

Better, faster, more versatile NMR diffusion measurements

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The range of applications and versatility of NMR diffusion measurements [1,2] increase with the speed, accuracy, and the practical lower concentration limits that can be used. For example, faster measurements expand the horizons of diffusion measurements to study reaction kinetics [3,4], as well as simply increasing throughput. Our group has been investigating various approaches for improving the performance of NMR diffusion measurements. Here we present some of our recent advances.

The absolute limit of detection will be determined by the spectrometer hardware and/or the ability to suppress nearby resonances [5], but even if a diffusion measurement is possible, it may not be practical due to the long experimental time required. Relatedly, some samples although easily providing adequate signal-to-noise ratios (SNR) can become tedious to perform experiments on due to long relaxation times (e.g., residual H₂O in deuterated solvents). Various methods have been presented for increasing the measurement efficiency, but most have ‘fatal’ flaws (e.g., limited to samples having only a single resonance, or to high concentration species, or the measurement no longer having a defined diffusion measurement timescale Δ). Further, diffusion measurements of low concentration species are especially difficult in the presence of multiple large solvent resonances as in chromatographic samples.

We have proposed two techniques to increase efficiency: the first is to run the experiment in a steady state mode [6] which requires only a trivial modification to the pulse sequence. The second is an obvious but seemingly unutilised approach in which the number of scans (NS) is varied through the array of experiments that constitute the diffusion measurement. Specifically, NS is varied as a function of the experimental parameter (typically the magnitude of gradient pulse amplitude g) and the signal normalised by the number of scans used at each iteration [7]. Conventionally, NMR diffusion measurements are performed with the same NS at each iteration of the experimental parameter despite the SNR being more than sufficient for many of the iterations. Hence, this new normalisation approach requires far less total scans.

Both approaches can shorten the experimental time by more than 70% without any loss in accuracy and unlike previous approaches, are totally general in their application. The methods can even be combined to further increase the experimental efficiency. We have also been exploring the optimal use of window functions in the analysis to maximise efficiency, and sophisticated multi suppression techniques [8].

References

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