Letter - application note

Long title: Transient Effect Determination of Spin Lattice (TEDSpiL) Relaxation Times using continuous wave NMR

Short title: T1 from CW-NMR transient effect (TEDSpiL)

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1. Introduction

The phenomenon of nuclear magnetic resonance (NMR) was first demonstrated as continuous wave (CW) NMR [1-7] which become unpopular due to the advantages offered by pulsed NMR. Conceptually more simple, but more challenging to reliably determine relaxation parameters from, for half a century CW-NMR has virtually been consigned to the undergraduate laboratory and magnetometers. In a typical CW-NMR system a sample is placed in a coil in a static magnetic field. The coil forms part of an oscillator circuit and sweep coils are used to vary the static field by a small amount. As the swept magnetic field corresponds to the Larmor frequency, the amplitude of the oscillator output rapidly falls, providing a shape and signature characteristic of the NMR spin-spin relaxation time T_2. CW-NMR has not been a particularly active topic of research for more than 50 years due to the advantages of pulsed NMR for measuring relaxation times. Some interest in the electronics development, in particular the development of oscillator circuits [8-10], has taken place and CW-NMR is used as the basis of sensitive magnetometers [11-13]. CW NMR has also enjoyed some success as an imaging tool for use on samples with very short T_2 relaxation times [14,15]. Commercial continuous wave NMR systems can be readily purchased although these are primarily used as teaching tools. In a 1981 article [16], Firth describes a technique to directly observe the spin-lattice relaxation time T_1 using a CW NMR system following recovery from saturation. In our work we have observed, using high speed data capture, that simply moving from static field only, to static field plus sweep coils, in a commercial CW NMR system resulted in a similar settling time related to the spin-lattice relaxation time. We corroborate our measurements against pulsed magnetic resonance on the same system and provide a means by which the continuous wave system can be used to determine the Spin Lattice relaxation times of unknown samples with greater simplicity and speed than is possible with the equivalent pulsed MR technique.

2. Experimental

A commercial continuous wave NMR setup from LD Didactic GmbH (fig 1) was used for all experiments (consisting of NMR supply unit (514 602), NMR probe (514 606) including sample coil, sweep coils and yoke, U-core (562 11) and two electromagnet coils (562 131)). The system was designed to operate between 16.0 MHz and 19.5 MHz by varying the current supplied to the electromagnet coils. The high current required to operate the magnet in that field range however caused significant heating of the samples during measurements affecting

the value of T_1. This was overcome using an additional 1m of coaxial cable between sample coil and oscillator causing the oscillator to operate at around 12MHz and requiring only 2.2A to generate the static magnetic field of the correct magnitude. Although the sweep coils would normally be powered by the NMR Supply Unit, the analogue output of a data acquisition card (NI USB-6211, National Instruments, TX, USA) was fed to a power amplifier built from a 2N3055H power transistor and LM358N buffer amplifier providing a gain of five. Data was collected using the same data acquisition device operating at 500kS/s integrated with a Labview program to generate appropriate waveforms and collect the resulting NMR signal. The analogue output of the USB-6211 produced a saw-tooth voltage waveform of maximum amplitude 1.25V and a frequency of 50Hz in five second bursts with a recovery time delay between bursts. All data were collected without changing the amplitude setting on the NMR unit or the current supplied to the static magnetic field coils. The samples used consisted of a range of PDMS oils of different viscosities, from 2cS to 30000cS, and different concentrations of copper sulphate solutions, from 5uM to 750uM, giving T_1 values in the range 0.5s to 2s. The T_1 values were measured on the same electromagnet (with the same current) and RF coil, with additional tuning and matching capacitors, using a pulsed NMR spectrometer (Kea^2, Magritek, NZ) running a stock inversion recovery pulse sequence with CPMG echo detection.

3. Results and Discussion

Figure 2 shows the NMR signal for a single sweep with the main peak followed by the characteristic 'wiggles' and a subsequent smaller peak on the fly-back of the saw-tooth (sketched over the data). A Labview VI produces the modulus of the data before finding the maximum value within each sweep. An example of the result of this process is shown in figure 3. The curve fitting routine in Labview then performs an exponential fit before writing out the exponential coefficients (amplitude, decay time (T_x) and noise) to a file. Before repeating the experiment, the system must be allowed to re-equilibrate. The time allowed for this to take place is known as the recovery time. The minimum recovery time required was determined experimentally by measuring a100uM aqueous copper sulphate solution 50 times for recovery times from 1s to 50s (data not shown). The standard deviation in the exponential fit was high for the short recovery times but reduced rapidly as the time was increased. The plateau was found at 15 seconds. To allow for a safe margin of error, 20s was chosen for use in all subsequent measurements. Figure 4 shows the T_1 relaxation time as measured by the pulsed system plotted against the exponential fit decay time from the CW-MR data using 50 averages. Whilst some scatter can be seen, there is a clear linear correlation between the two. It should be noted that the Tx value we determine is not the same as the value of T_1 in seconds. There are a number of parameters which change the gradient of this relationship including the amplitude setting of the oscillator. For the data presented we used the central 'sweet spot' where all the samples presented a sustained oscillation without changing the amplitude setting. As the relationship between T_1 and T_x is linear, unknown measurements are easily collapsed to a gradient of 1 by using two reference samples (one high and one low T_1 value) to provide the calibration factor.

Conclusion

In this work we have revisited a qualitative MR relaxation technique with modern data capture equipment to provide a rapid, low cost, quantitative measurement of relaxation times using the transient response which occurs following the start of a field sweep in a commercial CW-NMR system. We have demonstrated that a simple modification to such a system can lead to a method of determination of the spin-lattice relaxation time T_1 when a measurement commences with two known calibration samples. The advantages over pulsed measurements are primarily in the cost of the equipment with the setup presented here costing less than a tenth of the cost of the spectrometer required for an equivalent pulsed system.

Acknowledgments

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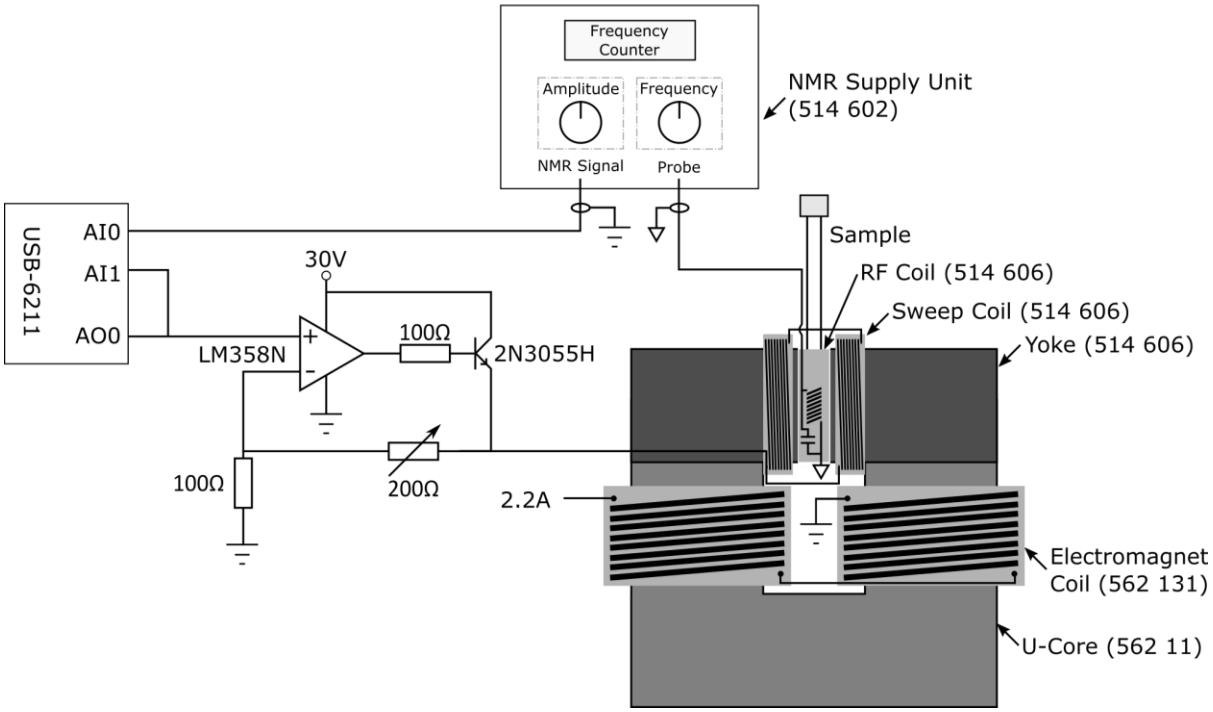

Figure 1. The modified commercial continuous wave equipment.

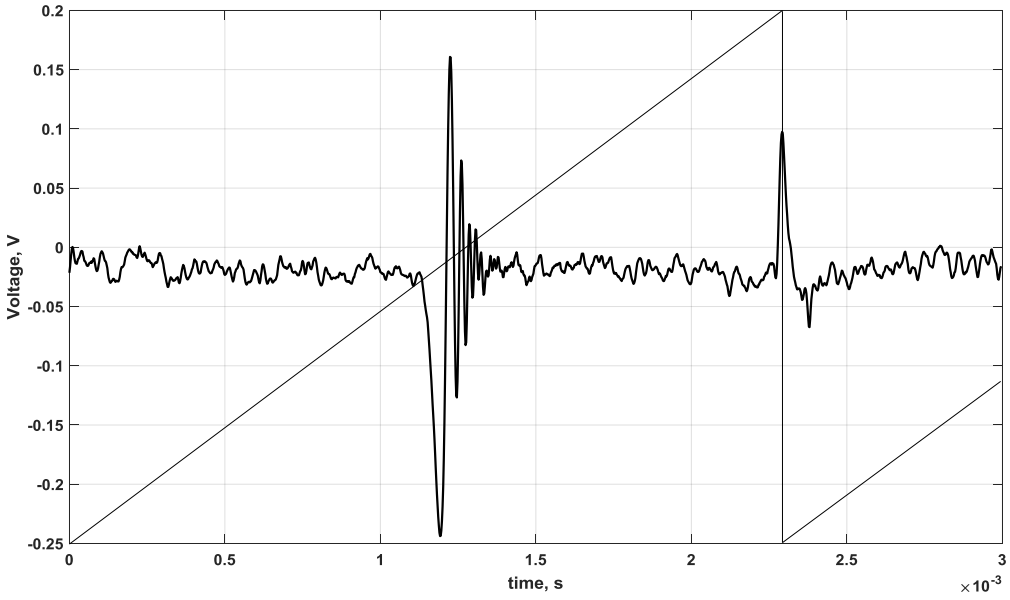

Figure 2. The NMR output signal for a single sweep of the saw-tooth applied (overlaid without scale) to the sweep coils also showing a smaller peak as a result of the fly-back.

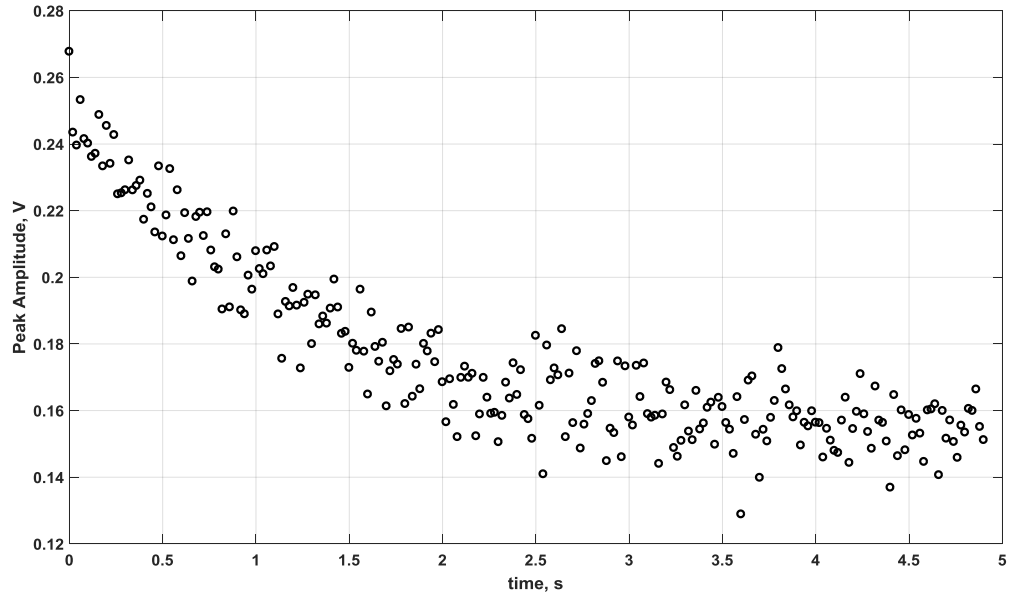

Figure 3. The peak amplitude of the NMR signal for each sweep of the saw-tooth shown for a five second burst. The Labview program fits an exponential to these data to give a characteristic time referred to here as T_x.

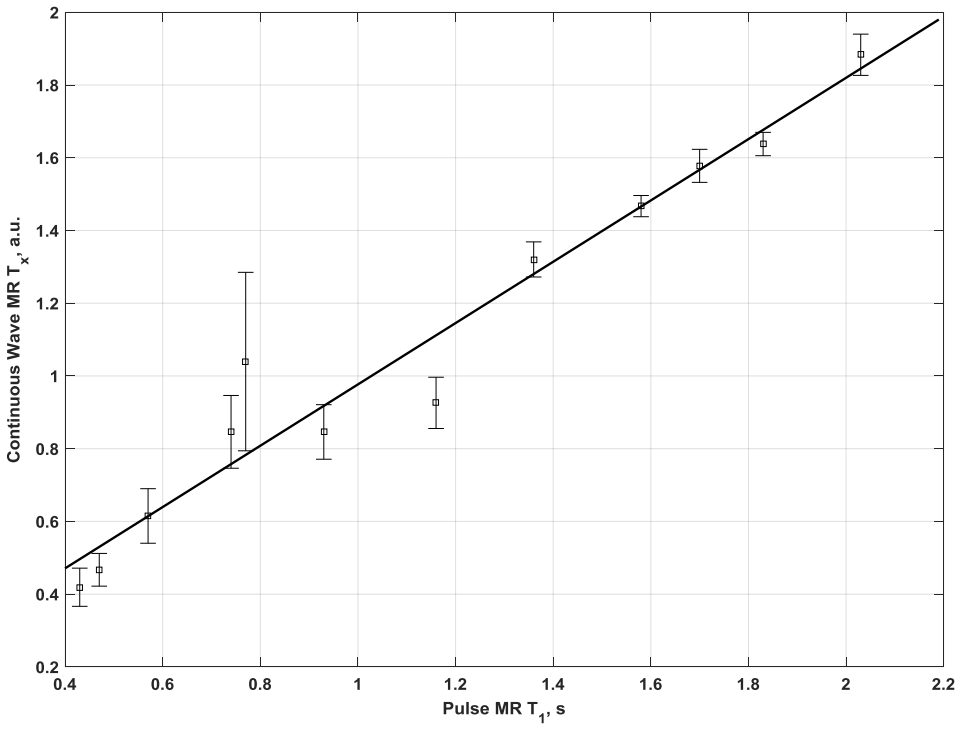

Figure 4. The value to Tx plotted against the value of T1 as determined by pulsed NMR.

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