A New Time-Domain Frequency-Selective Quantification Algorithm

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Introduction

In this paper, a new time-domain frequency-selective quantification algorithm, for quantitative analysis of MR spectra, is presented. By frequency-selective quantification, it is meant a quantification method which concerns only spectral components in a selected frequency region of interest, ignoring spectral components outside that region (1).

The usual frequency domain quantification, based upon a Fourier transform of the MR FID (Free Induction Decay), is frequency-selective by nature; however, it has some important limits: spectra require manual manipulations (e.g. phase adjustment, baseline correction); in the case of truncated time-domain data, the Fourier transform needs to be deconvoluted, before or during the quantitative data analysis (2). A new time-domain algorithm, denoted as FreSQuAl (Frequency Selective Quantification Algorithm), with in addition the advantage of to be frequency-selective, is presented. It consists in minimizing an opportune discrete value function of K continuous parameter (K being the number of the unknown signals' parameters which have to be fitted) obtained by the singular values of two opportune Hankel data matrices.

In order to test the FreSQuAl algorithm, both Monte Carlo simulations, which demostrate its ability to determine one signal in a selcted range of frequencies, for different Signal to Noise Ratio (SNR), both spectra of known contents, to test its ability for quantitative analysis, were considered.

Methods

The FreSQuAl algorithm is based upon the comparison of the singular values, obtained by Singular Value Decomposition (SVD) (3,4), of two opportune Hankel data matrices (5,6).

The first Hankel data matrix is obtained by the signal FID data (6), while the second is obtained by the signal FID minus the simulated signal to be tested. Due to Hankel matrix properties and the relation between the matrix and its singular values, singular values of the above mentioned matrices will have differences which are an opportune function of K continuous parameters (K being the number of the unknown signals´ parameters which have to be fitted), function which assumes only a discrete number of values. The algorithm concerns the minimization of this opportune discrete value function, defined in a continuous K-dimensional space. The discrete value nature of the function requires a multidimensional minimization procedure with only function evaluation and random choice of points to be tested. The first request can be satisfied by the downhill simplex method (7,8), while the second request by the method of simulated annealing (9,10,11). In particular, for the minimization of the function, a simulated annealing for continuous K-dimensional configuration space, which uses a modification of the downhill simplex method, has been used (12). This minimization procedure, due to Press et al. (12), has been little changed to take in account the discrete value properties of the function and the modified routines are presented.

Results

In order to test the FreSQuAl algorithm, both simulated FIDs and experimental 1H FIDs of known contents were utilized.

The simulated FIDs were generated by complex superposition of exponential decaying sinusoids with additive Gaussian noise. Each FID consisted of 2048 points with a dwell time of 249.6 ms. The program was written in Matlab and in order to generate random numbers, the randn Matlab function was used. Each FID consisted of 58 complex decaying sinusoids. The range of amplitudes, in arbitrary units, went from 50 to 13500, while the damping factor range was 5 – 250 Hz. The value of the phase, required only under particular experimental conditions, was set equal to zero (13). The noise amplitude, in the same amplitude arbitrary units, was varied from 30 to 210 and, for any noise amplitude value, 10 signals were fitted, one a time. For each noise amplitude value, the 10 tested signals were randomly chosen between the 58 signals, making attention to consider signals with amplitude such that the signal amplitude to noise amplitude ratio started from 4. Given, for each signal to be tested, a frequency range (20 Hz non symmetric large range), a large damping range (100 Hz linewidth non symmetric interval) and a large amplitude range (5000 a.u. non symmetric interval), the algorithm was able to find, for each signal and in a few minutes, the correct frequency (+/- 1 Hz), damping (+/- 1 Hz) and amplitude (amplitude error less than 5). Furthermore, the algorithm shows a good spectral resolution, because was able to distinguish signals only 4 Hz separated.

In order to test the FreSQuAl algorithm experimentally, a sample of known contents was considered. In particular, the sample contained 1.37 mg of Toluene in 2 ml of Chloroform, that is a 7.4 mM/l Toluene concentration. Five 1H NMR spectra were obtained using a Bruker digital spectrometer operating at 500 MHz. The experiments were carried out with a 90° flip angle pulse and 64 transients of 4 K data points, corresponding to a ±3255.2 Hz spectral window, accumulated.

The FreSQuAl algorithm was used to obtain the Toluene concentration and it was able to obtain the correct concentration with an error less than 10%.

Discussion

In this paper the new time domain frequency-selective algorithm FreSQuAl for MR spectra was presented.

It is based on the minimization of an opportune function obtained by comparing the singular values of two Hankel data matrices. FreSQuAl is able to fit a single signal in a MR FID by obtaining its amplitude, damping, frequency and phase. It offers the advantages of a time domain algorithm with in addition the property of being frequency selective.

The algorithm was tested both by simulated FIDs, both experimentally by considering a FID obtained by a sample of known contents. Simulations shown that it is quite robust, due to its nature consisting in comparing singular values of a FID with the singular values of the same FID, less than the signal to be tested. In this manner the effect of noise are quite reduced.

Experimental test shown that it is useful to quantify real spectra with an error less than 10%. Furthermore, FreSQuAl can be very useful in quantifying MR spectra very crowded in the frequency domain, because it can be very easily extended to include prior knowledge.

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