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Saturation Recovery with Half-Echo Acquisition V.2

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We use this protocol and it's working

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Abstract

Purpose
To measure the longitudinal relaxation time, T_1, of resonances present in the sample when a significant background signal is also present.

Scope
This SOP should be completed after an initial 1D experiment has been completed, but before further experiments are performed. Upon completion of this SOP, the user will be able to set recycle delays appropriate for the purpose of later experiments, either to maximize signal per unit time, or to ensure quantitative intensities.

Guidelines

If acquisition of a 1D spectrum requires substantial signal averaging, this SOP may not be appropriate.

The addition of echo detection increases the minimum number of scans required per time increment to 3. If the sensitivity of the sample is sufficient to obtain adequate signal with one scan **and** there is no significant background signal, instead follow the SOP for measuring T1 via saturation recovery without echo detection.
If acquisition of a 1D spectrum requires substantial signal averaging, this SOP may not be appropriate.

This SOP is intended for a beginning user who has been trained on basic spectrometer safety and principles.

This SOP is written for acquisition using a Bruker console and TopSpin 3.6.2. It may be adapted to other TopSpin versions where appropriate. The basic process is the same on TopSpin 4.x, but requires a NEO-compatible pulse sequence. The sequence **satrect1_echo.neo.nmrfam** is compatible.

Materials

Definitions:

1. T_1: Longitudinal relaxation time
2. l20: Number of saturation pulse loops
3. d20: Presaturation loop delay

Appendix:

If the presaturation train is not completely effective, the recovery curve might initially decrease, and then follow the expected exponential curve. This is common behaviour and can be dealt with by discarding the initial points of the curve.

The values of the variable delay list T1_standard_array range from 0.25 to 128 s, increasing by a factor of two for each increment. This should provide adequate spacing to accurately determine T_1 values between 1 s and 64 s. If necessary, adjust the list for shorter or longer values of T_1.

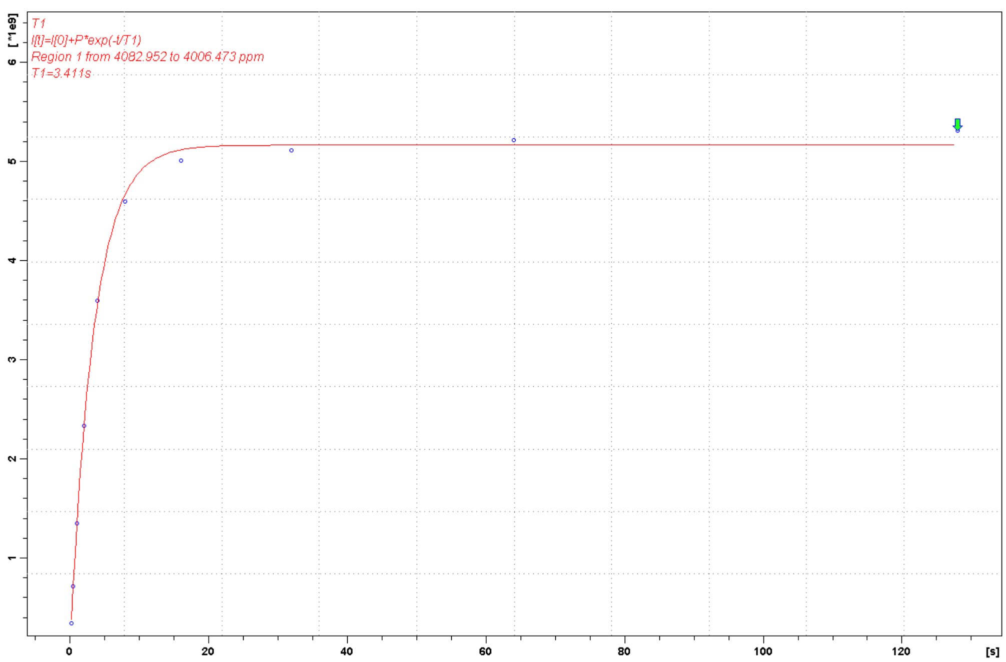

Figure 1. Example of a successful ^{7}Li saturation recovery experiment performed on a lithium silicate glass. The T_1 of this environment was found to be 3.4 s.

Safety warnings

The minimum length of **d1** for the 2D experiment will depend on whether decoupling is used during acquisition. If decoupling is used, **d1** should be about 20 times as long as the acquisition period, typically on the order of 1 s. If decoupling is not used, a **d1** value of 100 ms may be reasonable.

Before start

User is responsible for knowing the duty cycle of the probe and instrument being used.

User is responsible for knowing the high-power decoupling limits of the probe.

Expected time to completion: 1 hour or less

Procedure

1 Load the **satrect1_echo.nmrfam** pulse program; or, if using a NEO console, the **satrect1_echo.neo.nmrfam** pulse program.

2 Set values for the acquisition of an initial spectrum.

2.1 Set the 90° pulse length, **p1**, and the 90° pulse power, **plw1,** to previously optimized values.

1. The 180° pulse, **p2**, is automatically calculated as 2 × **p1**.

2.2 Set the recycle delay, d1, to a relatively long value, e.g., 10 s.

2.3 Set the number of saturation pulse loops, l20, to 0.

2.4 Set the spinning rate constant, **cnst31**, to the MAS rate in Hz.

1. If the sample is static, set **cnst31** to 1e6.

2.5 Set the rotor period loop counter, **l1**, to an initial value of 1.

1. If the sample is static, set **l1** to the desired echo delay in microseconds.

2.6 Set the pre-acquisition delay, **d7**, to the initial value calculated by **cnst7**.

2.7 If necessary, enable decoupling by setting the **-Ddec** flag in **zgoptns**.

1. Set the heteronuclear decoupling program, **CPDPRG2**, pulse length, **PCPD2**, and pulse power, **plw12**,to the value determined by following SOP ^{1}H Decoupling.

2.8 Set the variable delay list**, vdlist,** to T1_standard_array.

3 Acquire an initial spectrum. The number of scans should be as small as practicable to allow for adequate signal, ideally as low as 3.

3.1 Ensure that all expected resonances are visible. If some are not visible, either reduce the pulse length or increase d1, as appropriate.

3.2 If any background signal is sufficiently suppressed, proceed to the next step. Otherwise, increase **l1** and repeat this step.

3.3 Observe the baseline of the spectrum. If a significant first-order phase correction (> |60°|) is required, adjust **d7** until the required phase correction is minimized.

1. **cnst7** will typically overestimate **d7** by a few microseconds. Only small adjustments (1 µs – 10 µs) should be necessary.

4 Set the number of saturation pulse loops, **l20**, to an initial value of 20. Set the presaturation loop delay, **d20**, to an initial value of 1000 µs.

5 Acquire a spectrum. There should be no signal present.

5.1 If signal is still present, increase **l20**, up to a maximum of 100, and reacquire the spectrum.

5.2 If increasing **l20** does not result in a null signal, reduce the number of loops and retry with longer presaturation loop delays **d20**.

5.3 If increasing **d20** does not result in a null signal, retry with shorter presaturation loop delays **d20**.

6 Convert the experiment to a 2D experiment window. Set the following parameters:

6.1 **F1 TD**: 12
FnMODE: QF
F1 SI: 16
d1: A minimal value that respects the probe duty cycle, see Appendix.

7 Acquire the 2D experiment via the command **zg**.

8 Process the 2D experiment.

8.1 Transform the data using the command **xf2**.

8.2 Correct the F2 phasing of the slice with the longest delay period.

8.3 Do not transform or phase the F1 axis.

9 To process the data, launch the TopSpin utility **t1guide** and follow the workflow in the utility.

9.1 Extract the slice with the longest variable delay, *i.e.*, the most recently acquired slice.

9.2 Integrate each resonance. Save using the option "Export Regions to Relaxation Module and .ret".

1. If resonances are not resolved, attempt to select the regions of least overlap.
2. If resonances cannot be reasonably separated, integrating over all of the peaks will allow for the determination of the longest T_1 component.

9.3 Enter the relaxation window and set the Fitting Function Function Type to **uxnmrt1**.

9.4 Calculate fit for all peaks. If successful, the fitting window should resemble the example in the appendix.

10 Record the T_1 for each site. Use the longest value of T_1 for determining the recycle delay of future experiments.

Protocol references

Bruker Solid State NMR User Manual Z4D10641B, Section 16.2.4

Y. Nishiyama and N. T. Duong, "Practical guides for ^{1}H detected solid-state NMR under fast MAS for small molecules," Journal of Magnetic Resonance Open, vol. 10-11, p. 100062, Jun. 2022.
https://doi.org/10.1016/j.jmro.2022.100062

Example Data at 1.1 GHz: **usnan.org/ark:/83454/e1f28359ea-87ce-4107-b62e-5e4f79921537**
Example Data at 900 MHz: **usnan.org/ark:/83454/e165139178-91f9-409b-85f3-9e4694fbe8e3**
Example Data at 600 MHz: **usnan.org/ark:/83454/e147640572-2426-46ea-90da-4d3a5e293029**