

T1 Measurement on the U400

Knowledge of the T1's of a molecule could be important in the setup of many 1D and 2D experiments, in which the relaxation delay *d1* (or *sattime* in the cyclenoe experiment) must be set according to the T1's of the signals of interest. In some instances, the T1 values themselves are used as structural parameters in the characterization of a variety of compounds.

The T1's of a sample can be measured using the inversion-recovery method. For most applications, only a rough approximation of the longest T1 is needed for setting *d1* or *sattime*. In which case, no pw90 measurement would be necessary and the default pw90 can be used. However, if accurate T1 measurements are required, you should determine the 90° pulse width on your sample (see handout UVU423 for instructions) and set pw90 to the measured 90° pulse width.

If the measured T1's fall outside the expected range, you should rerun the experiment with a new expected minimum and maximum T1.

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1. ACQUIRE A PRELIMINARY SPECTRUM

*Select a standard parameter set and retrieve an appropriate shim file.
Lock and shim on the sample as usual. When done with shimming, enter:*

pw=pw90 <rtn>
nt=1 <rtn> (or minimum *nt* that would give a spectrum with acceptable S/N)
ga <rtn>

When acquisition is complete, phase and reference the spectrum as usual.

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OPTIONAL: *If digital resolution and data size are of concern to you, optimize the spectral window using the **movesw** command to include ALL the signals plus 2 ppm of empty baseline on either side of the spectrum. Then enter:*

gain='y' <rtn>
fn=2*np <rtn>
ga <rtn>

*When acquisition is complete, phase the spectrum and make sure that **sw** was reset correctly.*

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2A. AUTOMATED SETUP FOR THE T1 EXPERIMENT — dot1

The automated setup using the *dot1* macro is simpler and easier, and is recommended for most situations.

dot1 <rtn> command to set up the T1 experiment, which will prompt for the following:

ENTER MINIMUM T1 EXPECTED (SEC): **0.5** <rtn> (0.1 to 1 sec would be a good starting point)
ENTER MAXIMUM T1 EXPECTED (SEC): **5** <rtn> (5 to 10 sec are typical)
ENTER NUMBER OF TRANSIENTS (nt): **1** <rtn> (use minimum *nt*)

*After the above have been entered, an **d2** array list will be generated and printed in the text (or **dg**) window on the bottom left of the screen, along with the estimated experiment time. An example of the output is shown below:*

| ACQUISITION | ARRAYS |
|-------------|--------|
| array | d2 |
| arraydim | 10 |
| i | d2 |
| 1 | 0.0625 |
| 2 | 0.125 |
| 3 | 0.25 |
| 4 | 0.5 |
| 5 | 1 |
| 6 | 2 |
| 7 | 4 |
| 8 | 8 |
| 9 | 16 |
| 10 | 32 |

EXPERIMENT SET UP USING 10 TAU VALUES

NOTE: The dot1 command will also set the following parameters automatically:

pw=pw90

p1=2*pw90

d1=4*T1(max) (T1(max) is the **MAXIMUM T1 EXPECTED** entered above)

Check the parameters and start the experiment:

dg <rtn>

display parameters and make sure they are correct

ga <rtn>

start acquisition

2B. MANUAL SETUP FOR THE T1 EXPERIMENT

Use the manual setup procedure if you need to set d1 and the d2 array to some specific values.

pw=pw90 <rtn>

p1=2*pw90 <rtn>

d1=_____ <rtn> (should be $5 \times T1_{(\text{longest})} - at$)

d2=0.001,##,##,..... <rtn> (last d2 entry should be set to about $5 \times T1_{(\text{longest})}$)

da <rtn>

display the array list and make sure that are correct

vp=80 <rtn>

set vertical position of spectrum to 80 mm

ai <rtn>

select absolute intensity mode

ga <rtn>

start the experiment

3. VIEWING, PROCESSING, AND PLOTTING OF T1 DATA

T1 data can be viewed during and after acquisition by using one of the following two commands:

ds(#) <rtn>

display the specified spectrum in the array

dssh <rtn>

stacked display the completed spectra horizontally

To adjust the vertical scale of the stacked display:

ds(#) <rtn> (# = last array point)

display the last spectrum from the d2 array list

vsadj <rtn>

adjust the vertical scale

dssh <rtn>

stacked display the spectra

if phasing of the spectra is required:

ds(#) <rtn> (# = last array point)

display the last spectrum from the d2 array list

aph <rtn> (or manually phase it if necessary)

The stacked spectra can be plotted as follows:

dssh <rtn> (if you haven't displayed them yet)

stacked display the spectra horizontally

pl('all') pap page <rtn>

stacked plot the spectra as displayed with parameters (see example in Figure 1 on next page)

4A. ESTIMATION OF T1(longest) AND VALIDATION OF THE EXPERIMENT

If you are only interested in finding out the approximate value of the T1(longest), do the following:

- Find out $\tau_{\text{null}}(\text{longest})$: look for the spectrum in which the last peak of interest becomes null, the tau value of that spectrum is the $\tau_{\text{null}}(\text{longest})$.
- Calculate the T1(longest) according to the equation below:

$$T1(\text{longest}) = \tau_{\text{null}}(\text{longest}) / 0.69$$

IMPORTANT:

- If $d1 \geq \{5 \times T1(\text{longest}) - at\}$, your T1 data is valid and you may stop here.
- If $d1 < \{5 \times T1(\text{longest}) - at\}$, you may need to rerun the experiment with a different input for the **MAXIMUM T1 EXPECTED**, and perhaps for the **MINIMUM T1 EXPECTED** as well.

4B. CALCULATION OF T1 BY EXPONENTIAL CURVE FITTING

If accurate determination of T1 values are required, you should follow the exponential curve fitting routine described below:

ds(#) <rtn> (# = last array point) display the last spectrum from the d2 array list

NOTE: To avoid hanging up the computer, you should do the fitting for no more than 10 lines at a time.

*Expand around the signal(s) of interest and set the threshold to include a minimum number of lines necessary. (NOTE: For multi-line signals, only one line per signal is needed. Unwanted lines can be left out of the fitting later with the **fp(line indexes)** command below.)*

dll <rtn>

display listed line frequencies and intensities

fp <rtn>

measure the intensity of each line in the **dll** listing for the spectra in the array. This produce an output file which will be used for the curve fitting below.

NOTE: "**fp(line indexes from dll)** <rtn>" will measure only the lines specified. This can and should be used to exclude any unwanted lines such as the extra lines picked in a multi-line signal or those from the solvent or impurities.

t1 <rtn>

execute an exponential curve fitting to determine the T1 values for the lines selected by the **dll** and **fp** commands. The results will be printed in the text (or dg) window. See example in Figure 2 on next page. print the **t1** output tables to the printer

printon t1 printoff <rtn>

NOTE: The validity of the T1 experiment should be checked using the "**d1** or < {5 x T1(longest) - at}" criterion as described in 6A above.

The T1 value of a specific line (or lines) can be measured as follows:

t1(#) <rtn>

determine T1 value for the selected line

Any erroneous or unwanted d2 array point (or points) can be deleted as follows:

dels(##) <rtn>

delete two array points, for example

The exponential fitting curve for a specific line (or lines) can be displayed on the graphics screen as follows:

expl(#) <rtn>

display exponential fitting curve for the selected line

The exponential fitting curve for a specific line (or lines) can be plotted to the plotter as follows:

pexpl(#) **page** <rtn>

plot exponential fitting curve for the selected line.

Figure 1. Typical stacked plot of T1 data
 (Sample is the 1% CHCl3/CDCl3)

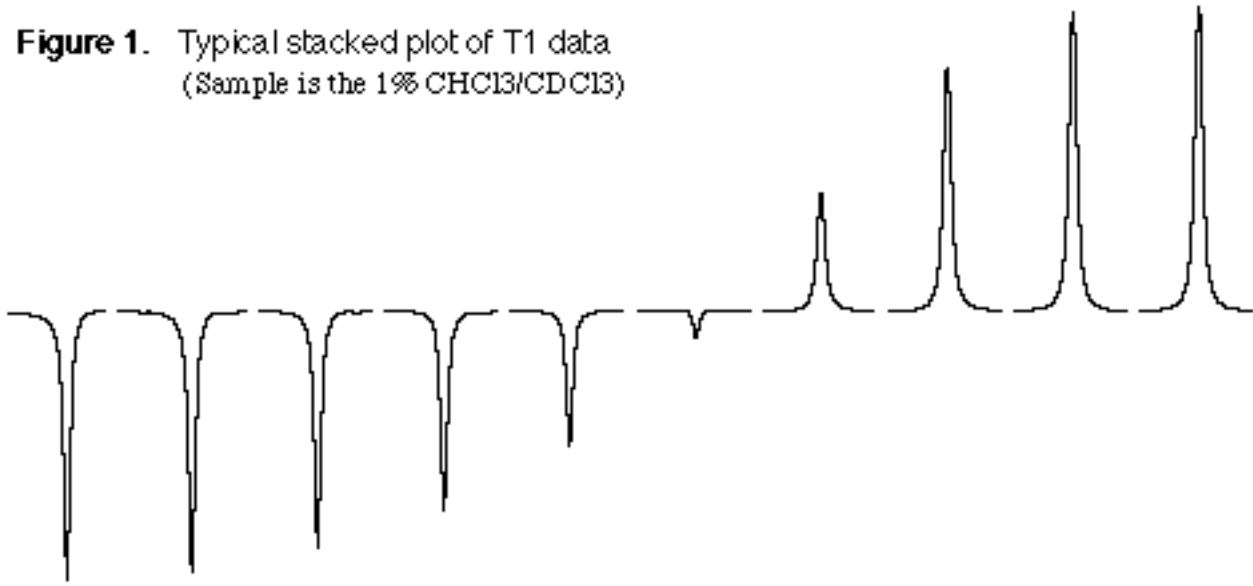


Figure 2. Typical output from a T1 analysis by exponential curve fitting
 (same data as above, acquired with expected T1(min)=1 and T1(max)=10)

Exponential data analysis:

| | | |
|------|-------|---------|
| peak | T1 | error |
| 1 | 7.042 | 0.07125 |

| | | | |
|---------------|----------|------------|------------|
| peak number 1 | | | |
| T1 = | 7.04 | error = | 0.0712 |
| time | observed | calculated | difference |
| 0.125 | -50.130 | -50.110 | -0.020 |
| 0.25 | -49.010 | -48.229 | -0.781 |
| 0.5 | -44.100 | -44.566 | 0.466 |
| 1 | -36.990 | -37.620 | 0.630 |
| 2 | -25.370 | -25.122 | -0.248 |
| 4 | -4.870 | -4.871 | 0.001 |
| 8 | 21.830 | 21.848 | -0.018 |
| 16 | 45.520 | 45.567 | -0.047 |
| 32 | 55.630 | 55.629 | 0.001 |
| 64 | 56.830 | 56.773 | 0.057 |