NMR NOTES #17
Measuring T_1 Values

Measuring T_1 values requires the use of acquisition arrays. If you are not familiar with using these arrays, please see NMR Note #16 which discusses their use. Inversion-recovery is generally considered to be the workhorse technique of T_1 measurements - it is robust and relatively fault tolerant. It requires calibrated 90° and 180° pulses, but small errors will not be fatal. You should calibrate pw90 on your sample before you start, however.

Measuring T_1 requires making an estimate of the T_1 value, both to insure sufficient time between pulses for the spin system to relax back to equilibrium, and to choose sampling times for the recovery. Too long a delay is not a problem, the experiment simply takes longer than necessary. If the delay is too short, the measured T_1 value will appear shorter than its actual value. This will require making a new T_1 estimate and running the experiment again. It is probably more time efficient to over estimate T_1 and only run the experiment once than to have to repeat the entire experiment several times.

The standard s2pul pulse sequence is used to implement the Inversion-recovery T_1 measurement. The **d1** delay time is set to 5*T1 to allow complete relaxation between pulses. the **p1** pulse, not normally used, is set to 180° to invert the magnetization along the -Z axis. This provides the perturbation of the spin system. Immediately after the inversion pulse, the magnetization begins returning to equilibrium along the +Z axis. At no time during this process is there coherent magnetization in the X-Y plane. By applying a 90° observe pulse at some time τ after the 180°, we can sample the magnitude of the magnetization along the Z axis. The **d2** delay is used to set this τ delay, and **pw** is used as the observe 90° pulse. By running a series of spectra at different τ values, we can plot the exponential recovery of the magnetization form the -Z axis to the +Z axis.

The processing software requires at leas 3 data points in order to fit the exponential recovery curve, but it is normal to use at least 6 or 8 different τ values to insure a good fit. In order to characterize the exponential recovery well, we should have data points sampling the magnetization where it is changing most rapidly. Points at times less than $0.1*T_1$ (fully inverted) or greater than $3*T_1$ (mostly recovered) don't give much information about the shape of the recovery curve. Consequently, given a sample with a range of T_1 values, you would want to choose a set of τ values ranging from a tenth of the shortest value to three times the longest value. In order to get a good distribution of values, you can either double the τ value at each step or use a 1,2,5 pattern. Assume that you have a range of T_1 values from 1 to 10 seconds, the τ values should range from 0.1 to 30 seconds. Either of these arrays would be fine:

Doubling: d2=0.1,0.2,0.4,0.8,1.6,3.2,6.4,12.8,25.6,51.2 (51.2 optional)

1-2-5: d2=0.1,0.2,0.5,1,2,5,10,20,50 (50 optional)

After the data is acquired and transformed, it can be fit to an exponential recovery curve and T_1 calculated. The first step is to get a line listing that includes all of the lines of interest in the spectrum. This is normally done on the last array element where (hopefully) all of the peaks are mostly recovered with good signal to noise. Set a threshold and use **dll** to display a line listing. This line listing is used to select peaks for exponential analysis. Next, the **fp** command (Find Peaks) is used to find the peak intensities from each spectrum in the array for each peak requested. Thus, **fp(1,3)** would extract peak intensity information from all 9 or 10 spectra in the data array for the frequencies given for lines 1 and 3 in the line listing. This information is written out to work file in hte current experiment directory. The **t1** or **t1s** command is then used to fit this data to an exponential recovery curve and display the results. The **t1s** command has a shorter output format, without all of the fitting details. Important things to look at here are the error on the T_1 values and the quality of the exponential fit. The **expl** command can be used to display the fit on the screen, but only data for the first 3 lines will be displayed. Also the S_0 and S_∞ values should be equal in magnitude and opposite in sign. These values are no longer displayed as part of the fitting data (although they should be), but S_0 is the intensity at time zero and S_∞ is the intensity at equilibrium. Both of these can be estimated from the exponential plot display. If the S_0 is not fully negative, it may be an indication that the 180° inversion pulse is not calibrated properly. If there is a data point that is far off the fit and seems to be erroneous, it can be removed from the fit calculation with the **dels** command (DELete Spectrum). For instance , **dels(3)** would remove the 3rd τ value from the calculation. The only way to restore a deleted data point is to re-run the **fp** command.

Hardcopy output of the spectral data can be done with the normal array plot commands. The exponential recover curves can be plotted with the **pexpl** command. Hardcopy of the T_1 analysis data can be done using the **printon t1 printoff** command sequence. This redirects the output of the **t1** command to your selected printer device.

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