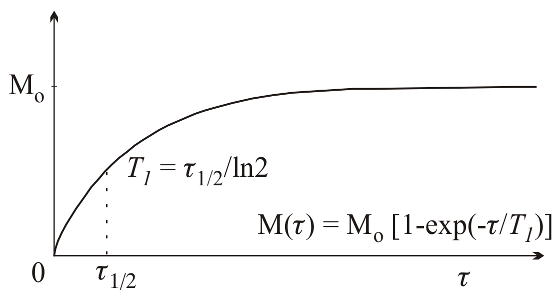
XIX. *¹H* Spin-Lattice Relaxation, T_1

(updated 02.07.01)

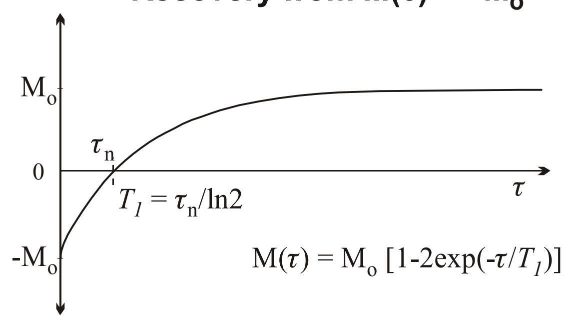
I. Discussion

- Spin-lattice relaxation, T_1, is nominally an exponential process, and is important as the determining factor in all experiments' repetition delay, **d1**. Suggestions for how "abusable" (borrowed from Varian) **d1** is for various experiments is provided at the end of this chapter.
- T_1 becomes critically important for quantitative, exchange, or cross-relaxation types of experiments such as NOESY. Spin relaxation, from zero magnetization and following an inversion pulse, are shown in the figures below.

Recovery from M(0) = 0



Recovery from M(0) = –M_o



- Usually a quick determination of T_1 is sufficient, allowing proper setting of the repetition delay, **d1**. For most liquids, use the rapid, inversion-recovery method in Section II below. This method involves finding the time at which the magnetization goes through a null, τ_n. For more accurate determinations of T_1, utilize the multi-point fitting scheme described in section III.

II. Rapid Determination of T_1 by Inversion-Recovery Null Method

(Adequate for most samples, but is semi-quantitative at best.)

- Obtain a reasonable quality *¹H* spectrum. Locate protons of interest for visual observation.
- 180° and 90° pulse lengths must be reasonably accurate. Typically, you should check the pw90 calibration prior to estimating T_1.
- set **p1=2*pw90 pw=pw90 nt=1**
  – If nt=1 does not provide sufficient signal-to-noise, then make certain $d1 \geq 3\times T_1$.
- **d2**=0.01 should give large negative peaks. Lengthen **d2** until peaks of interest are nulled (slightly shorter **d2** should give negative peaks; slightly longer should give positive peaks). For the time at which the null occurs, $\mathbf{d2_n}$, $T_1 \cong d2_n/\ln 2 = d2_n*1.41$.
- Find $\mathbf{d2_n}$ for other protons of interest.

III. Quantitative measurement of T_1 by Inversion Recovery Method

A. Comments

- A reasonable estimate of T_1 must be known to correctly setup the quantitative experiment: use the Inversion-Recovery Null Method in Section II.
- 180° and 90° pulse lengths must be accurate.
- For precise measurements, use **d1** = 10 T_1; **d1** = 5 T_1 will provide reasonable values if experimental times get too long. The number of **d2** values, nd2, can also be decreased to lessen experimental times ≅ nt*nd2*[2*(d1+at)].

B. Acquisition Set-up

1. Use the macro **dot1**; some randomization of the selected d2 values might be preferable to the macro setup.
2. Ensure that **d1** ≥ 5 * T_1 .

Table I. A reasonable grouping of VD delays for Inversion-Recovery T_1 sequence, where T_1^r is the T_1 estimate (from inv-rec estimate or a repetition-rate experiment).

$0.01T_1^r$	$0.5T_1^r$
$10T_1^r$	$10T_1^r$
$2T_1^r$	$5T_1^r$
$0.3T_1^r$	$0.1T_1^r$
$10T_1^r$	$0.01T_1^r$
$0.7T_1^r$	$1.4T_1^r$
$1.0T_1^r$	$10T_1^r$

C. T_1 Analysis (see the Varian Subject manual, Adv. 1d section)

1. Expand about the peak(s) of interest. Adjust the threshold with **Th**.
2. Enter **dpf** or **dll** then **fp** to locate the peak(s) of interest; find them throughout the relaxation set. **fp** writes a text file fp.out in the current experiment, e.g., ~/vnmrsys/exp1/ft.out.
3. If the dataset is a T_1 set, enter **t1**; for T_2 enter **t2**, or for a solid-state $T_{1\rho}$ enter **analyze('expfit','p3','t2','list')**
4. **t1** and **t2** will display the information on the bottom of the screen. To print this information out, repeat using, e.g.,

   printon t1 printoff or

   print the file ~/vnmrsys/exp#/analyze.list text file (same information) from the File Manager, or in vnmr with **ptext('analyze.list')**
5. Show a plot of the data using **expl**, and plot with **pexpl page**. Note that you can look at specific peaks using **expl(3)** and **pexpl(3) page** as an example for the 3rd peak. To make a smaller

plot use the sequence **expl center pexpl page**. To delete a point from the analysis, use **dels(<data#>) fp t1** or similar command.

D. T_1 "Abusability" vs Experiment Repetition (d1)

[from Varian course notes]

Likelihood of artifacts increases as go down column.

normal 1d	T_1 at 30° pulse
COSY (magnitude mode)	$< 1 \times T_1$
INADEQUATE	$> 1\text{-}1.5 \times T_1$ (^{13}C)
HMQC & HMBC	$> 1.5? \times T_1$
HOM2DJ	
HET2DJ	
HETCOR	
COSYPS	
TOCSY	
NOESY & ROESY (qualitative)	$\sim 2\text{-}3 \times T_1$
NOESY & ROESY (quantitative)	$> 3\text{-}5 \times T_1$
DQ-COSY* & MQ-COSY	$\geq 3 \times T_1$ (+ "homospoil")
Quantitative T_1	$\geq 5 \times T_1$

*The new DQCOSY experiment provided in VNMR 6.1c and newer can run with significantly reduced repetition delays: **d1** $\sim 2 \times T_1$ (perhaps even as fast as d1=T_1).