Homonuclear broadband decoupling of proton spectra is a challenging task since standard composite pulse decoupling (cpd) techniques cannot be applied. One possibility to achieve this decoupling are so-called pure shift or reset approaches.\textsuperscript{1,3} A new class of experiments uses a combination of small flip angle chirp pulses and a weak magnetic field gradient (PSYCHE, pure shift yielded by chirp excitation).\textsuperscript{4} This experiment shows improved sensitivity compared to similar methods.

\textbf{Experimental}

NMR spectra were acquired using a 50 mM Cyclosporine A sample in deuterated benzene (Z10092) on a Bruker AVANCE III HD 400 spectrometer equipped with a 5 mm BBO Prodigy probe at 298 K. The pulse program \texttt{reset\_psyche\_1d} was used with the shaped pulses \texttt{Bip720,50,20.1} for the 180° refocussing pulse and \texttt{Crp\_psyche\_20} for the PSYCHE element. The gradient strength of the magnetic field gradient during the chirp pulse was optimized in advance in a separate experiment (see corresponding chapter below). The length of the 90° proton pulse was 12 µs. 1024 complex data points were acquired in the direct dimension and the spectral width was set to 5 kHz resulting in an acquisition time of 205 ms and a dwell time of 100 µs. 32 to 2048 increments were acquired in the indirect dimension.

The number of complex points \( \kappa \) of each FID block is defined by \texttt{I31} and was set to values between 1 and 64, resulting in block lengths (\texttt{DELTA2}) of 200 µs to 12.8 ms per increment in \( t_1 \). Two complex points in the beginning of the FID were omitted (defined by \texttt{I30}).

Selected experimental parameters are shown in Table 1, the pulse sequence is shown in figure 1.

Processing of the data was done with the AU program \texttt{proc\_reset}. For a FID block size in the acquisition dimension of 8 and below, columns of the FID were back predicted and summed up to increase sensitivity. To increase resolution, spectra can be recorded using non uniform sampling (NUS).
Results

The PSYCHE experiment is a versatile tool to achieve homonuclear broadband decoupling of proton spectra. The effect of the decoupling and the apparent increase in resolution can be seen directly in Figure 2. Unfortunately, this increase in resolution results in a decrease in sensitivity. Compared to a standard 1D experiment, the sensitivity is decreased by a factor of 20 (depending on the experimental parameters). Nevertheless, the complicated multiplet pattern collapse to singulets and the number of different proton resonances can be identified unambiguously.

The pure shift interferogram (which is in principle the homonuclear decoupled FID) is reconstructed out of FID blocks with \( \kappa \) complex points that are acquired during each increment of \( t_1 \). The number of points of the interferogram depends on the number of \( t_1 \) increments and the block size \( \kappa \).

A long block size might lead to imperfect decoupling due to J-evolution during the FID block time \( \text{DELTA2} \), a short FID block size might lead to artifacts due to many discontinuities in the interferogram (compare Figure 3).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pulprog</td>
<td>Pulse program</td>
<td>reset_psyche_1d</td>
</tr>
<tr>
<td>ns</td>
<td>Number of scans</td>
<td>( 1 \times n )</td>
</tr>
<tr>
<td>I30</td>
<td>Number of complex points at the beginning of FID which are not included</td>
<td>2</td>
</tr>
<tr>
<td>I31</td>
<td>Number of complex points (( \kappa )) along the acquisition dimension used for reconstruction</td>
<td>1 - 64</td>
</tr>
<tr>
<td>dw</td>
<td>Dwell time</td>
<td>100 ( \mu )s</td>
</tr>
<tr>
<td>DELTA2</td>
<td>Length of FID block in seconds (( =2 \times \text{dw} \times I31 ))</td>
<td>200 ( \mu )s – 12.8 ms</td>
</tr>
<tr>
<td>cnst60</td>
<td>Sweep width of a single chirp element</td>
<td>10 000 Hz</td>
</tr>
<tr>
<td>cnst61</td>
<td>Flip angle of the chirp pulse</td>
<td>20°</td>
</tr>
<tr>
<td>gpz0</td>
<td>Gradient strength during chirp pulses</td>
<td>2% (optimize)</td>
</tr>
<tr>
<td>td1</td>
<td>Increments in ( F_1 )</td>
<td>( 2^n )</td>
</tr>
</tbody>
</table>

Table 1: Selected experimental parameters.
The PSYCHE spectrum with a FID block size of $\kappa = 64$ (corresponding to an evolution time of 12.8 ms) shows only little artifacts with good homonuclear broadband decoupling (blue). More artifacts will appear with a FID block size of $\kappa = 16$ ($\approx 3.2$ ms) which decrease in number but increase in intensity when using a FID block size of $\kappa = 8$ ($\approx 1.6$ ms).

Signal intensity in the PSYCHE spectra can be increased by summing up the first columns of the FID matrix. The idea behind this concept is depicted in figure 4.

**Figure 4**

Principle of increasing signal intensity via summation of the FID matrix. The chemical shift evolution in $F_1$ and $F_2$ dimension is identical, therefore the columns can be shifted to have identical chemical shift evolution in each data point in each row of the FID matrix. Afterwards, the missing points can be back predicted and the columns are summed up to generate a FID as if several scans were accumulated.

Points with the same color should have identical information with respect to chemical shift since the distance between data points in $F_1$ and $F_2$ is identical. Therefore, the FID matrix can be shifted, back predicted and summed up to increase the intensities of the signals. This can only be done with a small FID block size. Otherwise, back prediction will produce strong artifacts. As a rule of thumb, back prediction of up to 64 data points will give good results. For a block size $\kappa$ of 8, 8 columns can be summed up and the signal-to-noise ratio will increase by a factor of $\sqrt{8} = 2.83$. This can be seen in figure 5.

**Figure 5**

Comparison of PSYCHE spectra each with a FID block size of 8 and 256 increments in $F_1$. Blue: eight scans per increment, 50.5 min experiment time. Red: one scan per increment, 6.5 min experiment time. Green: FID sum of 8 columns with back prediction of the red spectrum. Spectra are manually scaled to the same noise level.

A PSYCHE spectrum with 8 scans is shown in blue while the spectrum with only one scan is shown in red. The decrease in sensitivity is clearly evident. If 8 FID columns of the red spectrum are summed up, the sensitivity increases and is even higher than in the blue spectrum. This procedure saves a factor 8 in measurement time and the spectrum can be acquired in less than 7 minutes instead of more than 50 minutes.

The method can be combined with non uniform sampling (NUS) as well to get a spectrum with sharper signals and less homonuclear coupling artifacts in a similar experiment time. Homonuclear coupling evolves during acquisition of the FID block. The longer the block size $\kappa$, the stronger the coupling evolution during that time. This will result in an unsteady interferogram and artifacts in the reconstructed spectrum. So a short block size would be preferable but requires many increments to get a well resolved spectrum.
Instead of acquiring a spectrum with a block size of $\kappa=16$ and 128 increments, one can acquire a spectrum with a block size of only 1 and 16 times more increments. To keep the measurements time in the same range, NUS can be used to acquire only $1/16\,(=6.25\%)$ of the increments. Another advantage is that 64 columns of the FID matrix can be back predicted and summed up to improve the sensitivity of the spectrum. Figure 6 shows a normal PSYCHE spectrum in blue and a PSYCHE spectrum with NUS and back prediction/column summation in red. The signals in the red spectrum are sharper and have a higher intensity due to less homonuclear coupling artifacts in the spectrum.

**Conclusion**

The PSYCHE experiment is a versatile method to achieve homonuclear broadband decoupling. Spectra can be acquired in short times with reasonable resolution and sensitivity. Sensitivity can be improved by applying back prediction and summation of columns of the FID matrix. To increase resolution and sensitivity, NUS in combination with back prediction and summation of columns can be applied to acquire spectra with a FID block size of only 1 and many increments.

**Optimizing the Magnetic Field Gradient Strength**

To achieve best results, the magnetic field gradient strength during the chirp pulses needs to be optimized. First a new experiment with only one increment in F1 is recorded and the first FID is processed with ft afterwards (PROCNO must not be 999). In the new 1D file, zoom into a signal or group of signals at the far right or left side of the spectrum. Save the displayed region to parameters F1/2 by right clicking in the spectrum and selecting ‘Save Display Region To…’ or by typing dpl into the command line. The gradient strength GPZ0 is then optimized with paropt from 0.5% to 3% with 0.1% increments to find the value for maximum signal intensity. An optimization profile can be seen in Figure 7.
References