Characterization of EPR spin-echo data for accelerated oximetry

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Target Audience: Researchers interested in characterizing or modeling the spin-echo response in pulsed electron paramagnetic resonance (EPR) to reduce the data acquisition time of EPR oximetry.

Purpose: The T2 decay constant of an exogenous paramagnetic probe is the metric that determines the oxygen concentration in EPR oximetry. In a spin echo sequence, the time *tau* between the 90 and 180 degree RF pulses is same time between the 180 degree pulse and the peak of a spin echo. As the time between pulses increases, the amplitude of the spin echo diminishes proportionally with a first-order exponential with rate constant T2. The traditional method varies the time between RF pulses and fits the decaying exponential using only the echo peaks. Each peak constitutes only one data point, whereas the entire echo could be utilized [1]. As a result, the traditional method used to evaluate the T2 decay constant in EPR is inefficient. In this work, we propose two methods for evaluating T2 decay in an EPR setting.

Methods: The first proposed method is based on the singular value decomposition (SVD) of measured echoes. The approach assumes that all echoes are identical in shape except for the amplitude and relies on finding the best rank-one approximation to the measured echoes. The resulting denoised echoes are then fitted with an exponential to find T2. Similar approaches have been used in MRI for image denoising [2]. The second proposed approach parameterizes the echoes, e.g., by using Gaussian or Lorentzian functions, and fits the measured echoes to find those parameters along with T2.

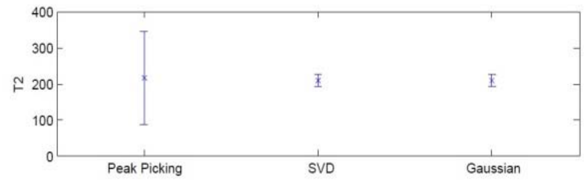

***Figure 1**: Comparison of the mean and three times the standard deviation of the T2 values (in nanoseconds) for the three methods for 10,000 trials. The standard deviations for the proposed methods are smaller than the traditional peak-picking method by a factor of 7.5.*

In the presented simulation study, a sequence of seven spin echoes were modeled to occur uniformly from *tau*=200 ns to *tau*=440 ns in increments of 40 ns. Each echo, 256 samples long, was modeled using a single Gaussian function with amplitude commensurate with the T2 (210 ns) exponential decay. Gaussian white noise with a variance of one percent of the peak amplitude was added. The seven-echo set was simulated and processed 10,000 times. For the traditional method, a T2 exponential decay was fitted using the echo peaks. For the first proposed method, SVD of 256x7 measured data matrix was employed. The left singular vector corresponding to the largest singular value was then fitted to the simulated echoes to estimate T2. For the second proposed method, echo was modeled using a Gaussian function with unknown variance and amplitude; these unknown parameters along with unknown T2 were jointly estimated by nonlinear least-squares fitting of the measured data.

Results: Figure 1 compares the performance of the three methods. The mean T2 values for the three methods are similar, but the error variances of the proposed methods were significantly lesser than that of the traditional peak-picking approach. The peak-picking method yielded a T2 of 216.2 ns, whereas the SVD and Gaussian modeling methods both revealed T2 values of 209.1 ns. On the other hand, the standard deviation of the estimated T2 for the traditional method was 43.2 ns, compared with 5.8 ns and 5.7 ns for the two proposed methods. Figure 2 illustrates the fitting process for the proposed Gaussian modeling.

In a preliminary measurement (data not shown), spin-echo data were collected from a paramagnetic sample (coal) on an X-band pulsed EPR spectrometer. The initial results show that the ratio of the first to the second singular values from the measured echoes was better than 10,000:1, which points to the validity to underlying rank-one structure. The echo shape for this particular probe was very accurately modeled by Gaussian. For other probes, shapes other than Gaussian can also be used to modeling.

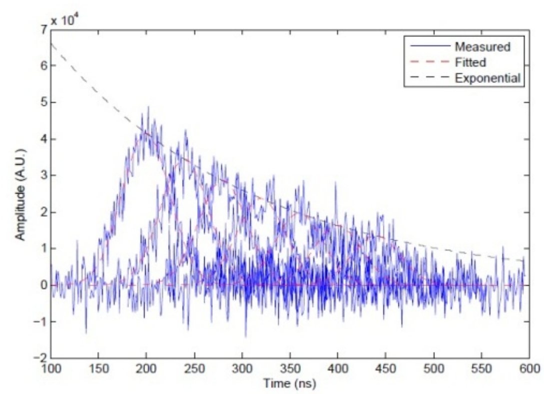

***Figure 2**: A set of seven noisy spin echoes fitted with Gaussian functions with exponentially diminishing amplitudes.*

Discussion: The traditional method is inefficient as it fails to utilize all the samples in an echo. The proposed methods facilitate the estimation of T2 in two ways. First, they use the entire echo in the estimation process. Second, they utilize a priori information that is not used in the traditional peak-picking method. For example, SVD exploits underlying rank-one structure (or repetitiveness) of the echoes, while modeling exploits parametric nature as well as repetitiveness of the echoes. The modeling approach provides a maximum likelihood estimation and slightly outperforms the approach based on SVD. However, SVD approach is more general and does not rely on finding or assuming a parametric model for the echoes.

For the simulation data presented, the standard deviations for the proposed methods are smaller than the traditional peak-picking method by a factor of 7.5. Since the standard deviation in the estimation of T2 is inversely proportional to the square-root of data acquisition time, the application of the proposed methods can accelerate the data acquisition for EPR oximetry by more than a factor of 50.

Conclusions: We have presented two methods to accelerate data acquisition for pulsed EPR oximetry. The methods are robust to noise and are predicated on exploiting the underlying structure in the measured echoes. In the future, the methods will be validated using experimental data.

References: [1] Tseitlin et al. *J. Magn. Reson.* **213**, 119-125. [2] Bydder, et al. *J. Magn. Reson. Imag*. **24**, 849-856. [3] Robinson, et al. *J. Magn. Reson.* **138**, 199-209.