



NMR

picoSpin User Guide

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NMR Spectroscopy

Readers of the picoSpin User Guide should become familiar with the basics of pulsed NMR spectroscopy of liquids. An introduction to this subject can be found in any college level organic chemistry textbook. There are also several excellent on-line resources available.

References

The Basics of NMR, by Joseph P. Hornak

Almost every section of this excellent text will be helpful to users of the picoSpin NMR spectrometers.

The NMR section of The Virtual Textbook of Organic Chemistry, by William Reusch

The basics in just a few pages.

NMR Web course, provided by Queen's University, Ontario, CA, Department of Chemistry, and maintained by Francoise Sauriol, Ph.D.

Basic NMR concepts are covered as well as extensive coverage of pulse sequences. This site includes animations.

NMR Tutor, by Charles B. Abrams

Interactive Flash animation of the basic concepts of NMR and pulse sequences.

NMR Lecture Course, by Hans Reich, Department of Chemistry, University of Wisconsin, Madison.

Advanced concepts in NMR.

NMR Databases and Resources

SDBSWeb, provided by the National Institute of Advanced Industrial Science and Technology

This site provides a searchable database that includes ^1H and ^{13}C NMR spectra as well as optical spectra.

WebSpectra, by Prof. Craig A. Merlic, UCLA Department of Chemistry and Biochemistry

Problems in NMR and IR Spectroscopy.

NMRShiftDB2, provided by the NMRShiftDB Project

These are searchable chemical shift databases for ^1H , ^{13}C , and other nuclei.

NMR Simulator, provided by NMRDB.org

A very nice interactive NMR simulator and database where one can draw structures and simulate their NMR spectra.

NMR Chemical Shift Tables, by Prof. Hans Reich, Department of Chemistry, University of Wisconsin, Madison.

A rich collection of chemical shift tables for ^1H , ^{13}C and other nuclei, as well as an extensive listing of J_{HH} and J_{CH} coupling constants.

System Operation

Web Browser Interface

The web browser user interface of the picoSpin is accessed by navigating to the unit's IP address, which is shown on the front-panel LCD display. An Ethernet connection can be made to the unit directly or through a local area network. See the Installation and Setup instructions to set up a connection.

We recommend Mozilla's free Firefox™ web browser for best compatibility with the picoSpin software, but most modern browsers will work nearly as well, including Google Chrome™, Safari™, and Internet Explorer™ 10 and 11.

When a web browser is directed to the unit's IP address, the instrument responds by displaying a splash screen with a large Thermo Scientific logo. You will be transferred to the Run page in a few seconds or you can go there immediately by clicking on the logo. If your connection is interrupted while you are operating the unit and the web interface becomes unresponsive, it may be helpful to restart the session by directing the web browser back to the IP address displayed on the unit's front-panel LCD.

The four main pages of the interface are **Run**, **Files**, **Temperature** and **System**. Orange links at the upper right of each page are used to navigate between them. A common message pane at the bottom of each page provides information about the currently running experiment and other operations. The content of the message pane is preserved when switching from one page to another.

Features

Interactive Zoom: Plots on the Files page have interactive zoom where a left mouse click-and-drag selects a rectangular zoom region. A single left click reverts to the previous zoom view and a double left click reverts to the original plot parameter settings. In addition, clicking on a data point in the plot shows its coordinates.

Drag and Drop File Management: The Files page implements a drag and drop file management system. It allows for creation of folders on the Files page under the Run Data section with the ability to drag and drop experiments between folders or to the trash bin. Folders with stored data files can also be moved to trash bin.

Auto tx Frequency: This setting is implemented in the autoShim and experiment scripts and allows the spectrometer to track and change the RF transmitter frequency while an experiment is running. When enabled, auto tx will use the auto tx offset parameter to place the weighted average of signals at the offset frequency.

Global tx Frequency: The tx frequency value is treated as a global parameter and shared across experiments script.

Run

The **Run** page is used to choose and run experiment scripts, and to monitor their progress. The name of the currently loaded script is displayed in the upper left corner of the page. Next to the script name is an information button (), which when selected displays information about the script.

The **script** and **shims** buttons are located at the top of the page. Clicking  opens a dialog window that allows you to choose between the available scripts. (To load a script with its default settings or with settings from a saved run, use the [Files](#) page.)

Clicking  displays the settings of the magnet shim currents, which are real numbers between -1.0 and +1.0. By filling in the Shims Name field and clicking , you can save a shim settings file, which can be examined and selected on the [Files](#) page. In addition to the three first order and five second order shims, there are also fields for a uniform field shim, Z^0 , and for a temperature. The temperature field on the Shim page has no effect on operation but it can be used to keep a record of the magnet temperature for which a particular set of shims is appropriate. The uniform field shift applies a uniform Z field, which can be used to offset the total magnetic field by a small amount. The value of Z^0 should remain set to its default value of 0.

The **Run** page contains a list of script parameters, two data plots and (optionally) a Run Name field. The Show less/show more button can be used to display only the most frequently used parameters or all parameters.  always appears near the top of the parameters list. This button changes to  while a script is running, providing a way to interrupt an experiment.

The script parameter fields are defined by the loaded script. Script parameters are grouped to make their function more apparent. The groupings are: acq. parameters, data processing, output format and plot parameters. Each field has a name that appears to its left and some have a unit that appears to the right. Hovering the mouse pointer over the field name will bring up a brief description of the field. Most fields are checked for validity; if an invalid entry is made a flag will appear on the field. This flag must be cleared by correcting the entry before the script can be run.

If you type a name into the Run Name field and then click , a saved data file with the run name supplied will be generated. When the script completes, a Download Data button () will appear next to Start Run. Clicking  will open a dialog window allowing for direct downloading of experimental data from the Run page.

In the onePulse script, if align-avg. data and JCAMP avg. are checked and Download Data is clicked, a browser dialog window will appear asking for user input. If the output format option JCAMP ind. is also checked, a file selection window will appear. Individual data files can be selected for download, or the Download All Data button can be selected to bundle and download all data files in single, compressed archive file. The saved run will also appear on the [Files](#) page after the script successfully completes. The saved run stores any data generated by the script and all of the settings.

The upper plot window displays time-domain free induction decay (FID) data and the lower window displays the spectrum.

Files

The **Files** page provides a way to examine and manipulate three kinds of information: saved runs with their data and settings, shim settings files, and scripts with default settings.

Menu Item	Description
Run Data	<p>Last Run – stores the settings of the most recent data acquisition</p> <p>Saved Run – named experiments with settings and JCAMP-DX data</p>
Shims	<p>Current – stores the shims currently set on the Run page</p> <p>Default – sets all shims to 0</p>
Scripts ^a	<p>autoShim – used for finding optimal magnet shim settings</p> <p>onePulse – used for collecting and analyzing data</p> <p>Search – used for finding the Larmor frequency when the approximate frequency is not known</p>

^a Factory default scripts. Instrument specific test report Larmor frequency and pulse length are not stored in these scripts.

The Files page implements a drag and drop file management system. It allows for creation of folders on the Files page under the Run Data section with the ability to drag and drop experiments between folders or to the trash bin. Folders with stored data files can also be moved to trash bin. The device should not be used for storing many data files but this helps organize what has not been downloaded yet.

Saved runs appear below the label Run Data. When **Last Run** is clicked the name of the script and the settings that were last used on the Run page are displayed. Below the settings appear any data files generated by the last run. The link **Use these settings at Run** will transfer operation to the Run page with the last-used script and all of its settings loaded. Clicking on a

data file will bring up a download dialog. Buttons are provided to download all of the generated data () and to delete the run (). The other saved runs behave similarly to **Last Run**. When any run is selected the time and date when it was saved appears to the right of the settings display.

Next to the Shims label the user can select the **Current** shims, the **Default** shims, or shims saved by experiment scripts. When a saved shim file is selected, buttons appear allowing the user to delete the file () or download it (). Downloaded shim files can be used to archive shim information. Saved shims can be moved to the Run page by clicking **Use these settings at Run**. If your system firmware was updated from version 0.8.1, an additional file name restored will be present. This file contains a set of saved shim values from the update process.

All experiment scripts currently available on the system appear next to the label Scripts. Clicking on a script name will display all of the settings fields with their names, default values, units and descriptions. Additional information about the script appears below the list of settings. To use the selected script at the run page with its default settings, click on **Use default settings at Run**. These are write protected factory-default scripts. Instrument-specific test report Larmor frequency and pulse length are not stored in these scripts. It is more convenient to select scripts by choosing a saved run or the last run or selecting the script from on the Run page.

Temperature

The **Temperature** page provides a convenient interface for the magnet temperature controller. The upper plot displays the magnet temperature in degrees Celsius, the middle plot shows the temperature of the magnet enclosure, and the lower plot shows the magnet heater setting. All plots show data over the previous six hours unless the unit has been on for less time or a system reset has been performed. Click to reveal fields for setting the magnet temperature controller parameters. The settings normally used are: (picoSpin 45) Set Point = 42.0, P = 10.2, I = 0.02, heater = on, closed loop = on; (picoSpin 80) Set Point = 36.0, P = 10.0, I = 0.01. If closed loop = off the controller is disabled and the heater setting is determined by the output field. Controller settings are not changed until is clicked.

The magnet heater setting varies from 0 to 65535. If the heater setting shown in the bottom plot is at zero, the setpoint temperature should be increased or the ambient temperature decreased. If the heater setting reaches its maximum value, the setpoint temperature should be decreased or the ambient temperature increased.

When the unit has been turned off and then turned on, it may take from 30 minutes to 4 hours for the magnet to stabilize at the Setpoint temperature. During this time it is normal for the heater setting to first be at zero and then to swing abruptly to its maximum value. Settings should not be adjusted until the system has stabilized.

System

Click the **Preferences** link to display three check boxes that can be used to control the display of information on the Run page. The Run Name box determines if a Run Name field appears above the script parameters. Checking this box enables saving of named runs. The Allow Named Run Overwrite box is a data file protect option. Checking this box allows the user to overwrite named Run files with the same name. Unchecking the box protects existing files from being overwritten, making users select a new Run name if it already exists. The **Mnova newer than 6.2.1** option formats JCAMP-DX data files for Mnova version's 6.2.1 and newer.

The **Settings** link provides access to fields for setting the default IP address when DHCP is not available. This IP address will not become effective until power is switched off and back on or the web server CPU is restarted. It will appear on the front panel LCD display after power-on or restart only if no DHCP server is available. The date, time and time zone may also be set under the **Settings** link. The clock time is used to label saved runs and data files.

The currently installed software and firmware versions may be inspected by clicking on the **About** link. The About page displays information about disk space usage for volatile and non-volatile memory, as well as web browser information for the computer connected to the picoSpin spectrometer. This information is useful when communicating with technical support.

Click the **Restart** link to restart the web server CPU inside the spectrometer. This should be done with caution when operating remotely since it will interrupt the web browser connection.

The **System Update** link is used to update the system software, including the web browser interface. Click this link only when you have received an update file and installation instructions from us.

Samples and Sample Preparation



WARNING Avoid personal injury.

- Needles and syringes should be considered regulated waste regardless of use
- Follow your local EH&S guidelines for disposal
- Never throw these items into the regular trash or dumpsters



CAUTION Avoid personal injury.

- Wear eye protection at all times when handling liquid chemicals
- Do not breathe hazardous vapors
- Avoid skin contact with hazardous liquids and vapors
- Eliminate ignition sources and prevent significant waste volume buildup

Viscosity

The 400 micrometer inside diameter of the cartridge tubing limits the viscosity of the sample one can inject without exceeding an upper pressure limit of 100 PSI. If you have difficulty drawing the sample into the injection syringe you will likely also have difficulty injecting it into the cartridge inlet. Adding a small amount of a low viscosity solvent may dramatically reduce the viscosity of a sample. Liquids with kinematic viscosity of 40 cSt (centistokes) to 45 cSt at approximately 35 °C to 40 °C represent the upper limit on sample viscosity before dilution should be considered. For reference, cooking oils such as olive oil have viscosities of 35 cSt to 45 cSt in the temperature range from room temperature to approximately 45 °C. Online viscosity tables may be consulted for guidance on other common liquids.

Concentration

The signal strength in proton NMR spectroscopy is directly proportional to the concentration of hydrogen nuclei in the sample. To maximize the signal-to-noise ratio (SNR), samples should be prepared with the highest possible concentration of the analyte of interest. In some situations, following this guidance may lead to samples which are too viscous or which have broadened spectral features. In these cases, begin with the highest possible concentration and then add solvent as necessary.

The exact SNR depends on the quality of the magnet shim, the data acquisition parameters and on choices made when filtering or apodizing the data. (picoSpin documentation uses the spectroscopic definition of signal-to-noise ratio: maximum height of the peak divided by the root-mean-square noise of the baseline.) In exceptional cases, the SNR may also depend on intrinsic sources of peak broadening. However, it is usually possible to estimate the SNR by comparison with the signal from pure water. We have specified SNR for pure water for a single scan. (Consult the factory test report for the water SNR measured with your unit at the factory.) Since the SNR is directly proportional to concentration, you can scale from pure water to estimate the SNR for any spectral peak. The concentration of water molecules in pure water is 55 M (55 moles/liter). When scaling it is necessary to include a factor for the “weight” of the peak of interest relative to the water peak. The weight is the number of protons per molecule contributing to the peak multiplied by the peak’s normalized intensity within the multiplet. (The normalized intensity is 1 for a singlet, 1/2 for each peak of a doublet, 1/2 for the middle peak of a triplet and 1/4 for the outer peaks of a triplet.) For example, the water singlet has a weight of $2 \times 1 = 2$, a CH_3 singlet has a weight of $3 \times 1 = 3$ and one peak in a CH_3 doublet has a weight of $3 \times 1/2 = 1.5$.)

Suppose, for example, that the analyte molecule has a concentration of 0.55 M and we would like to estimate the SNR of one peak in a CH_3 doublet. If the single-scan SNR for pure water is 1,000, the result will be $1,000 \times (0.55/55) \times (1.5/2) = 7.5$ (for the picoSpin 45). The single-scan SNR can be increased by averaging multiple scans. Because the SNR increases as the square root of the number of scans, it is not generally practical to increase it by more than a factor of 30 above the single-scan value; in most cases, the sample concentration should be increased if the estimated single-scan SNR of an important peak is less than 1.

Neat liquid samples are the most favorable case. They should generally be analyzed without dilution unless peak broadening or viscosity are a concern.

Solid samples must be fully dissolved in a suitable solvent. The effective lower limit on sample concentration is approximately 0.5 M for the picoSpin 45 and 0.2 M for the picoSpin 80, as shown by the estimation method above. Since only about 30 to 40 μL of sample is needed, one typically needs to mix only about 250 μL of solution. Many small organic molecules being analyzed have a molar mass between 100 and 300 g/mol. To make a 1 M solution, 25 to 75 mg of material needs to be dissolved in 250 μL of solution.

Solvents

For both solid and liquid samples, either deuterated or undeuterated solvents may be used to prepare sample solutions for analysis. Deuterated solvents are more expensive, more difficult to obtain, they are light and moisture sensitivity, which limits their shelf life. Protonated solvents can be used if the proton solvent signals do not overlap or otherwise interfere with other signals of interest. If a protonated solvent cannot be used, then one should select a deuterated NMR solvent that affords the highest solution concentration for sample analysis. In selecting a deuterated solvent one should keep four considerations in mind:

Concentration — To achieve the highest quality spectrum one should choose the deuterated solvent for which the solute has the highest solubility. Note that chemical shifts can depend somewhat on sample concentration and the solvent environment.

Proton-deuterium (H-D) exchange — When using a deuterated solvent one must be aware of the presence of labile or acidic protons in the sample that can suffer from H-D exchange with the solvent. H-D exchange has the effect of removing signals from the NMR spectrum, and sometimes this is a desirable effect. For partial or incomplete H-D exchange a residual proton signal may still be present and can affect integration ratios. The most common functional groups that undergo H-D exchange are hydroxyl (-OH), amine (-NH, -NH₂), thiol (-SH, -SH₂), and carboxylic acid (-CO₂H) groups.

Solvent polarity — The chemical shift and spin-spin splitting of proton NMR signals can depend on the dielectric constant of the solvent. There are many excellent texts that describe applications where one can benefit from a judicious choice of solvent.

NMR solvents most commonly used are: CDCl₃, C₆D₆, D₂O, acetone-*d*₆, DMSO-*d*₆, MeOD and methanol-*d*₄. Since the magnet is typically temperature stabilized at 36 °C (picoSpin 80) or 42 °C (picoSpin 45), methylene chloride-*d*₂(CD₂Cl₂) cannot be used directly in the picoSpin due to its low boiling point (39.75 °C). It can still be used as a co-solvent. Many NMR solvents can be purchased with added internal reference substances, such as DSS (4,4-dimethyl-4-silapentane-1-sulfonic acid) for D₂O or TMS (tetramethylsilane) for organic solvents, and which are defined to have a chemical shift of 0.0 ppm. NMR solvents with 1% TMS are desirable when an internal reference is needed.

Sample Handling

Samples are manually injected into the picoSpin using a glass syringe, as shown in [Figure 1](#), or using a polypropylene syringe, as shown in [Figure 2](#). Gas tight glass syringes are recommended for general laboratory use, whereas plastic syringes are preferred for teaching purposes or when it is not practical to re-use a glass syringe.

Figure 1. Sample injection with a glass syringe



Figure 2. Sample injection with a plastic syringe

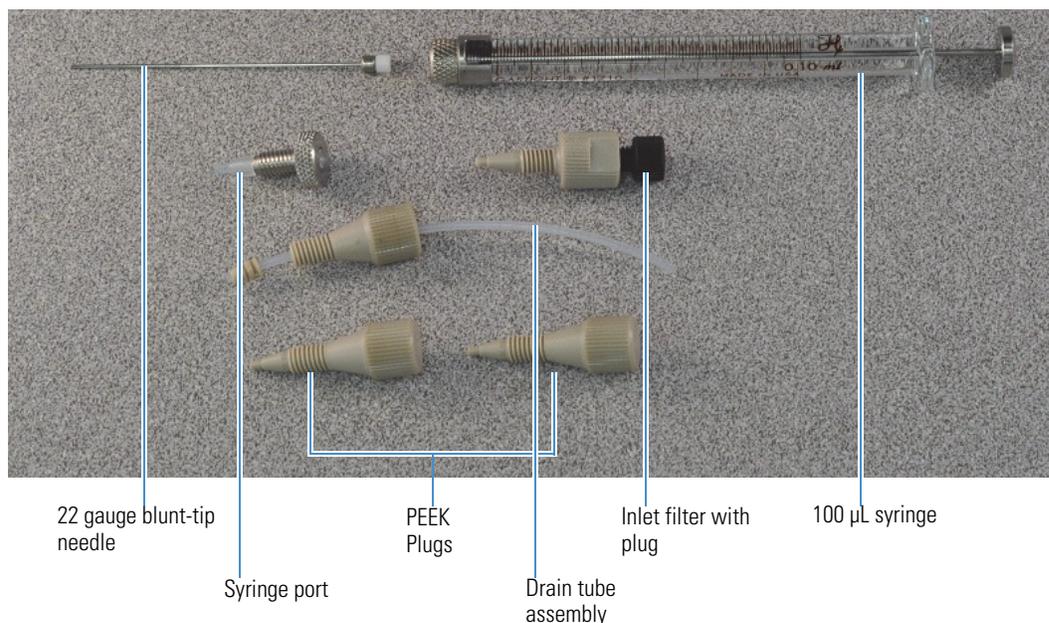


Complete sets of sample handling supplies are available from us. The Laboratory Kit contains a gas-tight glass syringe and related accessories, while the Teaching Kit contains plastic syringe accessories.

Sample handling accessories must be compatible with the cartridge fittings. The inlet is a 1/16-inch stainless steel bulkhead fitting with an external stainless steel frit filter.

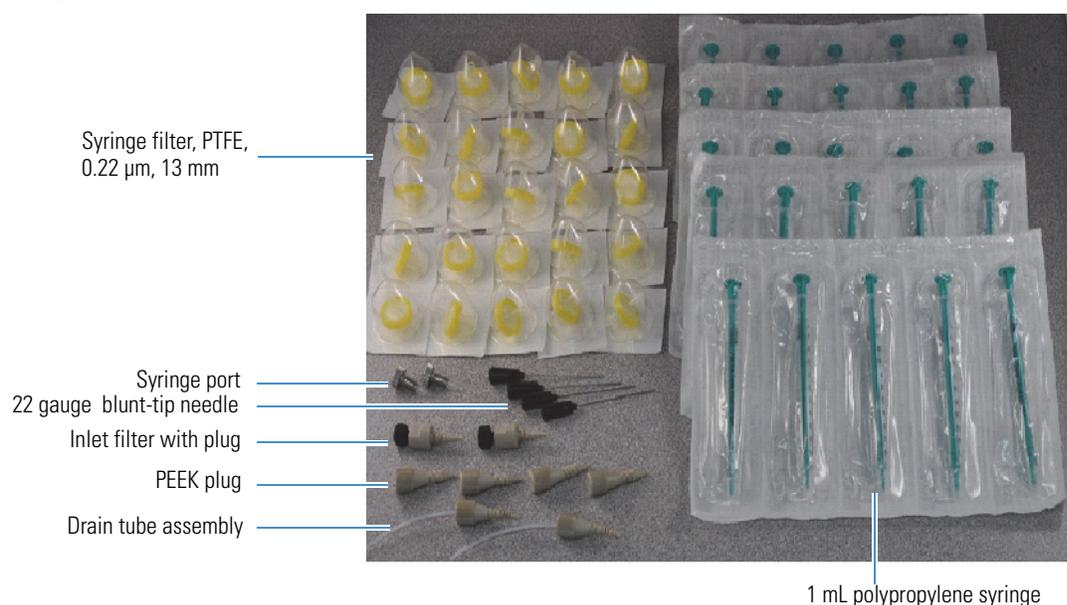
Glass syringe accessories suitable for use with the picoSpin are shown in [Figure 3](#). The 100 μL syringe has a PTFE gas-tight plunger and a removable 22 gauge blunt-tip needle. The needle is inserted into a syringe port. The drain tube uses a PEEK nut, a grooved PEEK ferrule crimped onto a length of 30 gauge PTFE 0.030-inch OD tubing. An optional 0.22 μm stainless steel frit inline filter with PEEK body is also shown.

Figure 3. Glass gas-tight syringe and other accessories for sample injection



An example set of plastic syringe accessories is shown in [Figure 4](#). The 1 mL polypropylene syringes are shown with optional 0.22 μm PTFE filters. Connection to the inlet fitting is made with a syringe port.

Figure 4. Plastic syringe and accessories



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Experiment Scripts

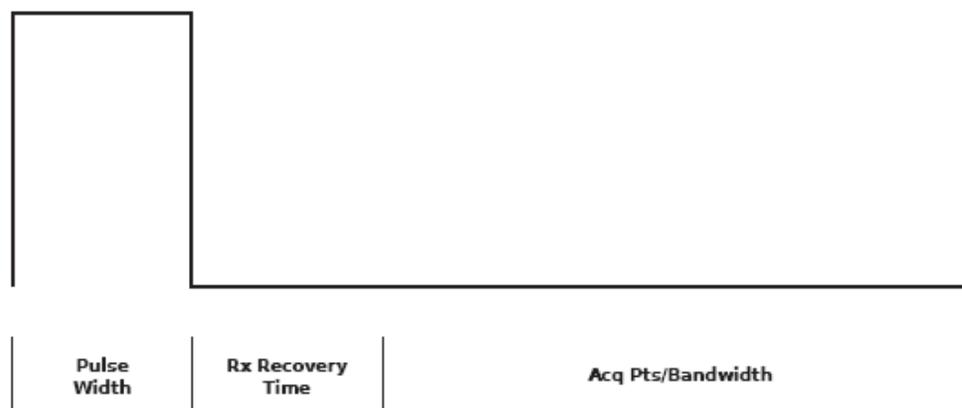
All experiments on the picoSpin spectrometers are implemented by means of factory defined scripts. The scripts are responsible for loading pulse sequences to the NMR Engine, retrieving data from the NMR Engine, and sending the data to the embedded web server for plotting to a browser window.

There are three scripts distributed with the spectrometer software: onePulse, autoShim, and Search. Of the three only the onePulse script is generally used to acquire data. The Search and autoShim scripts are used to find the Larmor frequency of the sample and improve the peak shape, respectively.

onePulse

The onePulse script is the experiment that will be used for collecting and analyzing data. It implements a single-pulse acquisition sequence as shown in [Figure 5](#).

Figure 5. onePulse pulse sequence



The sequence transmits a single pulse, waits for a receiver recovery delay time, then begins recording data. The sequence is executed in the NMR Engine hardware so its timing is highly accurate and precise. Once the sequence is complete, the onePulse script retrieves the data from the NMR Engine, processes it, and sends the data to the browser window and/or JCAMP-DX file if requested. If the user has requested multiple scans, the script then checks how much time has elapsed since the start of the last pulse sequence and attempts to wait the

necessary time as defined by the recycle delay before attempting to start the next sequence. If the specified recycle time is long enough for the script to start the next acquisition sequence in the requested time, a statement indicating “processing complete; waiting x s before sequence repeat” will be shown in the message window. If the target time has already passed due to the time it took to do the processing, the script will report to the message window, “processing extended repetition delay by x seconds”. Process extension delays can be minimized by increasing the recycle time or reducing the value of the “max plot points” parameter.

When multiple scans are acquired the user has the choice to save the data from each pulse separately or to have the data averaged together. To achieve the best possible resolution it is necessary to align the data before subsequent spectra are averaged. With the onePulse script, when spectra are averaged, the data are always aligned before averaging. The alignment algorithm requires that there be at least one high SNR peak present in the spectrum. If you are trying to observe a very low SNR peak by averaging many scans, make sure there is at least one high SNR peak present elsewhere in the spectrum.

Parameters

Acquisition Parameters Group

tx frequency (MHz) — The RF transmitter frequency specified in MHz. This frequency corresponds to the 0, or center, frequency of the spectral plot.

auto tx — When enabled in the onePulse script, auto tx uses the auto tx offset parameter to place the weighted average of signals at the offset frequency. For each pulse executed, the full bandwidth is evaluated for spectral signals above a minimum signal threshold and the tx frequency is automatically adjusted to honor the user supplied auto tx offset value. If the signal, however, is outside the bandwidth of the acquisition this procedure auto tx may fail to track properly. Aliased signals can also cause auto tx to improperly track real signals.

Aborting the script or allowing it to go to completion will write the last adjusted transmitter frequency value to the tx frequency parameter. It will be treated as a global value and be written to other scripts that share the parameter.

auto tx offset (Hz) — The position, in hertz for where to set the transmitter frequency. The tx frequency written by auto tx and based on the auto tx offset supplied in the onePulse script, will be written as a global value to other experiment scripts. Auto tx offset values can be different between scripts.

scans — The number of times to run the single-pulse acquisition sequence. If a certain target SNR is desired, run the script with a small number of scans at first to estimate the SNR per scan. Then compute the number of scans needed assuming that the SNR will increase as the square root of the number of scans.

pulse length (μ s) — The duration of the RF pulse in microseconds.

acquisition points — The number of points to acquire per acquisition. The acquisition time is this number divided by the specified bandwidth.

recovery delay (μs) — The time between the end of the pulse and the beginning of data acquisition. This delay time allows the system to recover from ring-down and RF switch transients.

recycle delay (s) — The requested recycle time between experiments. Since this is implemented at the script level the actual time between pulse-acquisitions will be extended if processing or server overhead require more time.

bandwidth (kHz) — The bandwidth of the receiver channel. This number determines the dwell time of the data acquisition. It is the rate, in kHz, at which the digitizer samples the signal.

post filter attenuation — The attenuation setting of the filter electronics.

Data Processing Group

zero filling — The number of Fourier transform points to use when aligning data by cross-correlation. Generally the aligning routine performs better the greater the number of points, but the longer the processing time required, which may affect the T1 relaxation delay request. Using a value that is the nearest power of 2 greater than four times the number of acquisition points works well for most cases. For example if 1000 points are acquired per scan then setting this to 4096 would produce a good alignment. If zero filling is less than the number of acquisition points, then twice the number of acquisition points are used for the alignment routine.

align-avg. data — Whether to align and average data that is acquired. The alignment routine performs a cross-correlation between the current scan and the aligned average of the previous scans before averaging the two together. When setting this parameter also be aware of setting zero filling appropriately.

phase correction (degrees) — The amount of zeroth-order phase correction to apply to the spectral data in degrees. This parameter only affects the displayed phase and not the phase of saved data.

exp. apodization (Hz) — If non-zero, applies an exponential apodization to the time series data (FID) specified in hertz. This parameter only effects displayed data and not saved data.

Output Format Group

JCAMP avg. — If align-avg data is set, this parameter determines whether a JCAMP-DX file of the aligned and averaged data is saved for the run.

JCAMP ind. — Determines whether to write individual JCAMP-DX files for each scan for processing with the user's analysis software.

Plot Parameters Group

max time to plot (ms) — The maximum time to plot for time series data (FID) in the browser. This parameter is useful when the user wants a long acquisition time but wants to have a zoomed in look at the beginning of the FID. This parameter does not affect the number of points saved to the data files.

min freq. to plot (Hz) — The minimum frequency to plot for spectral data in the browser. This parameter is useful when the user only wants to look at part of the acquired spectrum. This parameter does not affect the number of points saved to data files.

max freq. to plot (Hz) — The maximum frequency to plot for spectral data in the browser. This parameter is useful when the user only wants to look at part of the acquired spectrum. This parameter does not affect the number of points saved to data files.

max plot points — The maximum number of points to plot to the browser. If fewer points are specified than the number of acquisition points, the script will attempt to decimate the FID and spectral data down to a number of points that does not exceed this number. If greater than the number of acquisition points are specified, the script will plot the number of acquisition points to the browser. The purpose of this parameter is to decrease the load on the operating system. This may improve the ability of the operating system to accommodate the user specified recycle delay request. This parameter does not affect the number of points saved to data files.

live plot — Plots data to the browser for each scan acquired. Unchecking this parameter may improve the ability of the operating system to accommodate the user's requested recycle delay.

autoShim

The picoSpin contains a set of eight shim coils for improving the field homogeneity plus a ninth coil to apply a uniform Z field. These coils are contained in the user replaceable cartridge, which is included in the unit. The cartridge implements the following magnetic field gradients:

first order

- X
- Y
- Z

second order

- ZX
- ZY
- XY
- Z^2
- $X^2 - Y^2$

zeroth order

- Z^0

The orientation of the coordinate system is such that Y is coaxial with the capillary (perpendicular to the front face of the instrument), X is perpendicular to the side face, and Z is perpendicular to the base.

Due to very slight differences between magnets, shim cartridges, and shim electronics, different hardware components need different shim parameters. Although these shims can be set with the shim drop-down of the browser interface, this script automates the task. To do this it implements the Nelder-Mead (simplex) optimization algorithm to find the set of shim values that maximize the quality of the peak.

We refer to the size of the steps that the algorithm starts off with as increments. To reduce the complexity of the user interface it is only necessary to specify the size of the increments to use for all the first order shims and the size of the increments to use for the second order shims. If either of these are zero, that set of shims will be excluded from the optimization.

While the script is running the message window indicates the shim values that are being tried by the optimization algorithm and the LCD displays the iteration number of the simplex routine on the first line and the best value for the quality of the peak on the second line. The script also keeps a log file of all the shim values tried, the associated quality value, and the frequency of that peak.

When the script stops, either because it has reached the maximum number of iterations specified, it has passed the convergence criterion, or the run has been aborted, the best values of the shims found will be saved and will appear in the shim drop-down of the browser interface. The next time any script is run these will be the shim values used unless manually changed.

The shims found by the script can be saved to a file with the shims drop down on the **Run** page, entering a **Shims Name**, and clicking . Check to make sure the **Shims Name** field is clear when starting a new autoShim run or your previously saved shim will be overwritten.

Parameters

Acquisition Parameters Group

tx frequency (MHz) — The RF transmitter frequency specified in MHz. This frequency corresponds to the 0, or center, frequency of the spectral plot.

auto tx — When enabled, auto tx uses the auto tx offset parameter value to place the weighted average of signals at the offset frequency. Checking the test run box in the autoShim script overrides auto tx selection even if checked. That is, while test run is checked auto tx will not make changes to the tx frequency. Test run is designed for evaluating parameter values without changing them. Unchecking test run reestablishes auto tx control to discover and change the tx frequency.

For each pulse executed, the full bandwidth is evaluated for spectral signals above a minimum signal threshold and the tx frequency is automatically adjusted to honor the user supplied auto tx offset value. If the signal, however, is outside the bandwidth of the acquisition this procedure auto tx may fail to track properly. Aliased signals can also cause auto tx to improperly track real signals. Aborting the script or allowing it to go to completion will write the last adjusted transmitter frequency value to the tx frequency parameter. It will be treated as a global value and be written to other scripts that share the parameter.

auto tx offset (Hz) — The position, in hertz for where to set the transmitter frequency. The tx frequency written by auto tx and based on the auto tx offset supplied in the autoShim script, will be written as a global value to other experiment scripts. Auto tx offset values can be different between scripts.

test run — Whether to do a test run of the current script parameters and shim settings. No actual changes are made to the shims or transmitter frequency. This is provided as a convenient way to check that the acquisition parameters and location of the signal are suitable before actually trying to perform automatic shimming.

max iterations — The maximum number of times the Nelder-Mead algorithm should evaluate the simplex during the search. This is a number that is less than the number of times the data acquisition sequence is actually run because the routine may need to evaluate the quality of the signal at several shim settings for each iteration.

first order increments — The initial step size to use for the first-order shims in the Nelder-Mead method.

second order increments — The initial step size to use for the second-order shims in the Nelder-Mead method.

target rms — The criterion for convergence of the automatic shimming algorithm. When the algorithm reaches this value the script stops and reports the best shims found in the order shown at the beginning of the description of this script.

pulse length (μs) — The duration of the RF pulse in microseconds.

acquisition points — The number of points to acquire during an acquisition. The acquisition time is this number divided by the specified bandwidth.

zero filling — This parameter is no longer functional.

zero filling — The number of points to use for zero filling of the spectral data for evaluating the spectrum peak height.

recovery delay (μs) — The time between the end of the pulse and the beginning of data acquisition. This delay time allows the system to recover from ringdown.

recycle delay (s)— The requested recycle time between acquisitions. Since this is implemented at the script level the actual time between pulse-acquisitions is calculated by the spectrometer.

bandwidth (kHz) — The bandwidth of the receiver channel. This number determines the dwell time of the data acquisition. It is the rate, in kHz, at which the digitizer samples the signal.

post-filter attenuation — The attenuation setting of the filter electronics.

Data Processing Group

zero filling — The number of points to use for zero filling of the spectral data for evaluating the spectrum peak height.

phase correction (degrees) — The amount of zeroth-order phase correction to apply to the spectral data in degrees. This parameter only affects the displayed phase and not the phase of saved data.

exp. apodization (Hz) — If non-zero, applies an exponential apodization to the time series data (FID) specified in hertz. This parameter only affects the displayed spectrum and not the saved data.

magnitude — If set, uses the RMS spectral magnitude in the optimization routine instead of the intensity of the real part of the signal. This avoids having to worry about changes of phase when using large shim search increments.

Plot Parameters Group

max plot points — The maximum number of points to plot to the browser. If fewer points are specified than the number of acquisition points, the script will attempt to decimate the time and spectral data down to a number of points that does not exceed this number. If greater than the number of acquisition points are specified, the script will plot the number of acquisition points to the browser. The purpose of this parameter is to decrease the load on the operating system. This may improve the ability of the operating system to accommodate the user specified recycle delay request. This parameter does not affect the number of points saved to data files.

max time to plot (ms) — The maximum time to plot for the time series data (FID) in the browser. This parameter is useful when the user wants a long acquisition time but wants to look at the beginning of the FID in detail. This parameter does not affect the number of points saved to data files.

min freq. to plot (Hz) — The minimum frequency to plot for spectral data in the browser. This parameter is useful when the user only wants to look at part of the acquired spectrum. This parameter does not affect the number of points saved to data files.

max freq to plot (Hz) — The maximum frequency to plot for spectral data in the browser. This parameter is useful when the user only wants to look at part of the acquired spectrum. This parameter does not affect the number of points saved to data files.

Search

The search script is used to find the Larmor frequency of the sample. It is often used when a new cartridge has been installed in the spectrometer or the temperature set point of the magnet has been changed. The pulse sequence this script loads to the NMR Engine is the same as the onePulse script. The difference is that this script steps the transmitter frequency before running the sequence and checks the spectrum for a peak that passes a user specified signal-to-noise ratio (SNR) criterion. The SNR is calculated by taking the magnitude of the tallest peak and dividing by the standard deviation of the points in a user specified window of the real part of the spectrum. No checking is done to see whether the peak itself is in that window, so the frequency step size should be chosen to be less than the acquisition bandwidth and greater than the width of the noise window. While the script is running the LCD indicates the current frequency that is being probed.

In situations where the signal is very strong, it is possible that the SNR criterion is exceeded for an aliased signal. This might be the case when the system is already shimmed well. Therefore when a search stops because a signal was found it is worthwhile to use the onePulse script with transmitter frequencies that push the signal to the left or right side of the acquisition bandwidth to see that whether the signal is reduced in amplitude or vanishes altogether. If the signal gets larger instead, the original window displayed an aliased signal.

Parameters

Acquisition Parameters Group

start frequency (MHz) — The frequency in MHz at which to begin the search.

stop frequency (MHz) — The frequency in MHz at which the search is to end.

frequency step (kHz) — The size of the frequency steps in kHz to take during the search. Negative or positive values are allowed, appropriate to the starting and stopping frequencies, to scan either up or down in frequency.

SNR — The signal-to-noise ratio at which the search will consider that it has found a peak. When this threshold is exceeded the search stops and the message window reports the magnitude, SNR, and frequency of the tallest peak found.

noise window start — The frequency of the lower limit of the noise window for estimation of SNR. Due to the discrete nature of the spectrum, the actual frequency boundary may differ. The message window will indicate the actual frequency used.

noise window end (Hz) — The frequency of the upper limit of the noise window for estimation of SNR. Due to the discrete nature of the spectrum, the actual frequency boundary may differ. The message window will indicate the actual frequency used.

pulse length (μs) — The duration of the RF pulse in microseconds.

acquisition points — The number of points to acquire during an acquisition. The acquisition time is this number divided by the specified bandwidth.

recovery delay (μs) — The time between the end of the pulse and the beginning of acquisition to wait for the receiver electronics to recover from ring down.

recycle delay (s) — The requested recycle time between acquisitions. Since this is implemented at the script level the parameter is calculated by the spectrometer.

bandwidth (kHz)— The bandwidth of the receiver channel. This number determines the dwell time of the data acquisition. It is the rate, in kHz, at which the digitizer samples the signal.

post filter attenuation — The attenuation setting of the filter electronics.

Data Processing Group

zero filling — The number of points to use for zero filling of the spectral data.

phase correction (degrees) — The amount of zeroth-order phase correction to apply to the spectral data in degrees. This parameter only affects the displayed phase and not the phase of saved data.

exp. apodization (Hz)— If non-zero, applies an exponential apodization to the time series data (FID) specified in hertz. This parameter only affects the displayed spectrum and not saved data.

Plot Parameters Group

max plot points — The maximum number of points to plot to the browser. If fewer points are specified than the number of acquisition points, the script will attempt to decimate the time and spectral data down to a number of points that does not exceed this number. If greater than the number of acquisition points are specified, the script will plot the number of acquisition points to the browser. The purpose of this parameter is to decrease the load on the operating system. This may improve the ability of the operating system to accommodate the user specified recycle time. This parameter does not affect the number of points saved to data files.

max time to plot (ms) — The maximum time to plot for the time series (FID) data in the browser. This parameter is useful when the user wants a long acquisition time but wants to look at the beginning of the FID in detail. This parameter does not affect the number of points saved to data files.

min freq. to plot (Hz) — The minimum frequency to plot for spectral data in the browser. This parameter is useful when the user only wants to look at part of the acquired spectrum. This parameter does not affect the number of points saved to data files.

max freq. to plot (Hz) — The maximum frequency to plot for spectral data in the browser. This parameter is useful when the user only wants to look at part of the acquired spectrum. This parameter does not affect the number of points saved to data files.

live plot — Plots data to the browser for each scan acquired. Unchecking this parameter may improve the ability of the operating system to accommodate the user's requested recycle delay.

magnitude — Select whether to plot the spectral magnitude along with the real part of the spectrum.