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Use of Carr–Purcell pulse sequence with low refocusing flip angle to measure T_1 and T_2 in a single experiment

Fabiana Diuk de Andrade [a], Antonio Marchi Netto [b], Luiz Alberto Colnago [c,*]

[a] Instituto de Química de São Carlos, Universidade de São Paulo, Av. Trabalhador São-carlense 400, São Carlos, SP 13560-970, Brazil
[b] Instituto de Física de São Carlos, Universidade de São Paulo, Av. Trabalhador São-carlense 400, São Carlos, SP 13560-970, Brazil
[c] Embrapa Instrumentação, Rua XV de Novembro 1452, São Carlos, SP 13560-970, Brazil

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ABSTRACT

The Carr–Purcell pulse sequence, with low refocusing flip angle, produces echoes midway between refocusing pulses that decay to a minimum value dependent on T_2^*. When the refocusing flip angle was $\pi/2$ (CP_{90}) and $\tau > T_2^*$, the signal after the minimum value, increased to reach a steady-state free precession regime (SSFP), composed of a free induction decay signal after each pulse and an echo, before the next pulse. When $\tau < T_2^*$, the signal increased from the minimum value to the steady-state regime with a time constant (T^*) = $2T_1T_2/(T_1 + T_2)$, identical to the time constant observed in the SSFP sequence, known as the continuous wave free precession (CWFP). The steady-state amplitude obtained with $M_{CP90} = M_0T_2/(T_1 + T_2)$ was identical to CWFP. Therefore, this sequence was named CP-CWFP because it is a Carr–Purcell sequence that produces results similar to the CWFP. However, CP-CWFP is a better sequence for measuring the longitudinal and transverse relaxation times in single scan, when the sample exhibits $T_1 \sim T_2$. Therefore, this sequence can be a useful method in time domain NMR and can be widely used in the agriculture, food and petrochemical industries because those samples tend to have similar relaxation times in low magnetic fields.

1. Introduction

The Carr–Purcell pulse sequence (CP) is based on the spin-echo sequence introduced by Hahn in 1950 to measure the transverse relaxation time, T_2 [1]. The Hahn sequence uses two $\pi/2$ pulses separated by a time interval (τ), where $T_2^* \ll \tau < T_2$. Hahn had observed that this sequence was sensitive to molecular diffusion through the inhomogeneous magnetic field. To solve the effect of diffusion in the T_2 measurement, Carr and Purcell [2] introduced a pulse sequence that used a $\pi/2$ excitation pulse, followed by a train of π refocusing pulses using the same phase of the excitation pulse. The time interval between the refocusing pulses was doubled compared to time between the excitation and the first refocusing pulse. This sequence produced echoes with a maximum amplitude midway through the refocusing pulses. Each echo was dephased by 180° from the preceding echo. This sequence used a small τ value between the refocusing pulses, which minimized the effect of diffusion in the echoes' signals. However, Meiboom and Gill [3] observed that the adjustment of π refocusing pulses was critical and this problem was more pronounced for samples with long T_2 (liquid) values and using an inhomogeneous magnet. Thus, it was necessary to use short values for τ and a large number of refocusing pulses to eliminate the effects of diffusion. A small deviation from the exact value of π was cumulative; thus, the error of the refocusing pulses increased with the number of pulses and introduced error in the T_2 measurements as a consequence. To solve this problem, Meiboom and Gill [3] proposed a modification to the CP sequence by introducing a 90° phase shift between the excitation and the refocusing pulses. This improvement made the sequence very robust and insensitive to error in the refocusing pulse. Therefore, the sequence proposed by Carr–Purcell and improved by Meiboom and Gill, known today as CPMG, is the standard method to measure T_2. This sequence is so robust that we have recently shown that it is possible to measure T_2 using very low refocusing flip angles, as low as $\pi/4$ [4]. The major advantage in using CPMG with low refocusing flip angles occurs when it is necessary to reduce the applied power, as in online measurement [4] or in fast imaging techniques, to reduce the power deposition in the samples.

In this paper, the effect of low refocusing flip angles in the CP pulse sequence is shown. The use of $\pi/2$ refocusing pulses produced signal similar to continuous wave free precession (CWFP), a special condition of the steady state free precession (SSFP) regime [6]. The sequence was named CP-CWFP because it is a CP sequence with $\pi/2$ pulses and produced results similar to CWFP. Therefore CP-CWFP sequence can have similar CWFP applications, e.g. be

* Corresponding author. Fax: +55 16 21072902.
E-mail addresses: fabianadiuk@yahoo.com.br (F.D. de Andrade), nettomarchi@gmail.com (A. Marchi Netto), colnago@cnpdia.embrapa.br (L.A. Colnago).

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used to measure T_1 and T_2 in a single experiment. CP-CWFP sequence is less sensitive to signal-to-noise in measuring T_1 and T_2 in a single experiment compared to CWFP when T_2 is similar to T_1.

2. Experimental

The samples studied were deionized water, acetone, dimethyl sulfoxide (DMSO), soybean oil and castor bean seeds.

The CP sequence with $\pi/2$ refocusing pulse was $\pi/2_x - \tau/2 - (\pi/2_x - \tau)_n$ (Fig. 1).

The experiments at 9 MHz for ^{1}H were performed at 25 ± 0.5 °C on a SLK-1300 spectrometer (SpinLock, Córdoba, Argentina) based on 0.23 T Halbach magnet, using a 100 mm diameter probe. The sequence used a $\pi/2$ refocusing pulse width of 9.5 µs, τ = 0.3 ms, 5 KHz offset frequency equivalent to $\psi = 3\pi$, a recycle delay >5T_1 and 16 scans. For a good analysis of the signal composition for CP with $\pi/2$ pulse it was used τ = 3 ms ($\tau > T_2^*$). In this condition the sequence was named CP-SSFP due to be composed of a spin echo and steady state free precession (SSFP) signal.

The experiments at 85 MHz for ^{1}H were performed at 22 ± 1 °C using a CAT-100 transceiver (Tecmag, Houston) and a 2.1 T Oxford superconducting magnet (Oxford, UK). The sequence utilized a $\pi/2$ refocusing pulse width of 14 µs, τ = 0.3 ms, 5 KHz offset frequency equivalent to $\psi = 3\pi$, a recycle delay >5T_1 and 4 scans. T_2^* measured from FID was 1.2 ms and 13 ms for 9 and 85 MHz, respectively.

The T_1 and T_2 values were measured using the Inversion-Recovery sequence (IR) [7] and CPMG pulse sequences [3], respectively. The IR intervals varied from 0.15 s to 25 s for acetone, deionized water and DMSO and from 1×10^{-6} s to 2 s for soybean and castor bean seeds. The CPMG echo times were 500 us for acetone, deionized water and DMSO and 50 µs for soybean and castor bean seeds.

3. Results and discussion

3.1. CP with $\pi/2$ pulses

Fig. 2 shows the real component of the soybean oil signal at 9 MHz, obtained with a CP sequence using $\pi/2$ refocusing pulses (CP_{90}) and $\tau > T_2^*$. This figure shows the signal from the first echo to the signal after 500 pulses. The arrows (A–C) indicate three important regions of the CP_{90} signal. Arrow A points the spin echoes signals, which decreased to a minimum value. Arrow B indicates the increase of the signal to a steady-state value (arrow C). These features are better illustrated in the expansions presented in Fig. 3. Fig. 3A–C corresponds to the signals, from 0 to 0.016 s (2A), between 0.016–0.048 s (2B) and 0.640–0.660 s (2C), respectively.

Fig. 3A shows the real component of signal of the first eight echoes for the CP_{90} sequence. The first echo was stronger than the second one, as expected, but with the same phase. This was not observed in the conventional CP, which used π refocusing pulses. In conventional CP, each echo is 180° out of phase from the previous one. The third and fourth echoes have similar amplitudes and are 180° out of phase from the first and second echoes. The same pattern, 180° dephasing every two pulses, was observed up to the eighth echo. However, the amplitudes of the last two even echoes were bigger than the respective odd echoes. The presence of the odd and even echoes with same phase occurred because it is necessary to use two $\pi/2$ pulses to invert the magnetization. When considering the $\pi/4$ pulse (data not shown), four pulses were necessary to invert the phase.

After the eighth pulse (Fig. 3B), the CP_{90} signals were not echoes and showed a complex signal up to approximately 0.048 s. After this time, the signal start to form a periodic pattern (Fig. 3C); it consisted of a positive signal that decayed to zero at the midway

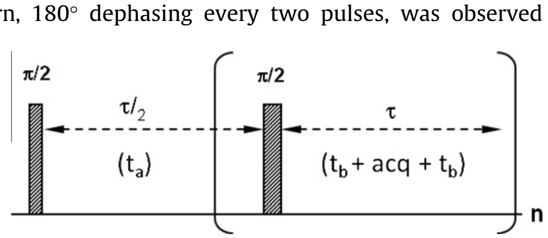

Fig. 1. Carr–Purcell sequence with $\pi/2$ refocusing pulses. When $\tau < T_2^*$: t_a = 144.5 µs, t_b = 67.25 µs and acq = 160 µs. When $\tau > T_2^*$: t_a = 1042.75 µs, t_b = 50 µs and acq = 2000 µs.

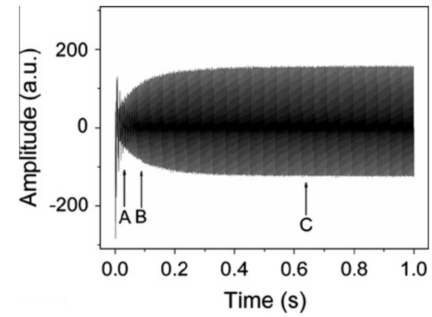

Fig. 2. Real components of the signal for the soybean oil sample obtained with CP sequence using $\pi/2$ refocusing pulses and $\tau > T_2^*$, from the first echo to the steady-state regime. The arrows A, B and C indicate three regions of the CP_{90} signal, which are expanded in Fig. 3.

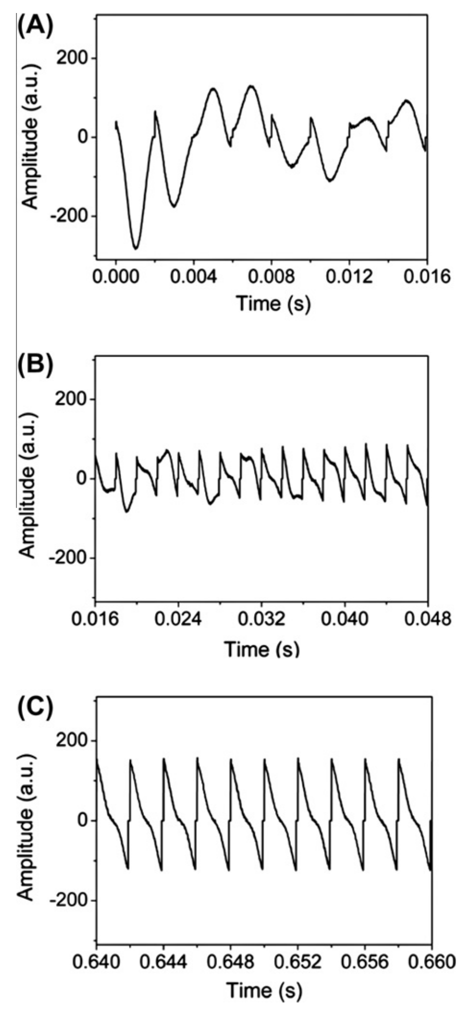

Fig. 3. Expansion of the real component of the signal for the soybean oil sample of Fig. 2. (A) 0–0.016 s, B) between 0.016–0.048 s and C) 0.640–0.660 s.