Positive Probability Ltd

Note N2: S/N Enhancement – C^{13} NMR Data

Introduction

No method can be particularly effective when the peaks in the data are very narrow. This is because there is very little difference in the frequencies that make up the signals (their width) and those that are found in the noise. However, both data reconstructions and non-linear filters provide significant gains over traditional filter methods. Here, the results of these new methods are compared with traditional Savitsky-Golay smoothing.

Data

The 13C NMR data presented here were obtained from a single pulse on a weak aqueous solution of codeine phosphate. The S/N was very low and there were also two strong artefacts that would have been cancelled if more pulses had been used.

Methodology and Data Processing

The data were filtered using standard 3, 5, 9 & 15 point Savitsky-Golay smoothing. For comparison, the original data were then filtered using ***Enchant™***. Although ***Enchant™*** is a filter, it is an iterative, non-linear method. It has been specifically designed to remove only high frequency information regardless of the noise characteristics in the data. Its behaviour is also independent of any baseline error and the vertical dynamic range. The method has two major advantages over linear filters. These are:

1. The method is fully automatic and there are no user inputs.
2. There is virtually no broadening of genuine signals.

However, there is a small dependence on the width of the peaks in the data and very sharp peaks will suffer very slight broadening. No broadening is detected for peaks more than a few data points wide. The special behaviour of ***Enchant™*** is achieved through a novel noise correlation technique that efficiently allows signals to be identified in noise so that the noise may be filtered independently. Therefore, noise over signals is filtered to the same extent as noise in the baseline. Finally, the data were deconvolved using the ***ReSpect™***-based fast reconstruction method - see Application Note P3 for a full description. The model width was assessed from the peaks to the right of the centre of the data and the shape was assumed to be Lorentzian.

Results and Discussion

Savitsky-Golay

Figure 1 below shows the data and the smoothed results using 3, 5, 9 & 15 point smoothing. Each result has been vertically scaled so that the average signal amplitude is constant. Because the peaks are narrow, they are also severely filtered and broadened. Therefore, the signal amplitudes are reduced almost as much as the noise and, as can be seen, there is little benefit to be gained by applying a conventional linear filter. Also, for narrow peaks no benefit would be obtained by using a Lorentzian to Gaussian Fourier filter and it would be necessary to adjust two parameters and perform a series of trials to obtain an acceptable compromise between peak broadening and the improvement in S/N.

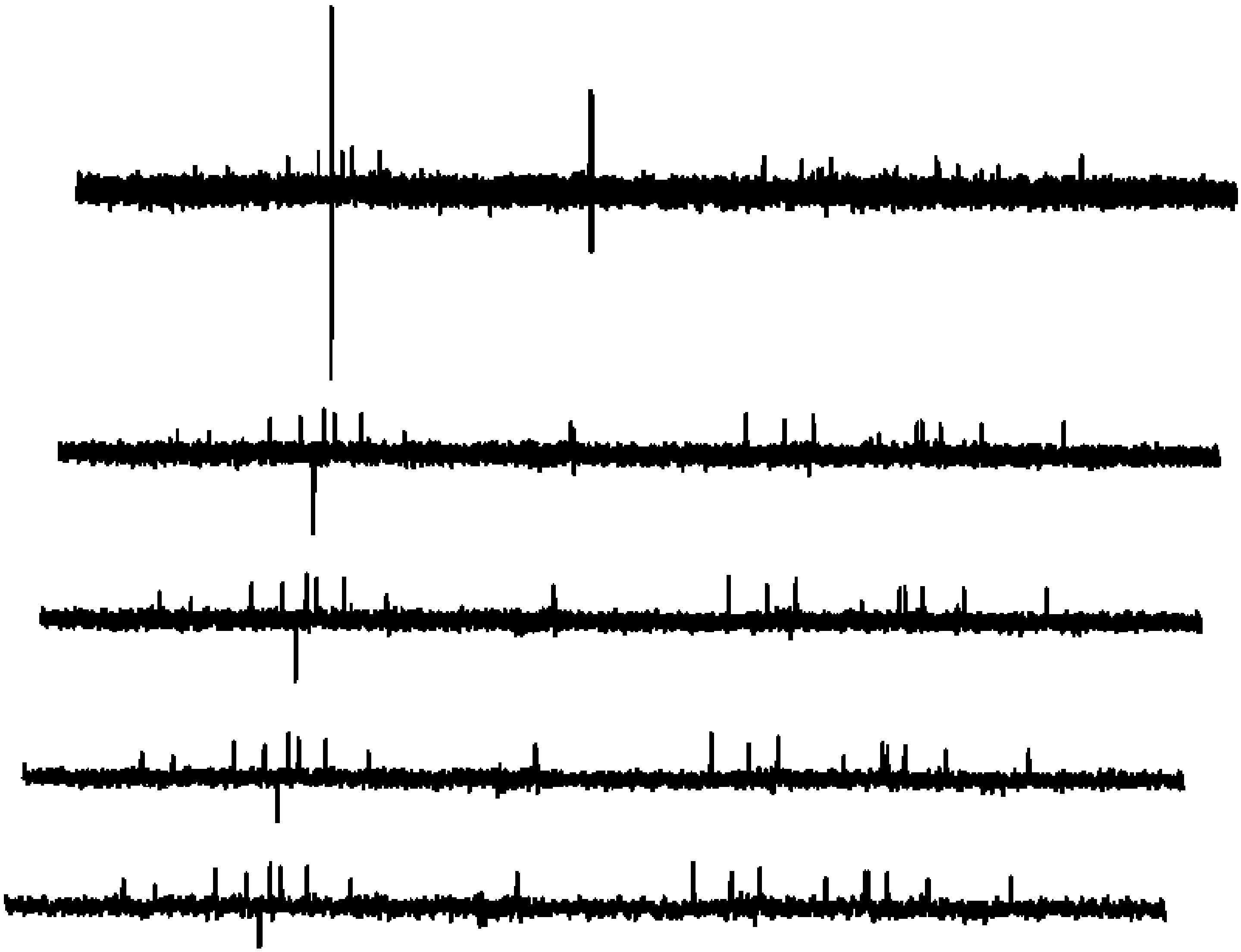

Figure 1: Top to bottom: Data, then 3, 5, 9 & 15 point Savitsky-Golay smoothing.

The instrument artefacts – identified by their positive and negative-going features – are very sharp and are heavily filtered even with a 3-point smoothing. Note that there is a genuine signal just to the left of the central artefact.

Enchant™* and *Enhance™

Figure 2 below compares the data with the results obtained from the ***Enchant™*** and ***Enhance™*** methods. The top trace is again the data and the centre trace shows the ***Enchant™*** result. There are two points to note.

1. Although there has been a dramatic improvement in the S/N, the amplitude of the instrument artefacts is virtually unaffected. Therefore, even for these very sharp features, there has been almost no peak broadening.
2. The S/N is almost twice that obtained using Savitsky-Golay filters and this was achieved with a method that has no input parameters.

The bottom trace is the reconstruction and it is apparent that there is virtually no noise in this result and that all 18 C13 signals are clearly visible. This demonstrates the advantage of data reconstruction methods over the more traditional methods commonly present in manufacturers' software. Of course, there is the penalty that the computation time is significantly longer but the improved results generally outweigh this disadvantage.

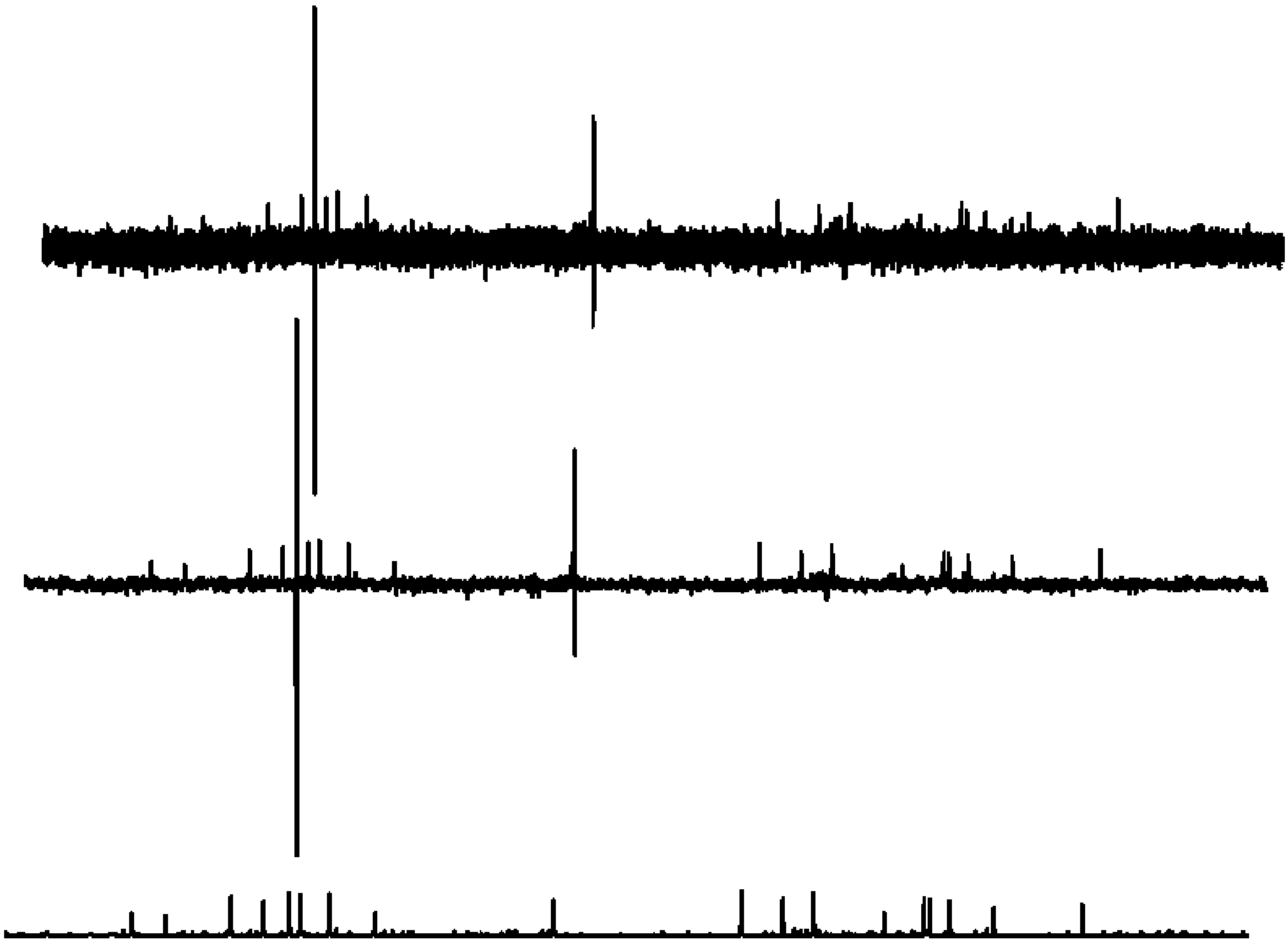

Figure 2. Top to bottom: Data; ***Enchant™*** *result;* ***Enhance™*** *reconstruction*

It is significant to note that the instrument artefacts are absent from the Reconstruction. The reason for this is that positive and negative features do not conform to the model and they are therefore correctly treated as noise. Depending on the data and the nature of any artefacts, data reconstruction methods will frequently eliminate artefacts to provide very clean results.

Conclusions

This example has demonstrated that an automatic, non-linear filter has the ability to provide significant gains in S/N without broadening genuine signals. Although the improvements are not as dramatic as those obtained using a data reconstruction method, the computation times are considerably shorter.