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An application of wavelet transform toward noisy NMR peak suppression

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Abstract : A shift-averaged Haar wavelet transform was introduced as a new and excellent tool to distinguish real peaks from the noise contaminated NMR signals. It is based on Haar wavelet transform and translation-invariant denoising process. Donoho's universal threshold was newly introduced to the shift-averaged Haar wavelet transform for the purpose of automated noise suppression, and was quantitatively compared with the conventional uniform threshold method in terms of threshold and signal to noise ratio (SNR). New algorithm was combined with a routine to suppress a large solvent peak by singular value decomposition (SVD). Combined algorithm was applied to the real spectrum that containing large solvent peak.

INTRODUCTION

In spite of the great development of instruments and techniques for the last few decades, efforts of NMR signal enhancement have been made in many challenging research areas. Many signal processing techniques and algorithms to improve the signal to noise ratio (SNR) and resolution have been developed together with the developments of more efficient hardware components.

Solvent suppression or noise elimination methods by singular value decomposition (SVD) and wavelet transform (WT) were developed in the previous works of our lab[1-3]. In these papers, both SVD and WT were introduced as a powerful data processing method. SVD has in general an advantage in solvent peak suppression while WT is effective in noise

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elimination.

Singular value decomposition (SVD) is defined as[4,5]

$$A = U\Sigma V^T, \tag{1}$$

where matrix U and V are phase related square matrices carrying $m \times m$ and $n \times n$ dimensional size, respectively. The upper capital letter T refers to the transverse matrix. The matrix Σ is a diagonal matrix that consists of the eigenvalues. These eigenvalues are magnitudes of the peaks.

For the suppression of large resonance peak, some of the largest diagonal elements of Σ matrix have to be replaced by zero.

Wavelet transform of a signal f is an inner product of f with building blocks $\psi_{a,b}$ called wavelets. These building blocks are obtained from a single function ψ called mother wavelet by dilations and translations, that is,

$$\psi_{a,b}(t) = \frac{1}{a}\psi\left(\frac{t-b}{a}\right), \tag{2}$$

where the dilation parameter $a > 0$, and the translation parameter $b \in \Re$ may be continuous or discrete. When the parameters are discrete values, the wavelet transform is DWT.

Haar wavelet transform[6] was selected for the noise suppression. Haar wavelet transform has several advantages for noise reduction of NMR spectra. At first, since Haar wavelet transform is an orthonormal transform, it is easy to estimate the statistical characteristics of noise of NMR spectra in the wavelet-domain. In the computational points of view, Haar wavelet transform provides a simple and efficient transform coding without requiring any boundary treatment. While the Haar wavelet approximation has the stair-step nature, this artifact can be significantly reduced through the averaging step in translation-invariant denoising process[3].

As a practical noise suppression step, the application of threshold in the wavelet domain is important, and the finding of appropriate threshold level is most important in this step.

Donoho and Johnstone suggested the universal threshold (λ) according to statistics[7]

$$\lambda \cong \sqrt{2\ln N}\hat{\sigma}, \tag{3}$$

where N is a number of data point, and $\hat{\sigma}$ is an expected value of standard deviation,

$$\hat{\sigma} = \frac{MAD\left|\bar{d}_{K-1,j}\right|_{1\le j\le 2^{K-1}}}{0.6745} \quad , \quad (N = 2^K) \tag{4}$$

where *MAD* implies a median of given data set.

We introduced Donoho's universal threshold into the shift-averaged Haar wavelet transform algorithm for the development of an automated noise suppression tool, and quantitatively compared the universal threshold with the conventional uniform threshold in terms of threshold and SNR. New noise elimination algorithm using the universal threshold was combined with the solvent peak suppression routine that based on SVD method as an attempt to make a more convenient and powerful post-processing tool, and the combined algorithm was applied to the noisy ^{1}H-NMR spectrum containing large solvent peak.

EXPERIMENTS

NMR Experiments

10*mM* Zinc binding Leuteinizing hormone releasing hormone (Zn-LHRH) dissolved in DMSO-d6 / H_2O mixed solvent. The large HOD peak at off-resonance region was used to test current NMR processing routine. NOESY spectrum were recorded on a Varian UNITY 500 MHz NMR spectrometer with 2048 data points, 256 *t*1 increments and 300*ms* mixing time. First FID of NOESY data was used to test 1D version of combined algorithm.

Program Coding

C/C++ routines were programmed on the PC with Microsoft Windows 2000 professional as operating system and SGI octane. Executable file was generated by visual C/C++ compiler and IRIX C/C++ compiler. FID was converted to HyNMR format or double precision text format. The program consists of two major part, water suppression part by SVD and noise filtering part by wavelet transform. Noise filtering part based on the shifted Harr wavelet algorithm is introduced in the previous work[3]. Both Donoho's universal threshold and uniform threshold functions were programmed in. Overall procedure of processing algorithm is summarized in Fig. 1. At first, time domain FID data was processed to frequency domain, and phase was corrected. Toeplitz matrix was constructed from the frequency domain data set, and decomposed to obtain a set of eigenvalues, implying intensities of each peaks on the spectrum. After removing of the eigenvalues of water peak, Toeplitz matrix was reconstructed by matrix multiplication of an eigenvalue matrix with two matrices relate to phase of the peaks. As an input of noise suppression part, shifted data matrix was constructed from the Toeplitz matrix obtained at the previous step. After Haar wavelet transform, two types of threshold, Donoho's universal threshold and uniform threshold, was applied for the elimination of noise elements.

Noise-filtered matrix can be converted to a noise free pure spectrum by sequential execution of inverse Haar wavelet transform, shift-back operation and signal averaging of all slices. In the every step of data processing, SNR values were evaluated for the quantitative comparison.

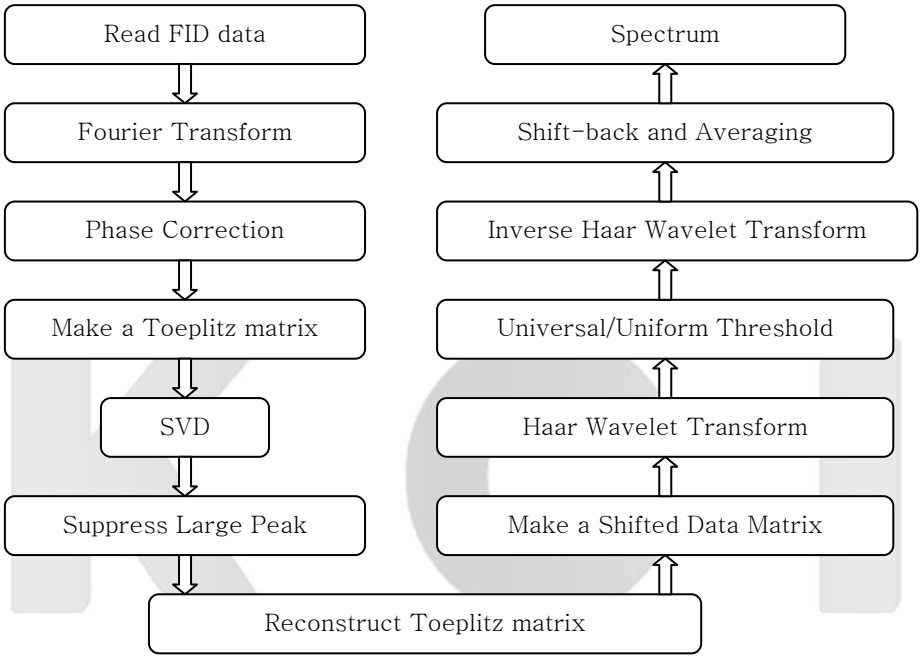

Fig. 1. Flow diagram showing overall procedure of the combined algorithm.

RESULTS

Toeplitz matrix was constructed with a rank of 100 in this work. Very first four eigen-values that are much larger than others are replaced with zero for the suppression of large water peak. The resulting spectrum was shown in Fig. 2 (B). In the part of noise suppression, two factors are important for the efficiency. The most important factor is a threshold level, and another factor is a number of shifted slices. To find an ideal threshold value automatically, Donoho's universal threshold was introduced and tested by multiplication with weight factor. Weight factor of 0.5 implies that half of the calculated universal threshold was used. Fig. 3 is showing the S/N ratio curve through the weight. Universal threshold gives a reasonable value near the ideal threshold. The case of 200 shifted slices is

more efficient about 7% than the case of 1024 slices.

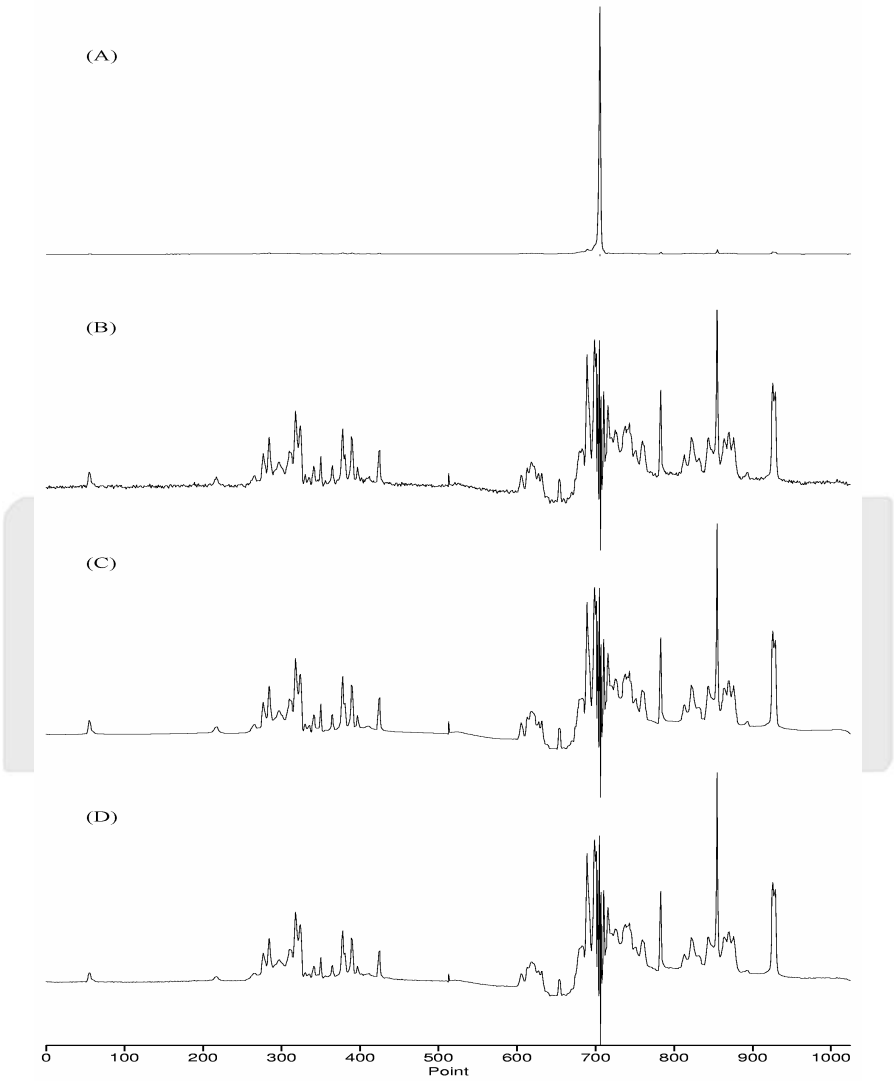

Fig. 2. 1D ^{1}H-NMR spectrum obtained from a first FID of NOESY data of Zn-LHRH complex has an off resonance large water peak (A). After application of a large solvent peak suppression routine using SVD (B). After application of noise suppression routine on the Fig. 2 (B) using uniform threshold (C), and universal threshold method (D), the noise on the baseline is eliminated.

Uniform threshold was also tested by measuring S/N ratio. As can be seen in Fig. 4, when a uniform threshold is applied, the number of shifted slices is not a critical factor because of the fact that the difference of S/N ratio between 200 and 1024 shifted slices is only 0.7%, and the S/N ratio value is larger than universal threshold about 19% at the most efficient threshold level, 2700.

Uniform threshold yields not only a larger S/N ratio, but also more sharp peaks, Fig. 2(C), than universal threshold, Fig. 2(D).

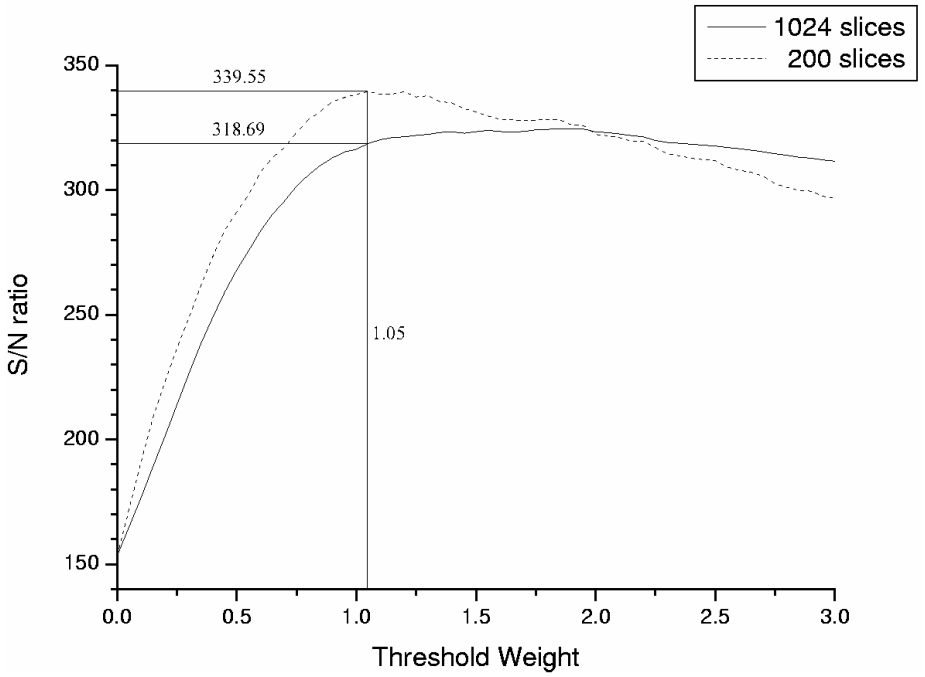

Fig. 3. S/N ratio curves according as the weight showing Donoho's universal threshold can find the believable optimal threshold level that giving maximum S/N ratio.

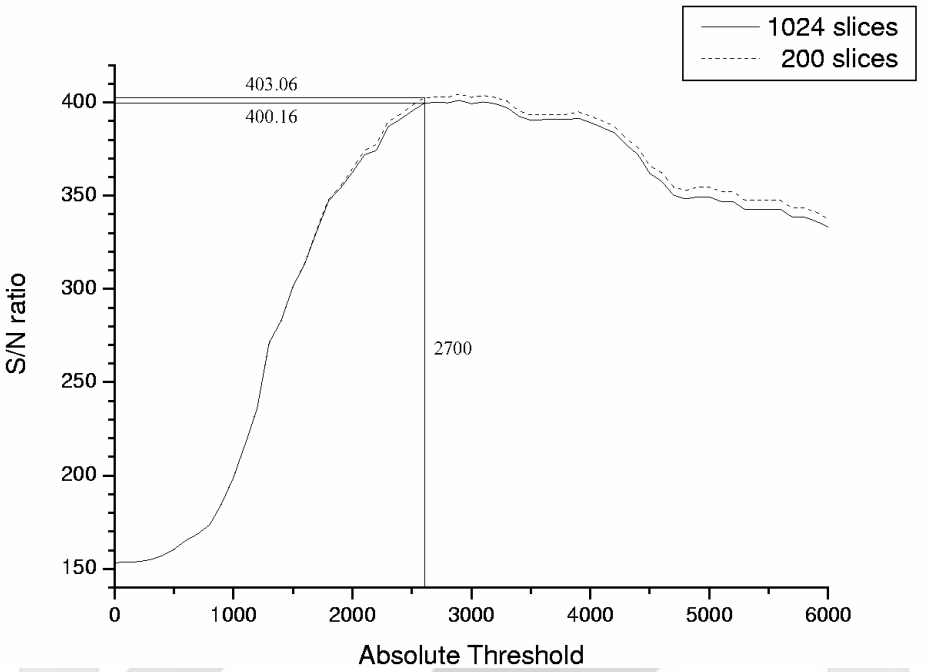

Fig. 4. Uniform threshold *vs* S/N ratio graph showing the nearly overlapped curves between 200 and 1024 shifted slices.

CONCLUSION

Small number of slices in noise peak suppression causes the wiggling of NMR peaks, therefore, the number of slices must be larger than minimum for the correct shaped peaks. On the other hand a large number of slices decreases efficiently, and consumes the computer resource and computing time. The most reasonable number of slices is about 200.

Uniform threshold is more efficient than universal threshold, but currently most efficient uniform threshold level can't be found directly. Universal threshold is less efficient than uniform threshold, but has a strong point that is applicable for automatic noise suppression.

Combined algorithm of SVD and Haar wavelet transform was optimized with 200 shifted slices and universal threshold. Combined algorithm using uniform threshold is also programmed for the best quality of spectrum. Newly developed combined algorithms were appropriate for complex ^{1}H-NMR spectrum, and can be expected to be applicable for other types of spectra, ^{13}C, ^{15}N, ^{31}P, 2D spectra, etc.

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