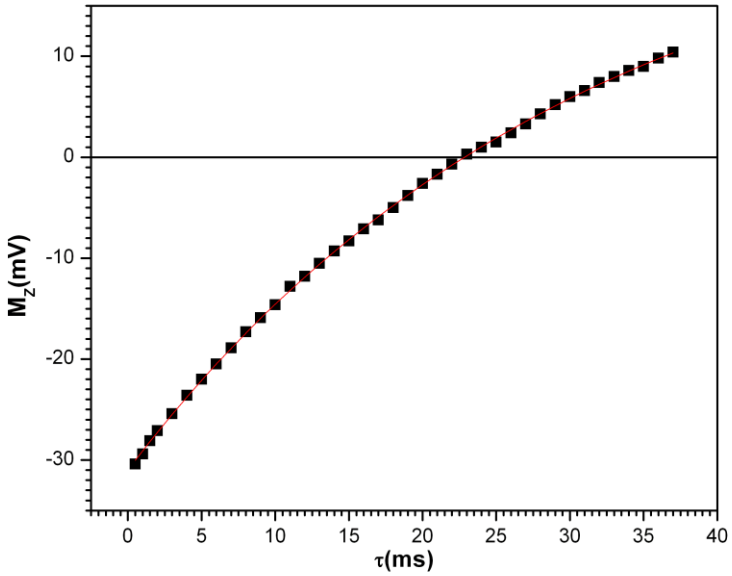

Fig. 6 The curve for petroleum shows a zero-crossing at a delay time of roughly 22 ms, corresponding to a T_1 value of 30.5 ms.

Table 1: The measured values of T_1 for all samples

sample	T_1 (ms)
mineral oil	20.3 ± 0.4
glycerin	47.7 ± 1.3
petroleum jelly	30.5 ± 0.5

As mentioned in the procedure section, the magnetization curves for both the two-pulse spin echo and the Carr-Purcell technique will both follow exponential decay curves. In the case of the two-pin echo technique, the exponential as a function of 2τ will produce a value of T_2 as the time constant. For the two-pulse spin echo technique, the curve was fit to

$$M_{x-y}(2\tau) = M_0 e^{-\frac{2\tau}{T_2}} + B,$$

where *B* is once again a background term. The data and fit are shown in Figure 7 for mineral oil. The results for all samples are shown in Table 2.

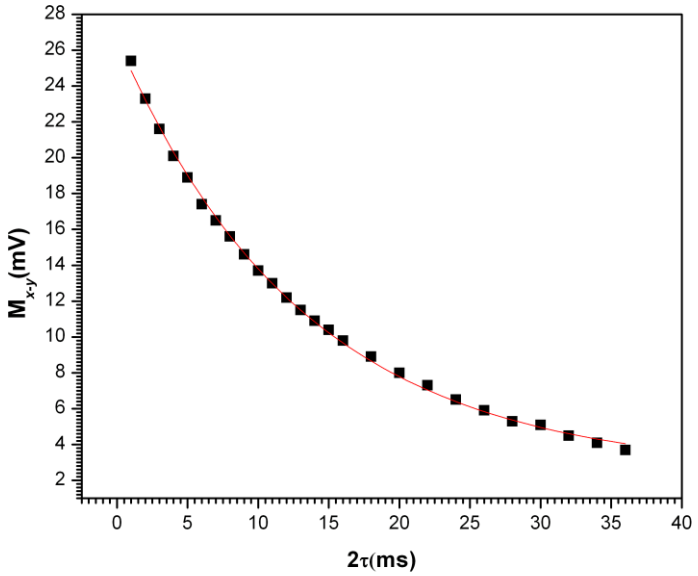

Fig. 7 The fit for mineral oil using an exponential decay curve produced a T2 value of 39.1 ms.

The Carr-Purcell method presents a standard exponential decay operating as a function of τ with T_2 as the time constant. A fit for the glycerin data appears in Figure 8 and the measured values for all samples appear in Table 2.

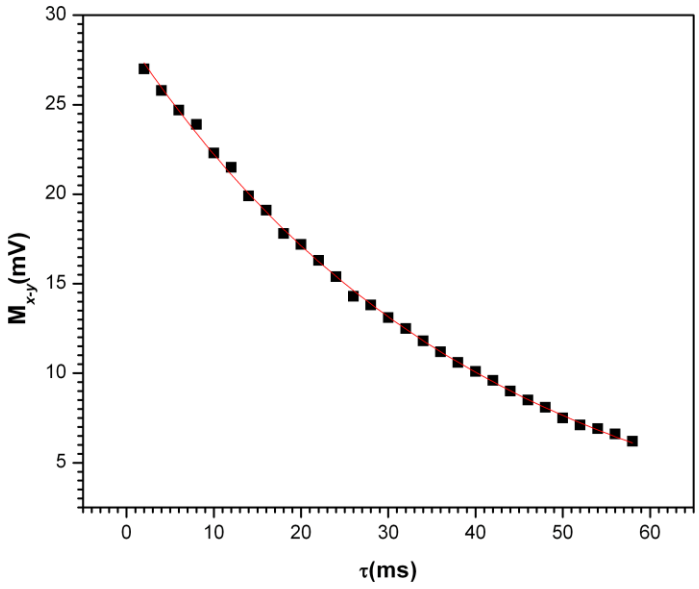

Fig. 8 The fit of an exponential decay curve for glycerin yielded a T2 value of 39.1 ms.

Table 2: The values for T_2 for all samples

sample	two-pulse spin echo T_2(ms)	Carr-Purcell T_2 (ms)	average T_2 (ms)
mineral oil	13.2 ± 0.3	12.2 ± 0.4	12.8 ± 0.2
glycerin	39 ± 1	40 ± 1	39.5 ± 0.7
petroleum jelly	17.4 ± 0.3	18.3 ± 0.6	17.6 ± 0.3

CONCLUSIONS

This experiment sought out to measure the spin-lattice relaxation time T_1 and the spin-spin relaxation time T_2 of various materials using PNMR techniques. The values of T_1 were determined by using a two pulse sequence, 180° then 90°. The spin-spin relaxation times were determined using two techniques, Carr-Purcell and two-pulse spin echo. The values of T_1 and T_2 were successfully determined for samples of mineral oil, glycerin, and petroleum jelly.