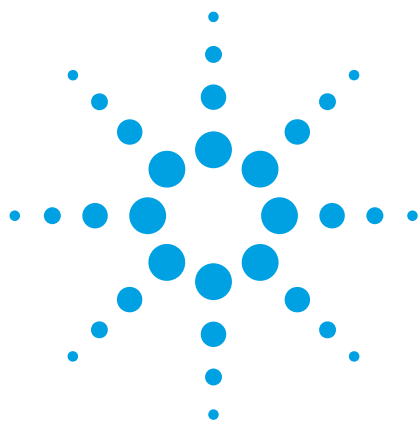




Shimming with VnmrJ 3.1 Software for Peak NMR Performance

Application Note

Author

Ron Crouch
Agilent Technologies
13000 Weston Parkway
Cary, NC 27513
USA

Shimming is the term used to describe the process of adjusting the shape of the effective magnetic field in the region of the sample in an NMR magnet, in order to yield good resolution in the NMR experiment. The term “shimming” is historical, dating to the very early days of NMR spectroscopy when scientists actually inserted mechanical shims into the magnet system to affect the shape of the applied field. Modern NMR consoles now provide adjustment through multiple coils controlled by computers and digital-analog converters (DACs) designed to correct virtually all field shape. Shimming is done in both a maintenance mode and sample-to-sample, in order to assure the highest resolution results. The Agilent NMR console offers a variety of technologies to provide facile control of the adjustment process. This technical overview describes the use of four easy-to-use tools in the VnmrJ 3.1 Software to perform both sample-to-sample and maintenance shimming and assure superior NMR performance.



Agilent Technologies

Sample-to-Sample Shimming

For best performance, shimming is done with each sample, using the appropriate tools in the VnmrJ 3.1 software. The default shimming technique is the use of Z-PFG to adjust the most important Z-shims that are axial to the long axis of the sample.

Z-PFG

Changes in the position of the NMR tube, the height of the sample, or the type of solvent can have significant effects on spectral line shape, due to changes in the magnetic field shape. These can be offset with Z-Axis Pulse Field Gradient Shimming (Z-PFG). There is a convenient menu entry point for managing all PFG shimming tools in the VnmrJ 3.1 software. The implementation of Z-Axis PFG shimming is fully automatic before any sample, as a routine step in data acquisition, and can be selected to be performed before any NMR experiment as well. The NMR operator has the choice to accept and use the default PFG shim map or a different one. For example, the spectrometer may be running in automation, with the default Z-PFG map set for ^2H observe, and the sample in pure H_2O . In such a case, the operator might select a ^1H PFG map for use with this sample.

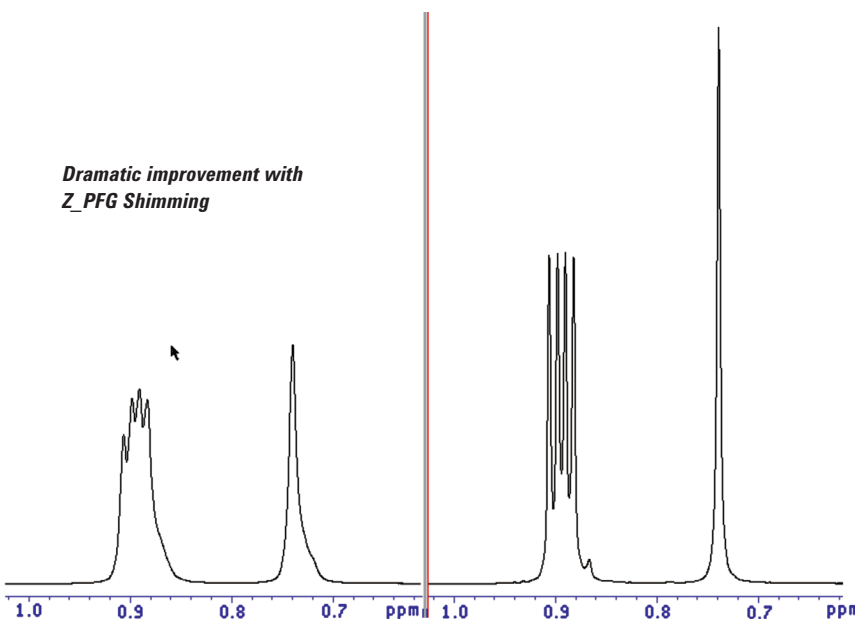


Figure 1. Automatic Z-PFG shimming of a spectrum improves resolution. The left spectrum was acquired before shimming, and the right spectrum was acquired following Z-PFG shimming. Both of these spectra are scaled identically.

Given a high lock sensitivity (which is the case with the OneNMR probe), ^2H Z-PFG shimming can be done with a single scan for any solvent. This means that the important step of doing Z-PFG shimming on a sample-to-sample basis typically takes only a total of 10 to 20 seconds. Also, when a series of multiple experiments is chosen to be run, each of which is quite long, each experiment can be quickly Z-PFG shimmed before beginning acquisition of data, at the choice of the operator.

Figure 1 illustrates a realistic loss of resolution and/or line shape due to differences in homogeneity between samples caused by different solvents and significantly different tube liquid column heights. The improvements in resolution and sensitivity resulting from an automatic Z-PFG shimming that was about 20 seconds in duration are remarkable.

Proshim

Proshim (introduced in VnmrJ 3.1) provides easy touch-up shimming along the x and y axes of the sample for best line shape. Proshim optimizes the shim values one at a time in a very fast manner. Available shim methods are in the menu list (Figure 2). After selecting a desired method, shimming can be initiated manually or on-demand. Proshim can also be used for maintenance shimming (see the Maintenance Shimming section). Proshim methods are simple text files

presented as a list of the shims to optimize in a given order, and can be run in automated mode. When an extensive Proshim method such as “allshims” or “4th-order_xyz” is used, it can be helpful to follow it with a final Z-PFG shim. The user can define custom methods that will also appear on the menu (see the VnmrJ 3 Automation User Guide, Pub. No. 91001987 for details on creating methods). Proshim is provided in the VnmrJ 3.1 software to both complement and enhance the traditional Simplex lock autoshim.

Simply choose the desired method from the menu and click the Proshim Now button

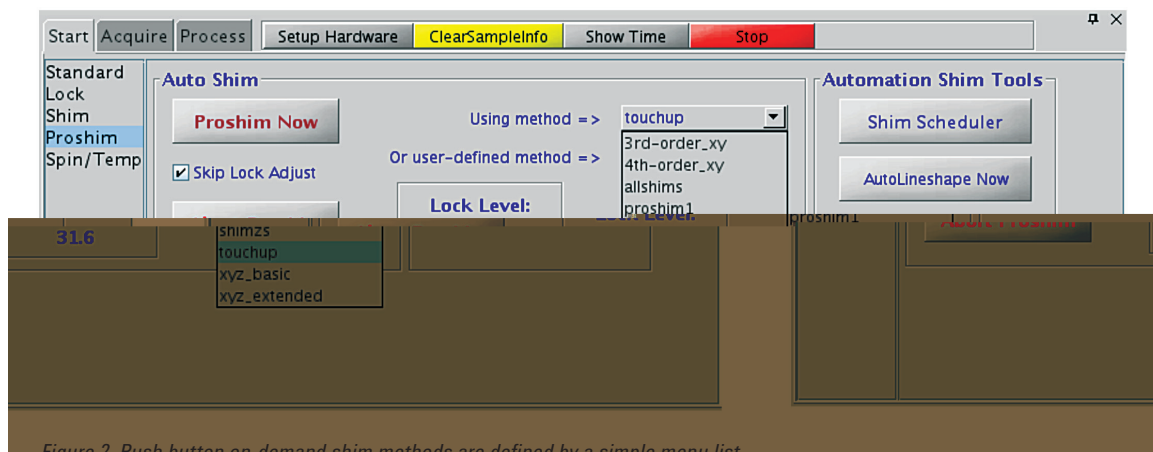


Figure 2. Push button on-demand shim methods are defined by a simple menu list.

Three-Dimensional Shimming

VnmrJ 3.1 provides a flexible and easy-to-use interface for adjusting all shims (along x, y and z axis) using gradient methods. 3D shimming can be done using any probe with or without gradient coils. 3D Shimming requires a very strong signal because of the large number of fids which must be acquired. For example, an 8x8 3-D matrix requires 128 fids for each shimming step. During the mapping process these 128 fids must be acquired for each of the 27 shims in a typical 27 shim set. Because of the lack of a sufficiently strong signal in an organic chemistry environment, 3D shimming is generally only useful for maintenance shimming. 3D Shimming is potentially usable for sample-to-sample shimming with Bio-NMR samples because they are typically in 90% H₂O solution and a strong signal is always available. Water suppression is an essential component for most Bio-NMR experiments, and optimal calibration of all of the shims using the 3D shim interface could be very valuable. Figure 3 demonstrates the value of 3D shimming using a sample of ubiquitin in 90% H₂O. The quality of water suppression with presaturation methods is a direct reflection of the quality of shimming. Note the nearly complete lack of residual H₂O near 4.6ppm and the sharp appearance of the protein methyl resonances near -0.2ppm. Figure 4 shows a series of two-dimensional NOESY experiments acquired with or without 3-D shimming. The quality of information is best in the experiment obtained after 3-D shimming with this ubiquitin protein sample.

Simplex Lock Autoshim

The traditional Simplex lock autoshim has been a feature with Agilent NMR systems for several years. It can still be employed to do shimming, using a large selection of provided shimming methods. The VnmrJ 3 Automation User Guide contains detailed information on how to create a custom method.

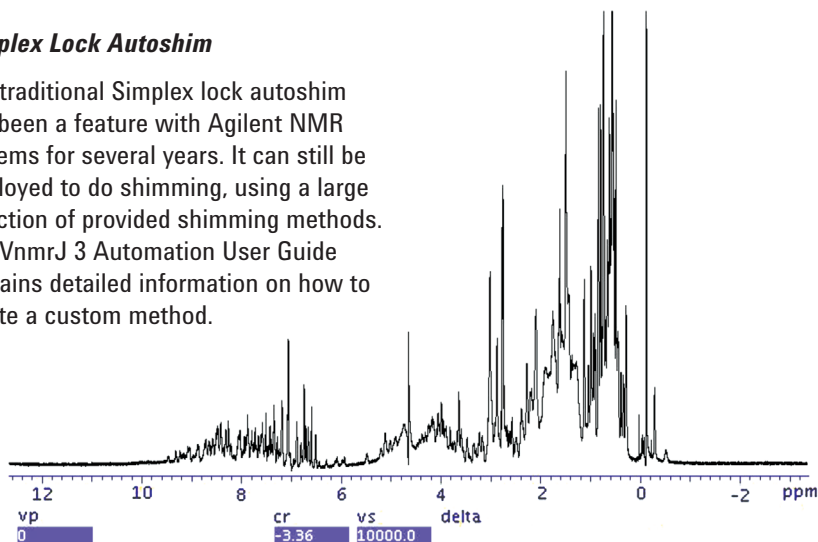


Figure 3. 1D spectrum of ubiquitin in 90% water in a Shigem tube using a normal presaturation, directly after 3D shimming. No processing methods for suppressing water were used. The total procedure was less than 10 minutes, after the sample temperature equilibrated.

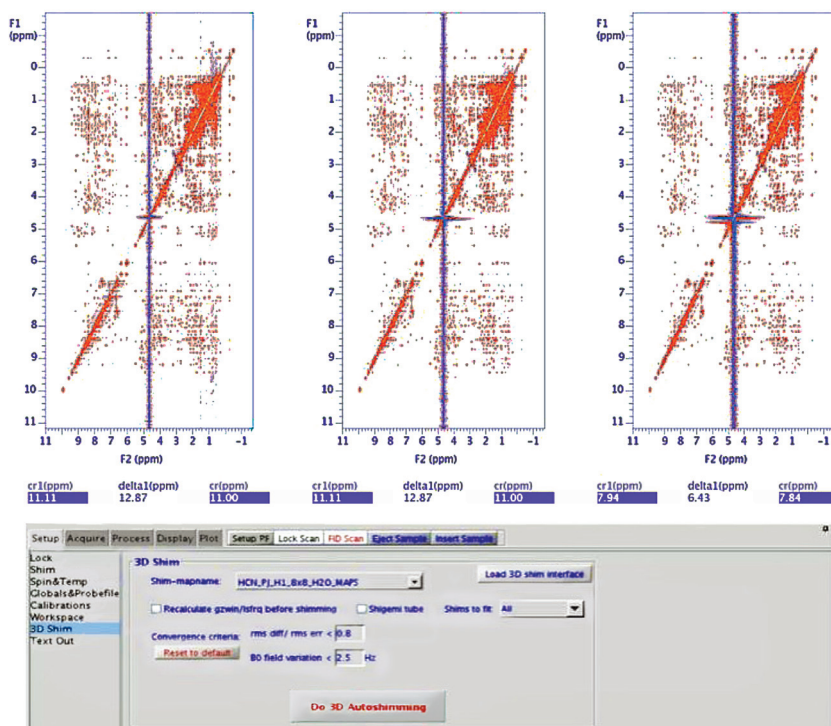


Figure 4. Shimming of three NOESY experiments using only presaturation for water suppression, and the 3D shim interface. The shims were first significantly altered to give bad shims before shimming. For the left spectrum, 3D shimming was performed before the NOESY experiment. Normal Z-PFG gradient shimming was performed on the middle spectrum, along with some quick manual shimming of the x and y shims. For the right spectrum, only manual shimming was done. There is an obvious improvement in water suppression from right to left, and spectra features are improved with better shims.

Maintenance Shimming

Maintenance shimming should be performed on a regular basis to assure proper operation over the long term. The easy-to-use maintenance tools accessed through the intuitive interface of the VnmrJ 3.1 software provide for efficient maintenance shimming. The need for maintenance shimming often dramatically decreases as a newly installed magnet settles in. Some touchup shimming might be desired on a daily basis in the first weeks after a magnet is commissioned, and this interval typically reduces with time.

Three-Dimensional Shimming

VnmrJ 3.1 provides a flexible and easy to use interface for adjusting all shims using gradient methods. 3D shimming can be done using any probe with or without gradient coils. It is important to note that use of 3D shimming as a maintenance tool is tied to a specific sample and that use on a sample-to-sample-basis (other than for Bio-NMR samples in 90% H₂O) is not appropriate. However, for maintenance shimming performed with a specifically selected sample 3D shimming is very powerful. The 3D shim interface is fully automatic and provides menu selection to tailor to a list of suggested samples. Perhaps the most convenient sample to use is a sample in 90% H₂O because of the speed with which the mapping process can take place. Once the sample type is selected from a menu, all calibrations, mapping steps, and shimming are carried out without further input from the operator. A variety of samples is supported and use is routine, even with probes that have no PFG gradients at all. 3D shimming can also be used for probe installation and affords a very rapid and thorough probe maintenance procedure. In essence, 3-D Shimming is the ultimate maintenance shimming tool.

Figure 5 illustrates the power of 3D Shimming to adjust a magnet that is very far from optimal values. For this figure a map created with a 90% H₂O shim map was used. The 3D shim on the water sample was followed by submission of the line shape sample with only the automatic Z-PFG adjustment. There is

a dramatic improvement in line shape. After magnet installation and the settling-in period are completed, typical monthly shim maintenance with 3D Shimming on a 90% H₂O sample provides good line shape results and assures ongoing magnet homogeneity for optimal performance (Figure 6).

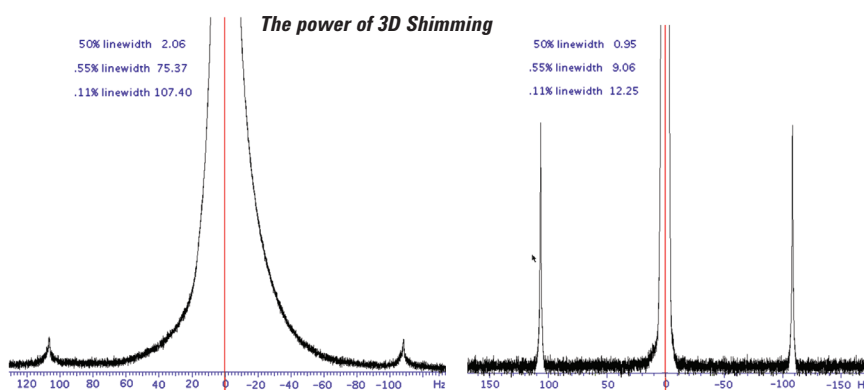


Figure 5. 3D Shimming can correct a magnet that is very far from optimal values, and give very significant improvement in line shape. The figure on the left shows line shape with a very poorly shimmed magnet. The figure on the right shows the same line shape sample after a 2 minute 3-D shim on a 90% water sample followed by just Z-PFG shimming with the line shape sample.

An excellent method for fast maintenance shimming

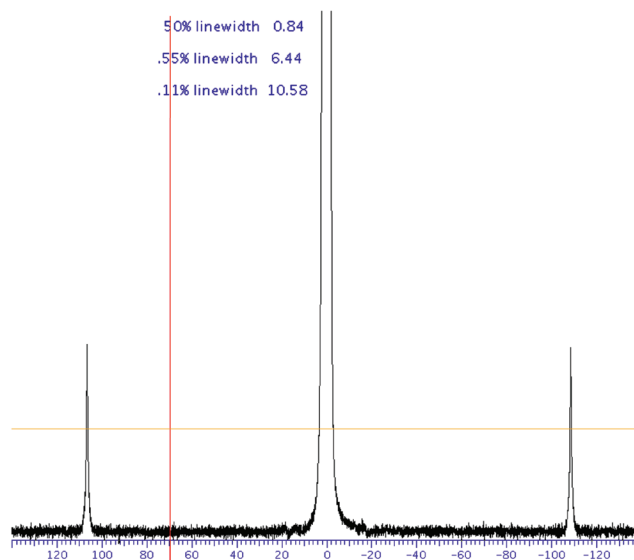


Figure 6. Monthly shim maintenance with 3-D Shimming on a 90% H₂O sample provides good line shape results and assures magnet homogeneity for optimal performance. The spectrum shown is from a 5% CHCl₃ sample in acetone-d₆.

Proshim

Proshim provides both on-demand and scheduled maintenance shimming. It utilizes a straightforward scheduling interface to enable the administrative user to define a shimming method for a line shape sample reserved in the sample tray. Proshim tells the console

to conduct unattended maintenance shimming at any time/day desired, either as a single event or on a recurring schedule (Figure 7). Once the job is defined (revealed by the Delete button being active and the Create button being grayed out), the day, hour and minute for desired maintenance shimming are entered and set by clicking

the Shim Scheduler button (Figure 7). Using a line shape sample with the Fast Lineshape automated method, which includes a final Z-PFG line shape adjustment, can provide scheduled magnet maintenance in an automated fashion. On-demand maintenance is also available with the push of a button.

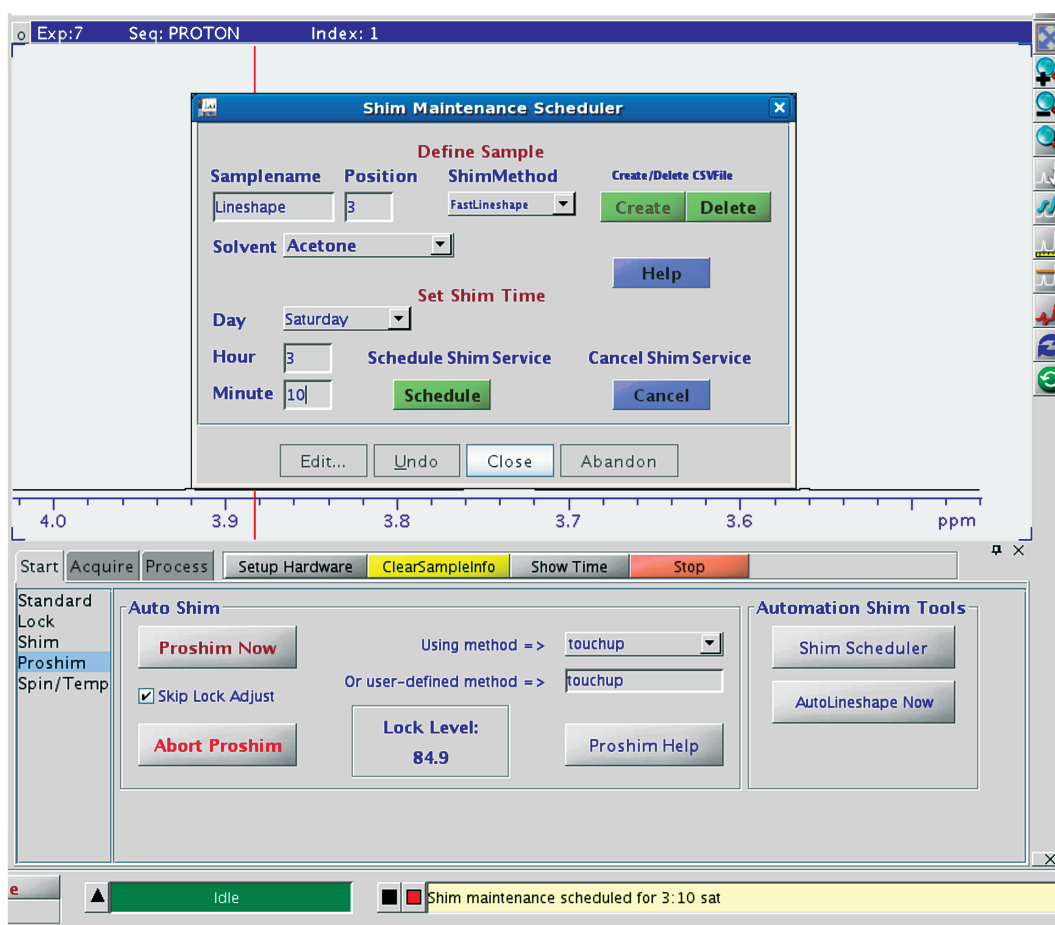


Figure 7. To schedule Proshim maintenance shimming, simply define the desired name for the shimming study and select the method from the choices in the ShimMethod menu in the Shim Maintenance Scheduler tool (top panel). In addition, the position of the line shape sample in the sample rack and the sample solvent are specified. Click Create and the shimming job is in place. Once the sample name, location, and shim method are set, the bottom portion of the scheduler can be used to define the time and frequency for the maintenance to be done. The Help facility guides the user through these steps.

Conclusions

The VnmrJ 3.1 software provides a variety of very powerful automatic shimming tools for both sample-to-sample and maintenance shimming. These range from simple Z-PFG for rapid routine shim adjustments for all samples, to a complete 3D PFG shimming interface for facile installation of new probes of any type. Proshim provides rapid, easy and automated fine adjustment of radial shims for both sample-to-sample and maintenance shimming, while 3D shimming is used primarily in the maintenance mode. Proshim is certainly preferred over the traditional Simplex shimming method, as it is faster and its methods are easier to create.

Maintenance shimming is made easy with the shim scheduling tool. It can be used to create a defined method to submit a study to automatically adjust homogeneity using the line shape sample, to run on any given day and at any given time. The VnmrJ 3.1 software provides powerful and easy-to-use tools to meet any and all sample-to-sample and maintenance shimming needs, in order to assure superior NMR performance.

For more information

Learn more:

www.agilent.com

Buy online:

www.agilent.com/chem/store

Find an Agilent customer center in your country:

www.agilent.com/chem/contactus

U.S. and Canada

1-800-227-9770

agilent_inquiries@agilent.com

Europe

info_agilent@agilent.com

Asia Pacific

adinquiry_aplsca@agilent.com

www.agilent.com

Product specifications and descriptions in this document are subject to change without notice.

© Agilent Technologies, Inc., 2011
Published in USA, April 8, 2011
Publication Number 5990-7860EN



Agilent Technologies