Quadrupole-Dips Measured by Whole-Body Field-Cycling Relaxometry and Imaging

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INTRODUCTION

It is well known that proton relaxation in proteins and other bio-polymers can be strongly affected by interactions with the quadrupolar nucleus ^{14}N, where ^{14}N–^{1}H groups act as "relaxation sinks". This gives rise to "quadrupole dips", reductions in the proton spin-lattice relaxation time which occur at the three NMR frequencies corresponding to the ^{14}N nuclear quadrupole transitions. This effect was studied extensively in the early to mid 1980s, and quadrupole dips were measured in hydrated proteins and various biological samples [1]. The first *in vivo* demonstration of the phenomenon was carried out by Kimmich et al., who studied living leeches [2]. To the author's knowledge, however, no other *in vivo* measurements of quadrupole dips have been made until now. In this work, quadrupole dips have been measured for the first time in human muscle *in vivo* using a whole-body sized field-cycling relaxometry and imaging system. Field-cycled inversion recovery images have also been obtained of the human forearm, enabling indirect NQR imaging via the quadrupole dip effect.

METHODS

Experiments were carried out using a whole-body field-cycling MRI system, originally developed for field-cycled PEDRI free radical imaging using the Overhauser effect [3]. The imager uses a whole-body permanent magnet with a vertical field of 59 mT (Field Effects Inc., MA, USA) which provides the detection magnetic field. Field cycling is accomplished by the field-compensation method: a resistive, saddle-shaped magnet (Magnex Scientific Ltd., UK) is fitted into the bore of the permanent magnet, and the field from this secondary magnet can add to or subtract from the field of the permanent magnet. A field change of 30 mT can be achieved in 10 ms. There are no problems with eddy currents because the permanent magnet is made of ferrite, and the support structures are also non-conducting. Field gradient coils are integrated into the structure of the permanent magnet, and the useable bore of the secondary magnet coil is 52 cm in diameter, sufficient for human subjects. In this work, a split-solenoid coil with i/d 14 cm was used for NMR transmit and receive at 2.5 MHz. The imager is controlled by a commercial NMR console (SMIS Ltd., UK). A field-cycled, interleaved inversion-recovery / saturation-recovery pulse sequence was used to measure T_1 values by a two-point method; the pulse sequence is shown in Figure 1. During the polarisation period (length T^{pol}) the magnetisation equilibrates at the measurement field. A 10 ms adiabatic fast passage (AFP) inversion is applied and the field is returned to the measurement value where the magnetisation recovers with the spin-lattice relaxation time. The saturation recovery part of the sequence is identical, except that the AFP is not applied. T_1 data was collected over the range 30 mT to 80 mT, at intervals of 1 mT. An interleaved field-cycled inversion recovery imaging pulse sequence was also used, collecting images at 57.5 mT and 65 mT using an adapted version of the sequence.

RESULTS

Figure 2 shows a T_1 dispersion plot of the author's forearm; two quadrupole dips at 49 mT (2.1 MHz) and 65 mT (2.8 MHz) can clearly be seen. The positions of the dips are in excellent agreement with previous work [1,2]. The timing parameters were: T^{pol} = 600 ms, T^{evol} = 150 ms, TR = 1500 ms. A copper sulphate solution with similar T_1 was also measured, and showed a roughly linear variation of T_1 with field. Figure 3 shows field-cycled

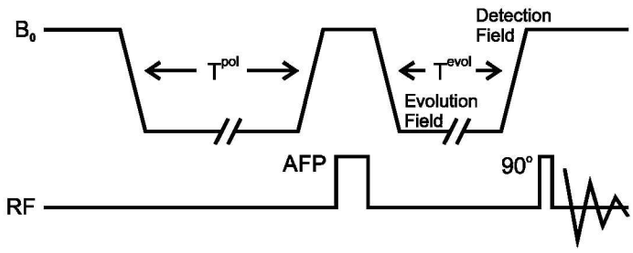

Figure 1: Field-cycled inversion-recovery pulse sequence.

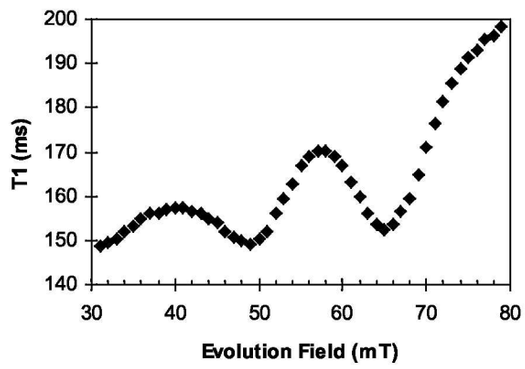

Figure 2: T_1 dispersion plot of author's forearm.

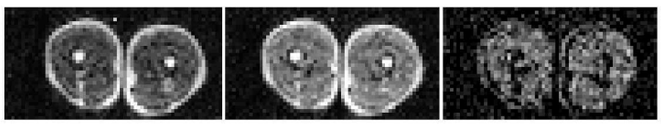

Figure 3: Field-cycled IR images of the author's thighs, at different evolution fields of 57.5 mT (left) and 65.0 mT (middle). Difference image is on right.

inversion recovery images collected at evolution fields of 57.5 mT (between the dips) and at 65 mT (on the high-field dip) with the same timing parameters as the relaxometry sequence. These show considerable differences in the intensity of muscle. Subtracting the images yields a difference image which highlights the regions where ^{14}N–^{1}H relaxation is most effective.

CONCLUSIONS

Whole-body field-cycling NMR relaxometry and imaging has been implemented. This has allowed quadrupole dips to be measured *in vivo* in the human for the first time. These techniques offer the possibility of studying relaxation mechanisms *in vivo*, and of NQR detection with the spatial resolution and versatility of MRI. It has previously been shown that the extent of the quadrupole dips (actually the magnitude of the change in $R_1 = 1/T_1$ at the dip) is proportional to the concentration of peptide bonds [4]. This is likely to give useful information on the integrity of muscle protein, and may be of use in the study of muscle-wasting diseases.

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