Measuring $^1$H $T_1$ Values in IconNMR  
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**Summary**

Knowledge of spin-lattice relaxation times, $T_1$, is important in many experiments in NMR:

a) **Quantitative assays** and **analyses of reaction kinetics** require having accurate knowledge of relaxation times. In particular the *longest $T_1$ of all protons of interest* must be known to properly optimize acquisition parameters and avoid systematic errors.

b) All **NOESY** and **ROESY** experiments require at least semi-quantitative knowledge of proton $T_1$ values for proper setup and interpretation.

c) **All NMR experiments** require qualitative knowledge of the *longest $T_1$ of the nuclei of interest* to properly setup repetition rates, typically equal to $d_1+aq$.

$T_1$ values accurate enough for b) and c) above can be obtained by an inversion-recovery null-crossing measurement. These were performed with regularity on our Varian spectrometers, with the array function in vnmr making such measurements straightforward. Similar procedures can be done in TopSpin (although to be honest, not as easy a manner), as detailed in a companion document: [http://www.chem.wisc.edu/~cic/nmr/Guides/Ba3vug/AV3_1H-T1null.pdf](http://www.chem.wisc.edu/~cic/nmr/Guides/Ba3vug/AV3_1H-T1null.pdf)

In this document, a simple method for obtaining *quantitative* $T_1$ values using IconNMR is presented.

**A. IconNMR's Inversion-Recovery Experiment – Setup and Acquisition:**

1. In IconNMR, **ADD** the **H1_T1invrec.UW** experiment.

2. In the main menu, select **PARAMETERS** → **EDIT ALL ACQUISITION PARAMETERS**

![IconNMR's Inversion-Recovery Experiment](image)

3. IconNMR will switch you into the **ACQUPARS** panel in TopSpin; you will see **ALL** parameters. Press $\text{F1}$ or type $\text{ased}$ to reduce the list to a reduced set (see Figure 1 next page).

4. Check the VDLIST by clicking $\text{puted}$ and if not already set, select **tluwchem** from the **SOURCE** = `/home/topspin3.1/uwchem/lists/pp` (in the upper right dropdown). Click **Set selected item in editor** then **Close** at the lower right. The list can be viewed and edited using the $\text{E}$ button.

5. The list of delays is a good one for typical organic compounds under normal atmosphere. See NMR staff for more assistance if you are working with very small compounds, paramagnetism, or samples sealed under inert atmospheres. Otherwise the default list should work ok.

6. The # of values in VDLIST must equal $\text{TD}[F1]$ (see Fig 1). On the command line, use $\text{TD}$.  

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Figure 1: **All** ACQU/PARS parameters.

![Image of ACQU/PARS parameters](image1.png)

- **2D exp switch to ased**
- **TD[F1] = # of vd values**
- **# 1D spectra**
- **# points in T₁ curve fits**

![Image of ACQU/PARS parameters](image2.png)

- **NS = 1 or 2, DS = 0 is fine**
- **select VDLIST and view/edit with E button**

Figure 2: **or ased reduced ACQU parameters.**
7. $D_1 = 15 \text{ sec}$ is the default. This value is too small for some compounds, and will need to be made longer when quantitative $T_1$ values are needed. If

$$D_1 + AQ \leq 5 \times T_1$$

[for nuclei of interest; i.e., ignore TMS or other solvent peaks]

is found to be true in the analysis (see below), then the results are at best qualitative. The experiment would need to be rerun to obtain accurate results. When $D_1 + AQ \leq 3 \times T_1$ the experiment should be rerun. For the most accurate results, using $D_1 + AQ = 10 \times T_1$ is recommended, as is randomizing the VDLIST values, and including 3 or more duplicates of the longest VD value.

8. Although the $t_{1ir}$ pulse sequences recommend $NS = 8 \times i$ and $DS = 4$, $NS = 1$ or 2 and $DS = 0$ will work fine on our spectrometers (assuming your sample is at sufficient concentration).

9. Optional: IconNMR will perform an automated analysis of the data. You can check the processing set by clicking on the PROCORS tab, then on the AUTOMATION link in the left-hand navigation bar. Make sure that a `1` is at the end of the AUNMP name: proc_2dt1.

10. Click on the RETURN TO ICONNMR tab, and SUBMIT the experiment.

Figure 3: The default VDlist (in $t_{1uwchem}$). $TD_1 = 11$

$D_1 = 15$ are other important default values.

NOTE: In ICON you will receive an error message after your experiment has run.

If you take a closer look, you will see that the data was acquired but not processed. You do not need to re-run the experiment!
B. Processing and Analysis of T1 data:

1. **MestreNova**: Working up the data for visually inspection is (mostly) straightforward.
   a) Some trouble occurs when importing raw data. Suppose the data folder name in TopSpin is:
      ```
      e.g., D1404180938_sucrose_1HT1 10 1
      ```
      If you drag the `D1404180938_sucrose_1HT1/10` folder into MNova, it identifies that the dataset is pseudo-2D (i.e., comprised of a series of 1D spectra) and auto-processes it, including performing an autophase.
      
      Recommended: drag the processed data folder in:
      ```
      i.e., D1404180938_sucrose_1HT1/10/pdata/1
      ```
      The phasing from TopSpin will then be used in MNova, and will (likely) be correct.
   b) or: To phase individual spectra in the stack, use the **Stacked Spectra** table view. Pin the spectrum you want to work on by checking the box under the pin icon or choose **Select → Select Active Only**.
   c) phase the first spectrum negative. If the inversion (+180deg) causes the spectrum to disappear, increase the intensity and manually phase the spectrum.
   d) click on **Stacked** again to display all and the phase will automatically be applied to all spectra in the stack.
   e) You should be able to visually observe where the nulls occur. The d7 delays for each spectrum will be listed in the **Stacked Spectra** table under the T/G column. $T_1 = 1.4 \times d_{7null}$.

2. **Automatic processing in TopSpin**: If AUNMP is set correctly (as described in step 9 above), TopSpin will automatically process the data. Setup and results can be found in the following text files:
   ```
   <datasetname>/10/vdlist ; contains the vdlist delay values
   <datasetname>/10/pdata/1/dt1t2.txt ; contains a brief summary of the T1 values
   <datasetname>/10/pdata/1/ct1t2.txt ; contains a detailed summary of the T1 values
   ```
   The automated processing is somewhat problematic, especially ascertaining which multiplet regions are solute peaks, rather than impurities and solvent. The required information can be obtained, especially on very pure and relative simple compounds. Otherwise, manual workup (MNova!) and processing will likely be preferred.

3. **Manual workup using TopSpin**: Bruker provides a good set of instructions in Chapter 8.2.4 of their “1D and 2D Step-by-Step – Advanced” manual, which can be accessed in TopSpin3.x by clicking the help button.
A brief summary of the steps (use the TopSpin guide initially, but then this will likely suffice):

a) **rsers 10** (last fid) → **ef** → manually phase **.ph** → store to 2D by clicking **mn** → **j**

b) return to the 2d experiment by clicking **j** and transfer with **xf2**

c) enter relaxation analysis with **T1/T2** which give the following menu:

d) click **Fid** → **SPECTRUM** → enter last fid # (10) → **OK**

e) click **Peaks/Ranges** → **MANUAL INTEGRATION** → **OK**

f) integrate all interesting multiplets/peaks → **then**

g) click **Relaxation** → **OK** to **RELAXATION PARAMETERS**

h) click **Fitting** → **CLOSE** → **OK**

i) click **Calculation** → **CLOSE** → **j**

j) note the **BRIEF REPORT**, or look at the full report by clicking **Report**