TopSpin

NUS Parameter

User Manual

Version 002

Innovation with Integrity

NMR

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1 Introduction

1.1 About this Manual

This manual is a short description of non-uniformly sampled (NUS) multidimensional NMR data available in TopSpin and its processing with „MDDNMR”.

„MDDNMR” is a program especially for processing of NUS multidimensional NMR data developed by Orekhov et al. and implemented in TopSpin (MDD means Multi Dimensional Decomposition). NUS data can be processed in TopSpin with the same processing commands (e.g. **xfb**, **ftnd**) as non NUS data; if required, "MDDNMR" processing is called automatically.

For detailed information about this program please refer to the original papers[1,2,3,4,5,6)] listed in chapter *References [▷ 15]*.

1.2 Conventions

Type of Information	Font	Examples
Shell Command, Commands, “All that you can enter”	Arial bold	Type or enter **fromjdx zg**
Button, Tab, Pane and Menu Names “All that you can click”	Arial bold, initial letters capitalized	Use the **Export To File** button. Click **OK**. Click **Processing**…
Windows, Dialog Windows, Pop-up Windows Names	Arial, initial letters capitalized	The Stacked Plot Edit dialog will be displayed.
Path, File, Dataset and Experiment Names **Data Path Variables** **Table Column Names** **Field Names (within Dialog Windows)**	Arial Italics	*$tshome/exp/stan/nmr/lists* *expno, procno,*
Parameters	Arial in Capital Letters	VCLIST
Program Code **Pulse and AU Program Names** **Macros** **Functions** **Arguments** **Variables**	Courier	`go=2` `au_zgte` `edmac` `CalcExpTime()` `XAU(prog, arg)` `disk2, user2`
AU Macro	Courier in Capital Letters	`REXPNO`

Table 1.1: Font and Format Conventions

File/Directory Conventions

<tshome> - the TopSpin home directory (default C\:Bruker\Topspin under Windows or /opt/Topspin under Linux)

Header Conventions

SYNTAX - only included if the command described requires arguments

USED IN AU PROGRAMS - only included if an AU macro exists for command described

1.3 Disclaimer

This guide should only be used for its intended purpose as described in this manual. Use of the manual for any purpose other than that for which it is intended is taken only at the users own risk and invalidates any and all manufacturer warranties.

1.4 Limitation of Liability

All specifications and instructions in this manual have been compiled taking account of applicable standards and regulations, the current state of technology and the experience and insights we have gained over the years.

- The manufacturer accepts no liability for damage due to:
- Failure to observe this manual.
- Improper use.
- Deployment of untrained personnel.
- Unauthorized modifications.
- Technical modifications.
- Use of unauthorized spare parts.

The actual scope of supply may differ from the explanations and depictions in this manual in the case of special designs, take-up of additional ordering options, or as a result of the latest technical modifications.

2 General Concept

Traditionally multi-dimensional NMR-data sets are collected using a linear incrementation of evolution times and require a FTT algorithm for processing. The data points acquired in the indirect dimension(s) form a grid where the distance between the points on the grid is given by the sweep width and the number of points by the TD for each dimension respectively.

The principle of NUS is to acquire only a subset of data points in a random manner while still using the same grid. Such data are generally processed by other methods. These can be:

1. Multi Dimensional Decomposition (MDD-NMR) by Orekhov et al. [1,3,4)]
2. Compressed sensing (CS) methods by Kazimierczuk & Orekhov (REFERENCES: K. Kazimierczuk, V. Y. Orekhov, Angewandte Chemie-International Edition 2011, 50, 5556-5559.; M. Mayzel, K. Kazimierczuk, V. Y. Orekhov, Chemical Communications 2014, 50, 8947-8950; K. Kazimierczuk, V. Orekhov, Magnetic Resonance in Chemistry 2015, 53, 921-926.)
3. Maximum Entropy (MaxEnt) methods
   - Rowland Toolkit by Hoch et al. [7,8,9,10)]
   - Forward Maximum Entropy by Wagner et al.[11)]
   - Azara (CCPN) by Laue et al. [12)]
4. Multidimensional Fourier Transformation (MFT) by Kozminski et al. [13,14,15)]

Bruker decided to use the MDD-NMR, which implements MDD, CS, other modern algorithms. Among others this program produces quantifiable results.

Recording of data in NUS mode can save a lot of time, especially for nD datasets. After a spectrum is recorded and stored to a disk, it has to be processed. The processing of a regular NMR spectrum includes the following steps:

1. Fourier transformation in the directly detected dimension
2. Fourier transformation in all indirect dimensions, viewing of the result and, if necessary, fine tuning of the processing parameters

If a spectrum is recorded in the NUS mode, the indirect dimensions cannot be Fourier transformed right away. Here ‚MDDNMR' software intervenes after step 1. It replenishes the complete data matrix in all indirect dimensions with reconstructed points, which means resorting of recorded data points and extrapolation of the missing ones. Then the step 2 is performed.

For a regularly acquired dataset one point after the other (from beginning to end of the whole matrix) has to be recorded according to the sampling. Spectra recorded in NUS mode may be obtained for two and higher dimensional experiments where only a small amount of data points will be acquired which is randomly spread over the whole data space (see *Figure 21 [▶ 8]*). Therefore it is possible to process the dataset after only a few percent of the data is recorded to obtain a spectrum with the final resolution, provided S/N the is sufficient.

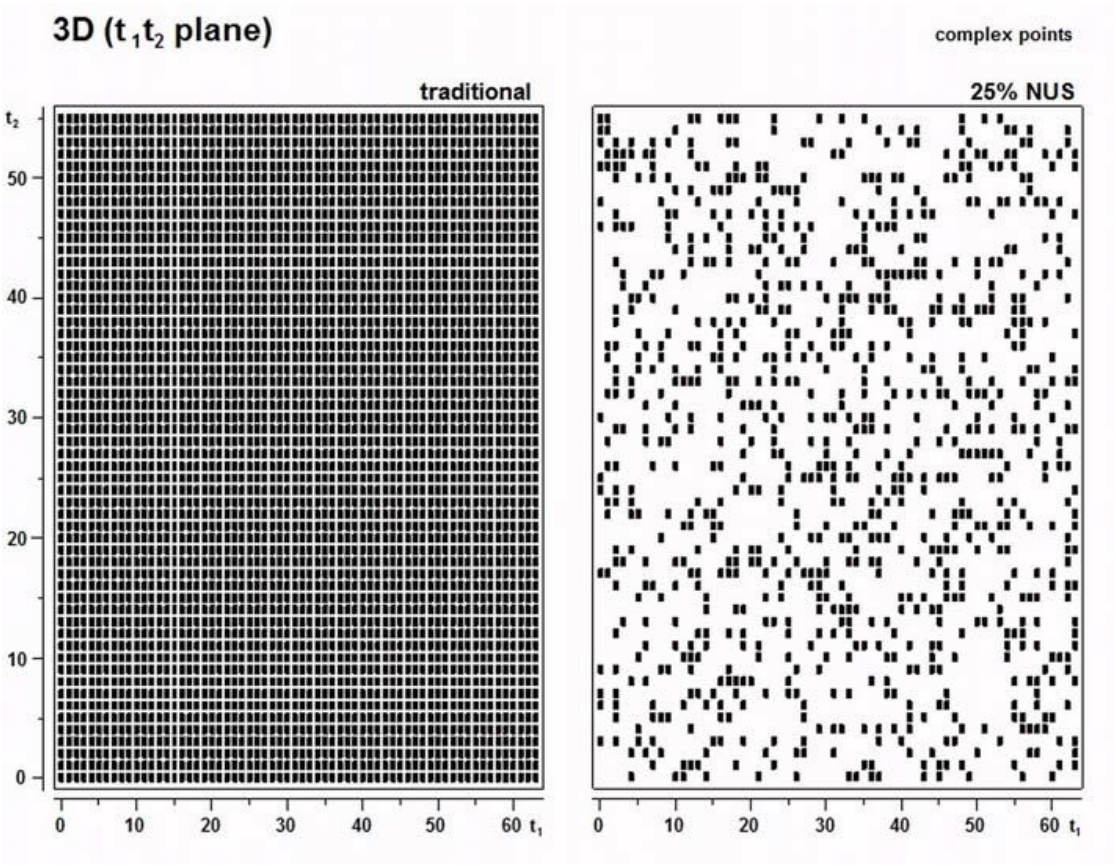

Figure 2.1: Distribution of complex points in traditional and NUS experiment

Prior knowledge about T2 or J-coupling is available, the position of the sampling points can be optimized (attach more weight to the strong parts of the FID).

2.1 Parameter Setup for NUS Experiments

First of all the parameters for the chosen experiment will be set as usually in the **eda** table. You can select the ‚FnType' which will set the nD acquisition mode. For a NUS experiment it is set to ‚non-uniform_sampling' as shown in the *Figure 2.2 [▶ 9]*.

In order to be used for NUS experiments the pulseprogram must be written using the appropriate mc syntax.

Figure 2.2: eda table for setup of a NUS experiment

After setting the ‚FnTYPE' to non-uniform sampling, click **NUS** from the listing on the left side of the **eda** table to get the additional acquisition parameters for a NUS experiment. They are shown in the figure 2.3.

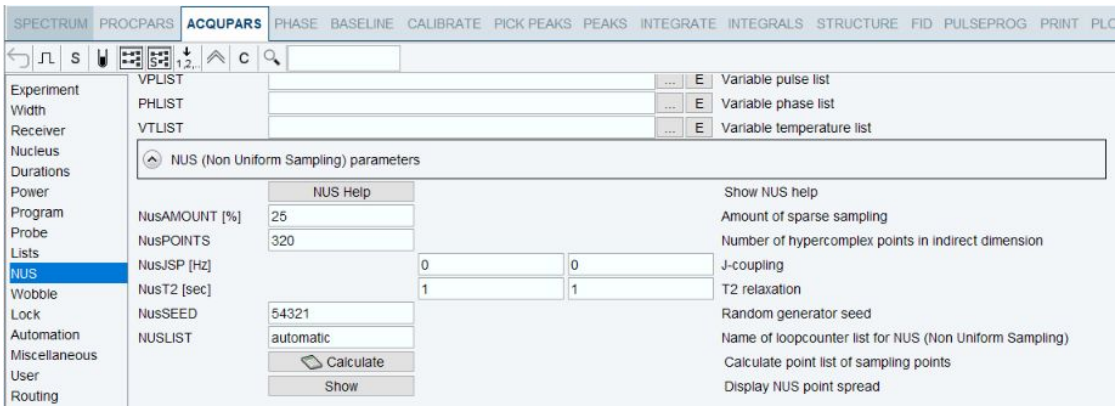

Figure 2.3: NUS acquisition parameter block

Acquisition parameters

NusAMOUNT[%] - percentage amount of sparse sampling, default is 25

NusPOINTS - number of complex fids to be recorded.

For a hypercomplex nD experiment it is [td1*td2...*td(n-1)*NusAMOUNT/100] / $2^{(n-1)}$ where hypercomplex means, that all values of acquisition parameter FnMODE are different from QF and QF(no-frequency).

As a rule of thumb the number of hypercomplex points should be at least twice the number of frequencies (signals in the spectrum slice through one point in the indirectly detected dimension).

Jsp [Hz] - J coupling, default is 0. In the case of J evolution in an indirect dimension the points acquired can be matched to the maxima of such a FID by setting this coupling constant.

T2 [s] - T2 relaxation time, default is 1. For indirect dimensions with so called real time evolution the FID in the indirect dimension will decay according to the T2 relaxation time of the spins evolving in this dimension. By setting the T2 parameter according to the relaxation time, parts of the FID with more intensity will be strengthened (exponential weighting of sampling scheme).

If an evolution period is implemented as constant time in the pulse program, exponential weighting must not be used.

seed - random number generator seed, responsible for the different distribution of data points, default is 54321

Calculate - allows to calculate and then view the distribution of points without starting the experiment.

Show:

- after the acquisition the show button displays the distribution of the measured fids (graphical representation of the file nuslist, which is stored together with raw data).

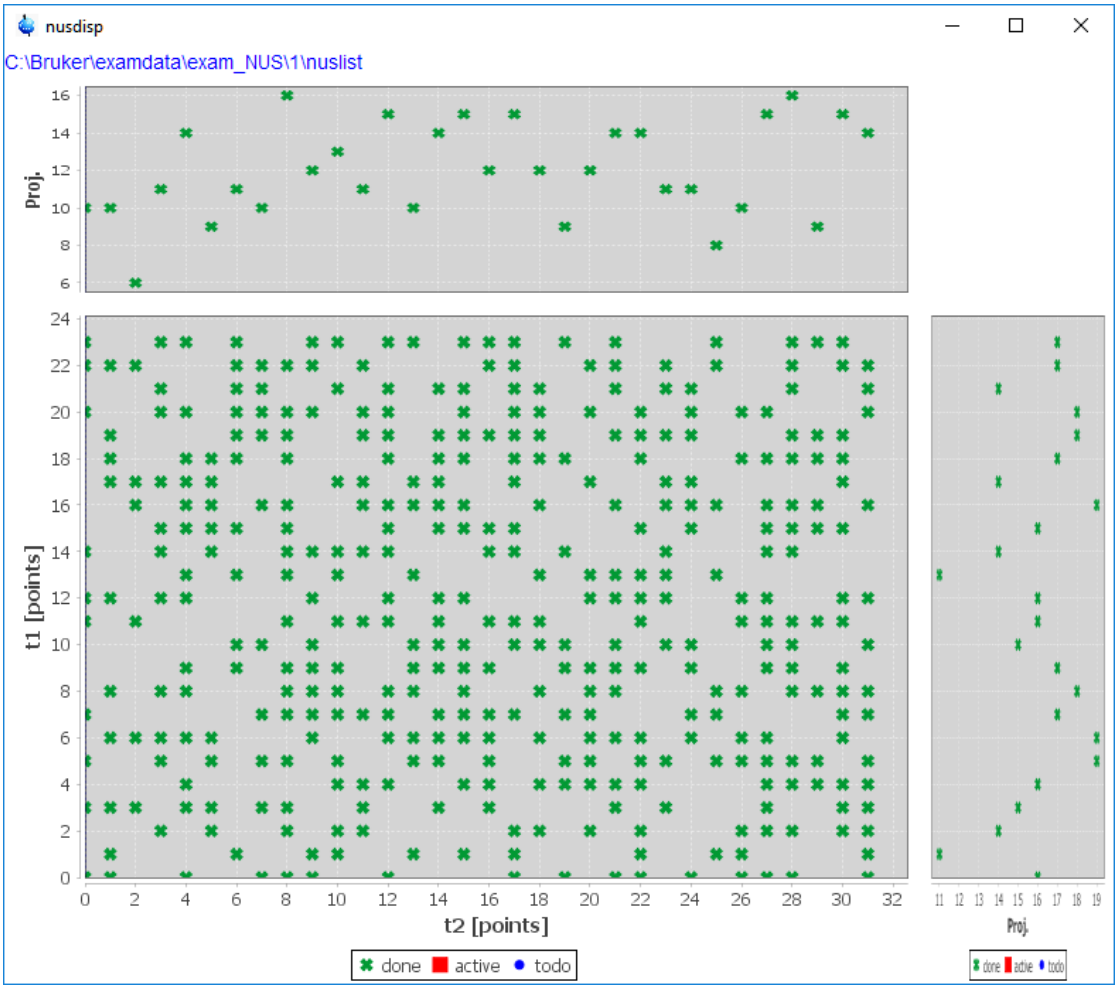

Figure 2.4: Result of command show after the acquisition.

- before or during the acquisition the show button displays a graphical representation of the file *exp\stan\nmr/lists\vc\automatic*

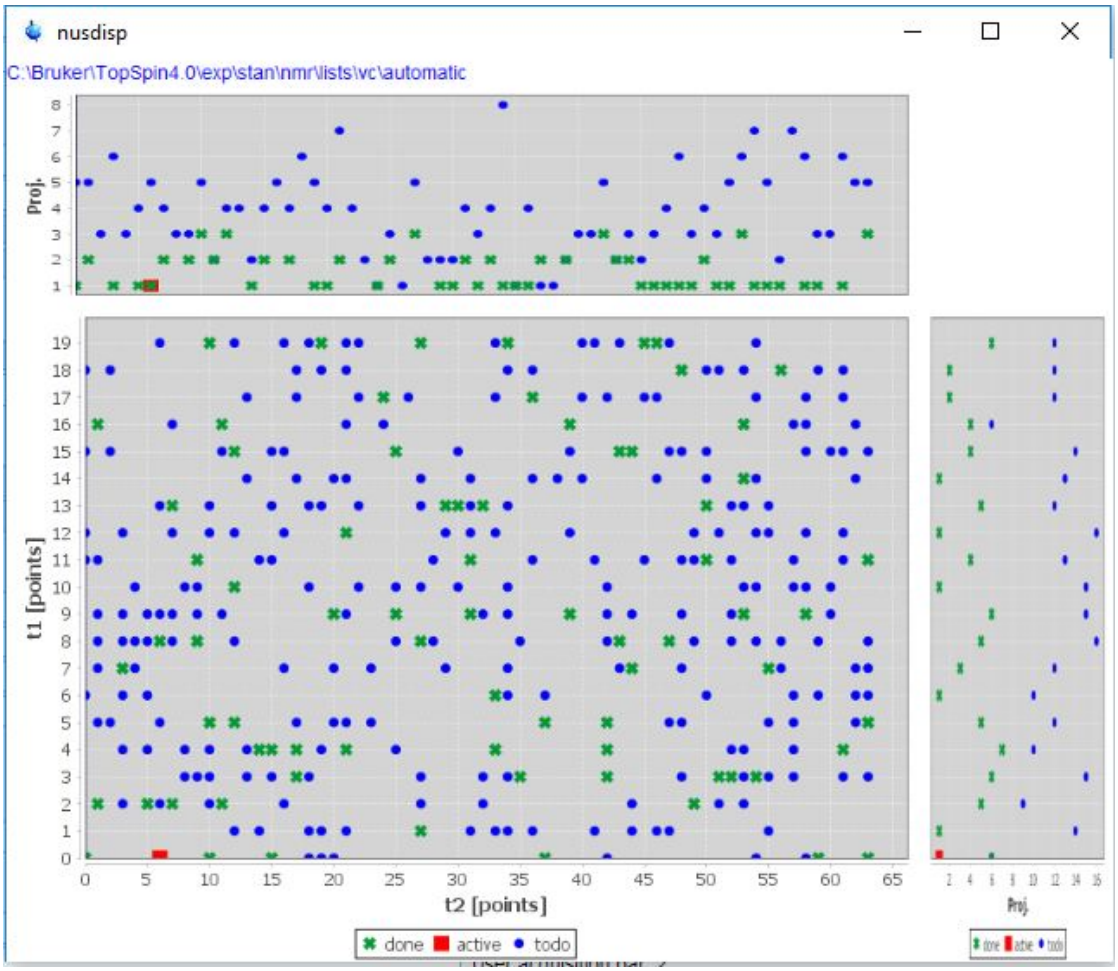

Figure 2.5: Result of command show during the acquisition.

Now make sure, that the parameter NUSLIST is called ‚automatic' (loopcounter list for NUS). You will find it together with other lists above the NUS parameter block (see figure *Figure 2.3 [▷ 9]*).

Processing parameters:

The processing parameters for a NUS experiment will be found in the **edp** table. Click **NUS** in the listing on the left side and the edp parameter list is scrolled to the NUS parameter block (see *Figure 2.6 [▷ 12]*).

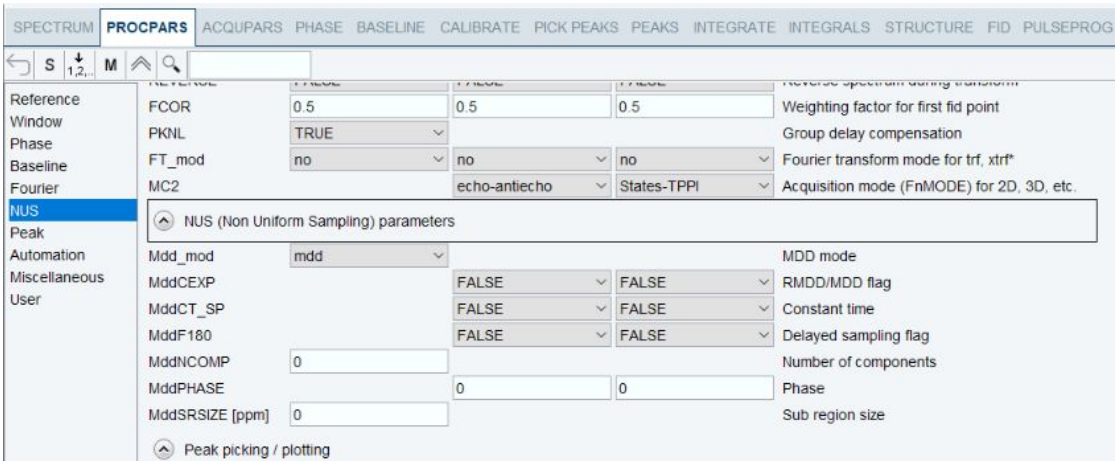

Figure 2.6: NUS processing parameter block

MddCEXP - recursive MDD/MDD flag, default is false in all dimensions (true = recursive), selecting true takes more time, for 2D spectra recursive MDD is mandatory in F1

MddCT_SP - allows to specify constant time direction, used as in the original MDD, false = non constant time direction, true = constant time direction, default is false in all dimensions, in the case of being true mirror image processing is used

MddF180 - delayed sampling flag, default is false in all dimensions; false = no delayed sampling, true = delayed sampling (first value for delay = 1/2 increment or t1(0) = in/2

MddNCOMP - number of components, default is 0 which uses the internal default of 25 components, if peaks are missing NCOMP should be increased

The increase of NCOMP leads to disproportional increase of calculating time

MddPHASE - zero order phase for correction for indirect dimension, default is 0 in all dimensions. Has to be set if virtual echo is used.

MddSRSIZE [ppm] - sub region size, for 1H 0,15 ppm are sufficient, for other nuclei the value might be larger. The default of 0 uses the internal default of 0,15 ppm.

Mdd_CsALG - CS algorithm: IST (1) or IRLS (0). IST is faster and less memory consuming for large datasets. IRLS can provide slightly better results, but is more demanding. For 4D only IST is available.

Mdd_CsLAMBDA - Sparsity of the spectrum. For IRLS can have any value, for IST between 0 and 2. Default is 1. Increase if high t1-noise-like artifacts remain after reconstruction. Decrease, if thermal noise is turned into too intense “spikes” or small “false peaks”

Mdd_CsNITER – number of iterations in CS algorithm. Default is 200 for IST and 20 for IRLS. Increase to 600 and 30, respectively, for spectra with high dynamic range of peak intensities (NOESY, TOCSY etc).

Mdd_CsNORM – norm in IRLS algorithm. Use default 0 for fast convergence. For IST the parameter is hard-coded to 1.

Mdd_CsZF – internal zero-filling in CS. Do not alter.

Mdd_Cs VE – virtual echo option. Use always when phase in indirect dimensions is known. Accelerates IST and provides better results for IRLS and IST. Obligatory in 4D IST. If Mdd_Cs_VE is set, MddF180 must be set correctly.

MddNOISE – scaling factor for the residual of a reconstruction added to the IST reconstruction (not used for IRLS).

See also

3 References

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References

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