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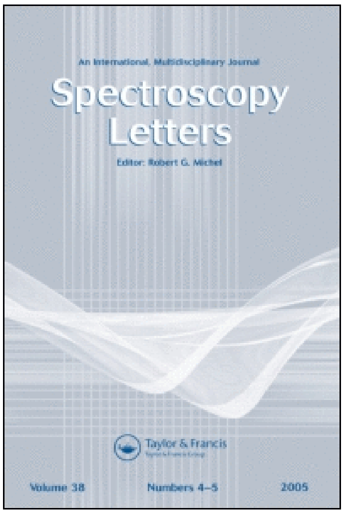

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Statistical Analysis of NMR Proton Spin-Lattice Relaxation Rates Measured at Various Pulse Repetition Times

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STATISTICAL ANALYSIS OF NMR PROTON SPIN-LATTICE RELAXATION RATES MEASURED AT VARIOUS PULSE REPETITION TIMES

Key Words: NMR T1, Pulse Repetition Times, Inversion Recovery, Non-linear estimation

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ABSTRACT

In this work, taking into consideration waiting time(WT) in successive automatic measurement, the effect of pulse repetition time(T_R) on spin-lattice relaxation time (T_1) was studied by a FT-NMR spectrometer. Inversion-recovery pulse sequence 180^o-τ-90^o(FID)+T_R +WT was successively applied for a set of 10 different τ . T_1 was calculated from non-linear estimation of inversion recovery formula, using partially relaxed recovery signals corresponding to different τ. Holding WT constant, T_R was set at 6 diferent values, ranging from nearly $6T_1$ to $0.7T_1$. T_1 measurements were repeated 20 times for each T_R. For comparison T_1 measurements were also repeated by the null method. Data showed that the intensity of recovery signals after total waiting (T_R+WT) has the same value for all T_Rs and comparison of T_1 groups corresponding to these T_Rs indicates no significant difference among T_1 values measured($p>0.2$). Keeping $T_R+WT>5T_1$, to reduce T_R more causes an imperfect signal. The results suggest that WT makes possible the use of a T_R shorter than $5T_1$ and saves experimental time.

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INTRODUCTION

The most commonly method for measuring nuclear spin-lattice relaxation time (T_1) by fourier transform spectroscopy is the inversion-recovery technique(1). The method is based on the well-known pulse sequence $[180^o\text{-}\tau\text{-}90^o(FID)+T_R]_n$. A waiting time $T_R > 5T_{1max}$ is allow to restoration of equilibrium after 90^o pulse, where T_{1max} is the longest longitudinal relaxation time to be measured, τ is delay time after inversion of signal by 180^o pulse and n, number of scans. The partially relaxed Free Induction Decays(FIDs) for various τ are collected and then fourier transformed each leading to a partially relaxed spectrum. If we call M_z, the amplitude of a line in the spectrum and M_o, the corresponding amplitude at thermal equiblibrium, the spin-lattice relaxation time can be deduced from the following equation:

$$M_z = M_o[1-2\exp(-\tau/T1)] \quad (1)$$

The applicability of this method is limited by its duration which depends on the number of scans, n, and on the pulse repetition time, T_R. This difficulty is particularly stringent for low sensitivity nuclei such as ^{13}C and ^{15}N because these nuclei may have long relaxation times and because extensive time averaging may be required even to obtain a single spectrum. The problem becomes less acute with methods based on 90^o pulses, so-called saturation recovery sequences which do not utilise a long T_R. These sequences can be obtained using a burst of 90^o pulses(2) or by field inhomogeneity gradients(3). A similar result to eliminate magnetization which causes saturation is more simply obtained by progressive saturation methods(4,5). However, saturation recovery methods entail a loss of dynamic range with respect to inversion-recovery. Therefore, the traditional two-pulse inversion-recovery sequence is modified to save time. The fast and modified fast inversion-recovery sequences are still most widely used for spin-lattice relaxation measurements(6,7), and the studies on experimental time saving in relaxation measurements have still been interesting(8,9).

Diagnostic NMR studies are often based on a set of inversion recovery images in which proton density, Rho and relaxation times constitute the source of con-

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trast (10,11). A long T_R causes longer acquisition time which is undesirable for patient examination and for image contrast. Although different techniques are being used to get the relaxation map of tissues(10-13), saving imaging time more will be useful for routine analysis.

In addition to pulse repetition times between pulse sequences, NMR spec - trometers use an additional waiting time(WT) for kinetic measurements using time. This is a characteristic of automatic measurement and its duration should change from spectrometer to spectrometer. In the presence of a long WT, the pulse sequence can be written as 180^o-τ-90^o(FID)+T_R +WT. By holding WT+T_R>5T_1, T_R can be reduced. This makes possible the use of a shorter T_R which saves experimental time in ^{13}C relaxation measurements and in MRI. However, T_R must be longer than acquisition time(*acqt*) and this can be satisfied by lowering sampling data points(*sampo*) of computer. The lower values of *sampo* lead to imperfect signals. This requires a knowledge on lower limit of T_R when WT is used. To the best of authors, in the presence of a WT, such a limit for T_R and saving time in relaxation measurements by reducing T_R have not been studied so far.

In this work, taking into consideration WT, the signal intensity of magnetization recovery after (T_R+WT) was measured for different T_R and comparison of T_1 groups corresponding to these T_Rs was made.

MATERIALS AND METHODS

The water sample was used for spin-lattice relaxation measurements. T_1 measurements were carried out on a JEOL FX- 60Q FT-NMR spectrometer operating at 60MHz for proton and 10-mm o.d. NMR tubes were used. Inversion-recovery pulse sequence 180^o-τ-90^o(FID)+T_R+WT was successively applied for ten different τ. Using partially relaxed inversion recovery signals corresponding to various τ, T_1 was calculated from non-linear estimation of magnetization recovery formula in Equation 1 by SYSTAT statistical programme (14,15). WT was 30s(>5T_1) and automatically set by spectrometer, but T_R was set at 6 different values, ranging from nearly 6T_1 to 0.7T_1. In this way 6 different T_1 groups, corresponding to different T_R each, were studied. The experiment was repeated 20 times for each group. To satisfy T_R>*acqt*, *acqt* was lowered by reducing *sampo*. Comparison of different T_1 groups corresponding to different T_R was made by using t-test(16). T_1 was also determined by the null method, using FT signals(17). The intensity of recovery signals after total waiting(T_R+WT) was measured by using [180^o-0.01s-90^o(FID)] + T_R+WT + [180^o-0.01s-90^o(FID)] pulse sequences, where T_R was altered from nearly 6T_1 to 0.5T_1. Probe temperature was maintained at $(20 \pm 0.5)^oC$ by means of a JNM-VT-3C automatic temperature controller unit. The experimental error for T_1 by inversion-recovery was estimated to be about $\pm$0.03s.

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RESULTS AND DISCUSSION

The intensities of inversion recovery signals for two different series of [180^o-τ-90^o(FID)+T_R+WT pulse sequence versus τ are shown in Figure 1. Ratio of recovery signal(M_z) after total waiting to M_0 at thermal equilibrium (Mz/Mo), the average of relaxation rates measured by inversion-recovery for each group and the relaxation rates by the null method are shown in Table 1.

Fig.1 shows that the data obtained for both series (T_R=20 and 3.3) fall on the same curve and give just one 1/T1. This indicates that the waiting time replaced by the spectrometer provides full recovery of magnetization for T_R= 3.3 as in T_R=20. The data in Table 1 confirm Fig.1 for all T_R, where each T_R corresponds to one group. It is seen that all the groups have the same average for 1/T1 and comparisons of groups do not give any significant difference (P>0.2). It is also seen that M_z is equal to M_0 for all groups. The results indicate that M_z is fully recovered after total waiting (T_R +WT) between pulse sequences so that it can give just one 1/T1 for all T_R. However, WT should change from spectrometer to spectrometer. Therefore, the contribution of WT to T_R should be examined carefully .

In the present case,*acqt* and *sampo* for T_R=2.2s were 2s and 4000 respectively. Reducing T_R more requires shorter *acqt* in order to satisfy P_R > *acqt*. This was achieved by reducing *sampo*, but smaller values of *sampo* lead to imperfect recovery signals and likely false 1/T1. Even if WT has a suitable value (30s) for reducing TR more, the shortest TR was nearly 2.2s for the present case.

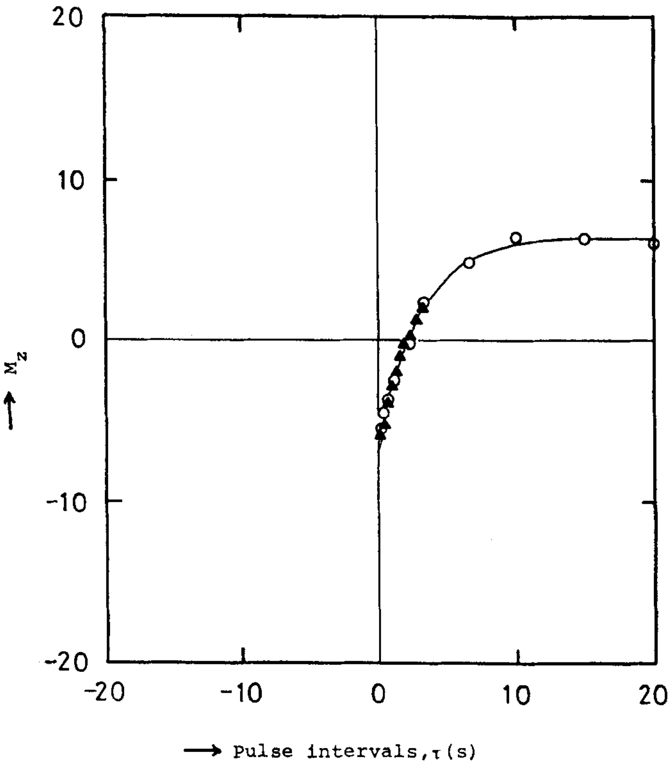

Figure 1: magnetization Recovery curves of various 180^o-τ-90^o Pulses for TR=3.3s(triangles) and for TR=20s(circles).

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It was shown that elimination of systematic errors in fast inversion-recovery makes possible the use of a short $T_R(\cong 2T_1)$ and to extract τ from T_R provides faster inversion recovery sequences for T_1 measurements(6,7). It is also noted that the determination of the number of nonacquisition and dummy pulses is important to minimize the errors in experimentally determined values of T_1(18). Single-scan fourier transform methods are also designed to save time(19,9). Our data are convenient to these results.

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TABLE 1

The average of relaxation rates measured by inversion recovery technique, relaxation rate by FT-null method and the ratio of recovery signals after total delay time (T_R+WT) to initial magnetization.The relaxation rate is given(1/ms) and T_R in second units.

T_R	$(1/T_1)_{IR}$	$(1/T_1)_{null}$	M/M_0
20	341 ± 30	341	0.99
15	340 ± 15	340	0.99
10	340 ± 15	340	1.00
6.6	341 ± 15	340	1.01
3.3	339 ± 20	340	1.00
2.2	341 ± 15	340	1.00

In conclusion, the present results suggest that T_R can be chosen shorter than $5T_1$ in the presence of a significant WT, and this provides experimental time saving.

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