Use of the Filter Diagonalization Method in the Study of Space Charge Related Frequency Modulation in FTMS.

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The Filter Diagonalization Method (FDM) is a recently developed signal processing algorithm based on quantum mechanic’s mathematical formalism of the harmonic inversion problem¹⁻³. FDM is shown to provide extremely high precision in finding resonance frequencies with < 1ppm accuracy on small number of transient data points e.g. 10k. It was used in frequency shift chasing experiments for the purposes of determining intra-transient frequency shifts and using them for reference deconvolution and study of space charge effect.

In this study we used an in-house C++ implementation of the FFT Square Window FDM, which will be available as open source software in an upcoming release of the Boston University Data Analysis (BUDA) system. Theoretical spectra were generated by using in-house simulation software with 1 mega-point length and 1MHz sampling rate. Real spectra of Substance P were acquired on homebuilt ESI FTMS instrument (1 mega-point length with 1MHz acquisition rate). Frequency chasing experiments were performed on transient domains ranging from 1000 to 20000 data points starting with the 0 offset and shifting depending on the experiment from 1 to 200 data points into the transient. \(K_{\text{win}}\) used ranges from 4-11 points.

FDM shows amazing precision and high resolution on small number of data points. FDM is much slower and not as stable as FFT and for that reason cannot compete directly with FFT. However FDM proves to be a good tool for reconstructing frequency shift plots. On theoretical spectra it showed ability to trace frequency shifts of .005 Hz with signal/noise ratio of 2.

A substance P spectrum was used in the frequency chasing experiment (figure 1). The isotopic beat pattern is faithfully reproduced in both abundance and frequency shifts. Space charge, even for such a simple spectrum, are > +/- 400 ppm even though post FFT, it is possible to get 1ppm mass accuracy on this spectrum. This result indicates that the FFT effectively averages out these cyclic frequency shifts to achieve its results.

FDM, therefore, is a new tool for study space charge. The frequency shift plots, if they are shown to be consistent, could be used in reference deconvolution⁴⁵.
Figure 1. Frequency chasing experiment conducted on the Substance P mass spectrum. A) The first 0.14 Seconds of the transient signal. The 158906 Hz peak was followed using window of 1000 data points (1 millisecond) stepping 1 data point (1 microsecond) into the transient. B) Abundance vs. Time plot. C) Frequency (Hz) vs. Time plot.

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References: