

## NMR

# Determining Relaxation with the Inversion-Recovery Experiment

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### Innovation with Integrity

NMR experiments typically consist of RF pulses followed by a period of recording the resulting NMR signal. Very often, several such sequences are executed after another - for instance to increase the signal to noise ratio by averaging. It is important to wait with the application of a new pulse until the RF signal from the previous pulse has decayed.

The relaxation rate of a given sample determines the maximum repetition rate that can be realized to acquire a series of scans. Large relaxation rates make high repetition rates possible which increases the number of scans that can be accommodated in a given time and thereby increases the signal to noise.

As another example, quantitative NMR (qNMR) depends on thorough relaxation. Since most qNMR spectra are obtained from several scans, sufficient relaxation time is needed to assure the acquisition of uncompromised signals and integrals.

### The Relaxation Time Constant T1

When an NMR sample is introduced in an NMR magnet, an equilibrium magnetization builds up in the sample. This process is governed by a characteristic time constant T1, which is referred to as longitudinal relaxation rate or spin-lattice relaxation.

If the equilibrium magnetization is then disturbed by RF pulses and the system subsequently returns to its initial condition, the same relaxation mechanism applies again.

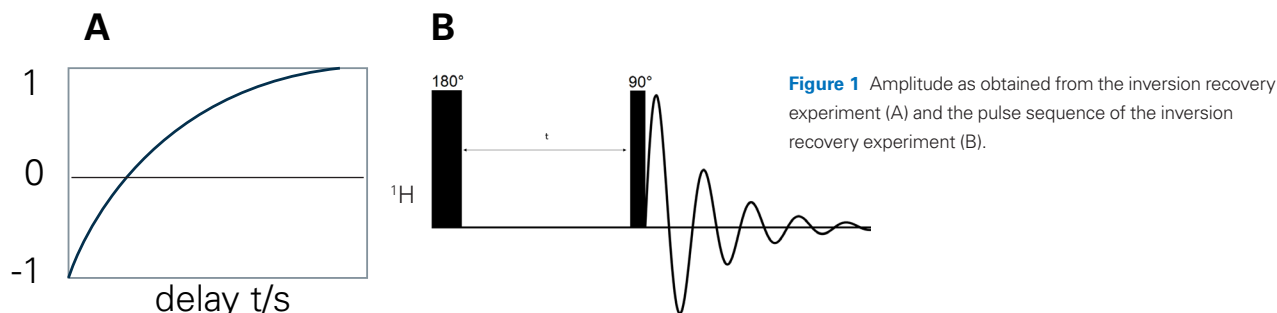
For liquid state NMR, the relaxation constant T1 is on the order of seconds and depends on various sample-specific properties such as:

- The sample viscosity
- The solvent
- Dipolar interactions
- The sample temperature

## The Inversion-Recovery Experiment

The inversion-recovery experiment is a two-pulse NMR experiment which is commonly used to measure the relaxation constant  $T_1$ .

The experiment consists of a  $180^\circ$  pulse, a relaxation delay  $t$  and a  $90^\circ$  read pulse (Fig. 1).



**Figure 1** Amplitude as obtained from the inversion recovery experiment (A) and the pulse sequence of the inversion recovery experiment (B).

The experiment is usually recorded as a series of several scans while varying the relaxation delay  $t$  from scan to scan, starting with a short delay, and then moving on longer delays. A typical inversion-recovery experiment will then lead to the following result (the underlying physics are explained in more detail below):

- For the first scan, a short relaxation delay  $t$  is chosen which leads to a negative signal (Fig. 1A).
- Upon increasing the relaxation delay the signal vanishes. This happens when the relaxation delay equals the relaxation time constant  $T_1$ .
- Upon further increasing the relaxation delay, the signal turns positive.

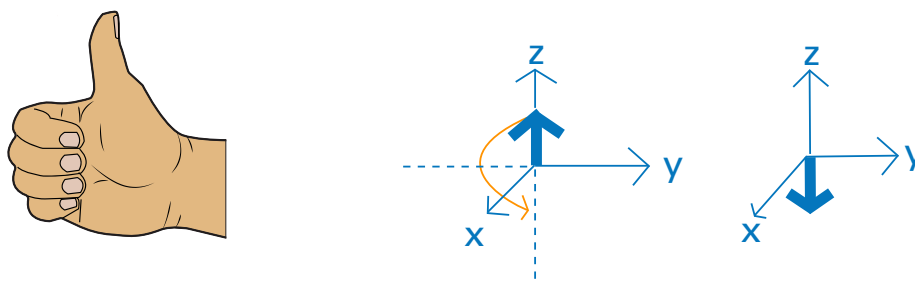
The  $T_1$  time constant can thus be easily determined from the zero-transition of the inversion-recovery experiment.

## The Evolution of the Magnetization During the Experiment

The amplitude behavior of the inversion-recovery experiment can be rationalized from the evolution of the magnetization while the pulse sequence is executed. In the 3-dimensional space (with  $x$ ,  $y$ ,  $z$  coordinates), Bloch's equations govern the spin dynamics and explain how RF pulses interact with the equilibrium magnetization and how the magnetization evolves over time. The result of this interaction is given by a vector product between the magnetization and the RF pulse and can be illustrated with a simple rule that is referred to as the "right-hand rule". The three phases of the inversion-recovery experiment are the following:

### 1) Creation of the Non-Equilibrium State

To probe the relaxation, a non-equilibrium state is created by applying a  $180^\circ$  x-pulse (this is a RF pulse with x-phase). Applying the right-hand rule, the thumb is oriented towards the rotation axis. For an x-pulse, this rotation axis is the x-axis. The remaining four fingers of the right-hand now all point in the same direction. This is the direction of the rotation of the magnetization. The  $180^\circ$  pulse moves the magnetization from  $z$  via  $-y$  to  $-z$  (Fig. 2). Note that the final state ( $-z$ ) would be reached regardless of the pulse phase.

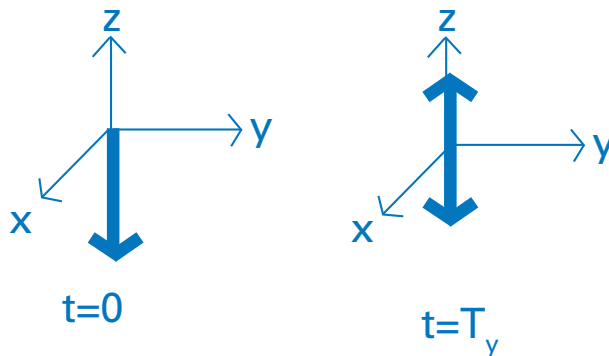


**Figure 2** Right-hand rule and rotation of the magnetization from  $z$  to  $-z$ .

## 2) Relaxation Delay

During the relaxation delay, the magnetization at  $-z$  decays. As the decay progresses, the magnitude of the magnetization along  $-z$  decreases and equilibrium magnetization along  $+z$  builds up (Fig. 3).

The experiment is repeated several times while incrementing the duration of the delay to sample the build-up curve.



**Figure 3** After the  $180^\circ$  pulse, the magnetization is located at  $-z$ . During the relaxation delay, it relaxes to  $z$ .

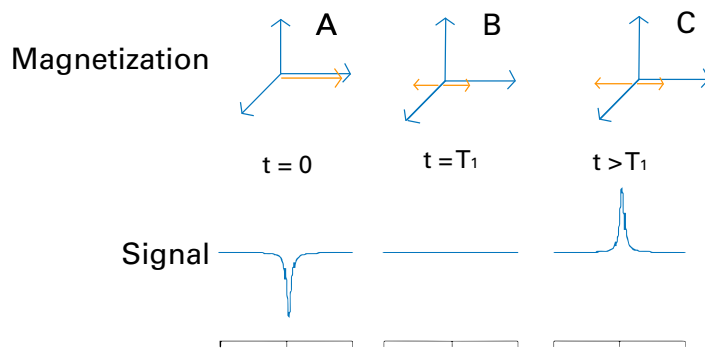
## 3) Readout Pulse

The readout pulse is a  $90^\circ$  x-pulse. Applying the right hand-rule, the thumb points in the direction of the rotation axis, which is again the x-axis. The remaining fingers point in the direction of the rotation. The  $90^\circ$  pulse does the following:

- 1) It moves the magnetization that remains along  $-z$  from  $-z$  to  $y$  and
- 2) it moves the longitudinal magnetization along  $+z$  from  $+z$  to  $-y$ .

Magnetization in the  $xy$ -plane can be detected. By definition, magnetization at  $-y$  creates a positive NMR signal. At the end of the pulse sequence, the following scenarios can thus be distinguished:

- 1) For a short relaxation delay (e.g.  $t = 0$ ), the entire magnetization is transferred to  $y$  which creates a negative signal with the maximal intensity (Fig 4A).
- 2) If the relaxation delay is equal to the  $T_1$  constant, equal amounts of  $y$  and  $-y$  magnetization cancel each other, leading to no detectable signal (Fig 4B).
- 3) For a long relaxation delay  $> T_1$ , the sum of  $y$  and  $-y$  magnetization is negative and leads to a positive NMR signal (Fig 4C).

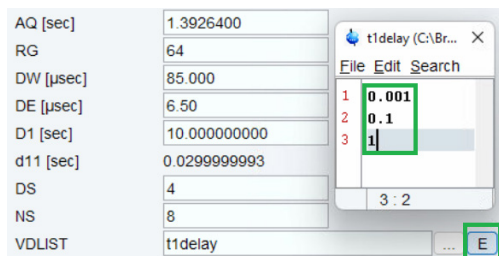


**Figure 4** For relaxation delays  $< T_1$ , negative signal amplitudes are obtained (A). If the relaxation delay equals  $T_1$ , a zero signal is obtained (B). For relaxation delays  $> T_1$ , positive signal amplitudes are obtained (C).

## Determining T1 on an AvanceCore

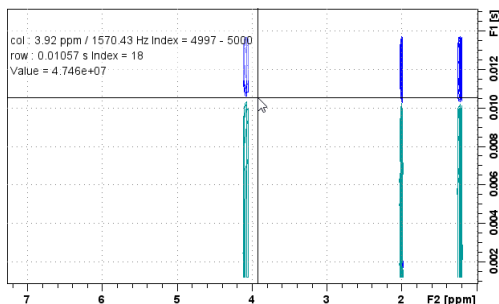
The T1 relaxation constant can be determined with the parameter set PROTONT1.

- Create a new experiment using the parameter set PROTONT1.
- Set the pulse parameters by typing "getprosol" in the TopSpin command line.



**Figure 5** A variable delay list (VDLIST) is used to set relaxation delays in the TopSpin software.

- Define a set of relaxation delays in the acquisition parameter tab. Click on Edit next to VDLIST and enter a set of relaxation delays. In the example shown in Figure 5, three different relaxation delays (0.001, 0.1 and 1) are entered in VDLIST.
- Continuing with this example, three T1 experiments will be recorded in a pseudo 2D experiment. Hence, the number of increments in the indirect dimension is set to three (TD(F1)).
- The pseudo 2D spectrum is Fourier transformed along F2 by typing "xf2" in the TopSpin command line.



**Figure 6** Pseudo 2D experiment for the determination of the T1 time constant recorded on ethyl acetate in  $\text{CDCl}_3$ . The zero-crossing is obtained at the increment 18 which translates to a T1 time of three seconds.

The T1 experiment shown in Figure 6 was recorded with a total of 22 different delays, i.e. with a correspondingly larger number of entries in VDLIST and a correspondingly larger number of increments in the indirect dimension. The data was acquired on a sample of 10% (v/v) ethyl acetate in  $\text{CDCl}_3$ . After Fourier transformation, the zero-crossing is found at the index increment 18. According to the VDLIST, increment 18 corresponds to a relaxation delay of three seconds. Hence, the T1 time constant for ethyl acetate is three seconds.

