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Measurements of Diffusion, T_1 and T_2 in One Shot by MMME

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Abstract

In this paper, we demonstrate a rapid simultaneous measurement of diffusion constant D, T_1 and T_2 relaxation times in just two scans. Theoretical standard deviations of D, T_1 T_2 for a wide range of T_1 and T_2 were predicted for given sequences with a random experimental error of 3%. By carefully selecting of sequence parameters for samples with different relaxation times, the error propagators in T_1, T_2, and D can be modified to within 10%.

Keywords

Coherence pathway, rapid simultaneous method, diffusion, relaxation rates, MMME

1. Introduction

The study of molecular dynamics, as well as rotational and translational diffusion requires the measurements of T_1, T_2 and diffusion constant which are typically measured in separate experiments, and therefore, requires a long experimental time.

In the presence of a constant gradient field (g), a sequence of n hard RF pulses will allow multiple coherence pathways (q) to produce multiple signals [1]. This class of sequences is called **m**ultiple **m**odulation **m**ultiple **e**choes (MMME). Different q creates different spatial phase modulation and yields an echo signal at different time. Consequently, in one scan of the sequence, different modulations with different diffusion, relaxation weighting and phase shift coefficients can be measured. Previous works have shown that the MMME sequence can be used as an effective method for the encodings of diffusion, flow and positional properties [2-7]. Here, we demonstrate the capability of MMME method for rapid simultaneous measurement of diffusion constant D, and relaxation rates T_1, T_2 with two scans without phase cycling in a few seconds.

2. Methods

The 4-pulse MMME sequence was used for simultaneous measurements of the diffusion and the relaxation rates. The time periods between adjacent *RF* pulses are τ, 3τ and 9τ, then

the echoes appear with equal time separation during the detection. The flip angles of the pulses were 54º - 71º - 71º - 110º, so that the echoes have more uniform amplitudes and simple shapes [2]. The magnetization of each echo coherence pathway (i.e. each echo q) is a product of three factors: the *RF* pulses (α), the diffusion (D), and the relaxations (T_1, T_2). It can be written as:

$$M_q = M_0 \cdot f_q(\alpha) \cdot \exp(-b_q \cdot D) \cdot \exp\left(-\frac{c_q^1}{T_1} - \frac{c_q^2}{T_2}\right) \tag{1}$$

where M_0 is the initial total magnetization, the symbols b_q, c_q^1, and c_q^2, are sequence dependent diffusion, T_1, and T_2 weighting factors, respectively, and they are determined by the sequence as:

$$\begin{aligned} b_q &= \int_0^{TE} k(t)^2 \mathrm{d}t, \quad k(t) = \gamma g \int_0^t q(t')\mathrm{d}t' \\ c_q^1 &= \int_0^{TE} (1 - |q|)\mathrm{d}t \\ c_q^2 &= \int_0^{TE} |q| \mathrm{d}t \end{aligned} \tag{2}$$

TE is the echo time, γ is the proton gyromagnetic ratio.

In practice, for two measurements with same RF flip angles, but different time delays, the ratio of the corresponding echo magnitudes will eliminate $f_q(\alpha)$. The amplitude ratios S_1/S_2 and weighting factors of the corresponding 13 echoes give sufficient data to uniquely determine D, T_1 and T_2 simultaneously.

3. Results and Discussion

Different echo spacing and gradient strength will result in different diffusion and relaxation weightings for each coherence pathway, thus offering a mechanism for optimization. For the sequence with the optimized parameters, synthetic data were generated by giving a random error of 3 % on each echo signal, and the standard deviation of T_1, T_2 and D were calculated for different T_1, T_2 in the range of 20 - 2000 ms ($T_1 \geq T_2$) with a constant D value. It can be seen, that using giving sequences, the error propagators in D, T_1 and T_2 can be controlled within 10 % (Fig.1).

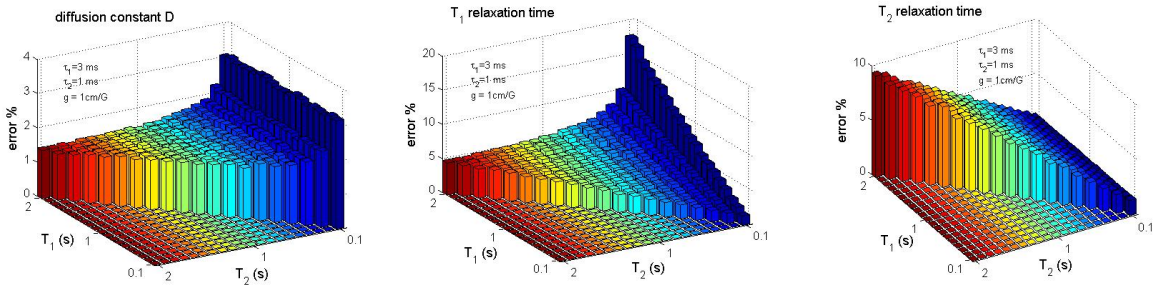

Fig. 1: Simulated standard deviations of D, T_1 and T_2 for optimized MMME sequences with a random error of 3 % on each echo signal. The results derive from 2 scans of (1) $\tau = 3$ ms, (2) $\tau = 1$ ms. The applied constant gradient is 1 G/cm.

Moreover, the simulation results show that the gain in less error propagator in relaxation times may result in a loss in more error propagator in diffusion constant, and the error in T_1 has opposite tendency to that in T_2 with the increase of the relaxation time. Therefore, the optimization of the experimental parameters should balance the diffusion and relaxation weightings for each coherence pathway. Fig.2 shows the contributions of T_1, T_2 and D to the

amplitude ratio S_1/S_2 of each echo and compares the experimental and simulated results of the sample with T_1 = 1002 ms, T_2 = 780 ms. The simulated values were derived from MMME method using T_1, T_2 and D values from standard NMR Inversion Recovery (IR), Carr-Purcell-Meiboom-Gill (CPMG), and Pulsed Field Gradient Stimulated Echo (PGSTE) measurements, respectively. The experimental data show excellent agreements with the theoretical data.

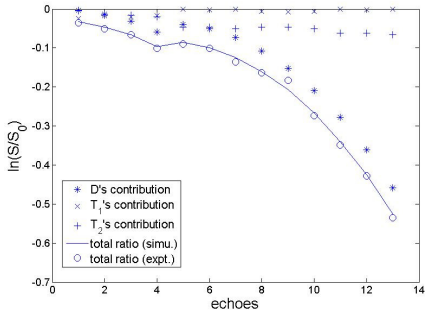

Fig. 2: The contributions of T_1, T_2 and D to the amplitude ratio of each echo for the sample of T_1 = 1002 ms, T_2 = 780 ms, $D = 1.69\times10^{-5}$ cm^2/s. Two scans of MMME measurements with (1) τ = 3 ms, (2) τ = 1 ms were performed. A constant gradient (g = 1.0 G/cm) along B_0 was applied in both scans.

Table 1 lists T_1, T_2 and D values with standard deviations from 10 separately repeated measurements by MMME method and those by the traditional methods for 5 samples with different relaxation times. It can be seen that the average values of T_1, T_2 and D from the MMME method with optimized parameters are close to that from the standard IR, CPMG and PGSTE methods, and the error propagators in T_1, T_2 and D are all within 10%.

IR/CPMG results (PGSTE: D=1.69 ×10^{-5} cm^2/s)	MMME results		
	T_1 (ms)	T_2 (ms)	D (10^{-5} cm^2/s)
T_1 = 1045 ms, T_2 = 807 ms	975±3.6%	760±3.6%	1.75±0.98%
T_1 = 741 ms, T_2 = 609 ms	796±3.6%	602±3.5%	1.73±0.35%
T_1 = 413 ms, T_2 = 329 ms	440±6.5%	329±6.9%	1.69±0.95%
T_1 = 134 ms, T_2 = 107 ms	134±5.3%	112±4.5%	1.60±1.48%
T_1 = 57 ms, T_2 = 50 ms	57±1.2%	50±2.0%	1.81±4.0%

Table 1. Experimental results of MMME measurements

4. Conclusions

We demonstrate a rapid simultaneous measurement of diffusion constant D, and relaxation times T_1, T_2 in just two scans without phase cycling within a few seconds. By optimization of sequence parameters for samples with different relaxation times, the error propagators in T_1, T_2, and D can be controlled within 10 %. This method can be used to detect the time-dependent processes in chemical reactions, production monitoring, and medical MRI.

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