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A spoiler recovery method for rapid diffusion measurements

Geir Humborstad Sørland[1], Henrik Walbye Anthonsen[1], Klaus Zick[2], Johan Sjöblom[3], and Sébastien Simon[3],

[1]Anvendt Teknologi AS, Trondheim Norway (www.antek.no)

[2] BrukerBiospin GmbH, Rheinstetten Germany [3]Ugelstad Laboratory, Department of Chemical Engineering, the Norwegian University of Science and Technology, Trondheim Norway

Abstract

A method for rapid acquisition of multiple scans of NMR sequences is presented. The method initially applies two RF-pulses in combination with two magnetic field gradient pulses of opposite polarity, different strength and different duration. The basic idea is to spoil any magnetization in any direction before by letting the system recover to some degree of restoration of the thermal equilibrium magnetization. Thereafter any pulse sequence can be applied, and the next scan may be run immediately after the end of the pulse sequence. Thus one avoids the 5 times T_1 delay between each scan. A set of PFG sequences are presented that apply the spoiler recovery method for significant reduction in acquisition time, and the method has been verified at 0.5 Tesla as well as at 11.7 Tesla.

Keywords: Pulsed field Gradient, NMR, diffusion, acquisition time, recycle delay

1. Introduction

Diffusion as measured by pulsed field gradient (PFG) NMR is an important parameter in research as well as for industrial applications and diagnostics [1-3]. Nevertheless, after more than four decades of development of the PFG NMR technique, new methods and applications within PFG NMR still appear. This only reflects the flexibility and yet unrevealed potential of this technique [4-11].

One of the major drawbacks of the PFG NMR has been the settling time needed for the system to regain thermal equilibrium of the net nuclear magnetization along the external magnetic field (~5 times T_1) between each scan. This settling time puts for example a limit to how many gradient values or relaxation time values one can use before the time of the experiment becomes longer than the stability of the system or what is feasible. Recently methods have been proposed to reduce this experimental time by saturating the magnetization before recording of the actual NMR experiment [4-6] or just do the diffusion experiment in the oneshot experiment [7-8]. The major draw back using these approaches is the significant loss in signal to noise and the fact unwanted coherence transfer pathways results in multi exponential decay from system that should give a mono exponential decay [4].

Instead of letting the magnetization reach thermal equilibrium before each scan, we apply a combination of RF-pulses and magnetic field gradients that aims at spoiling any magnetization in any direction. Then, using a waiting time equal to T_1 after the spoiling (SRD in figure 2.1), we have already regained 63% of the magnetization at thermal equilibrium. The waiting time between each scan is then reduced to practically nothing, and the total experimental time may be reduced by as much as 80% without any significant loss of signal to noise. Likewise we may use the spoiler approach to reduce the acquisition time of two dimensional experiments, as Diffusion-T_2 or T_1-T_2, from the order of hours to the order of minutes. Furthermore, the rapid T_1-T_2 is quantitatively correct which is not feasible using the saturation approach [5-6]. In the following we will focus on describing the set-up for acquiring a state of spoiler recovery, and how we combine it with diffusion measurements. The method has already been successfully implemented for the characterization of unstable emulsions [11]

2. The spoiler recovery (SR) method

The conventional approach for measuring diffusion and or relaxation is to let the magnetization recover back to thermal equilibrium after application of a set of RF- and gradient pulses. Improvements have been made to reduce this acquisition time, and are based on saturating the magnetization to a steady state before applying the pulse sequences [4-6]. Our approach is different as we initially do not assume any particular state for the net nuclear magnetization. Regardless of the initial state we apply two 90 degree RF pulses in combination a bipolar pair of magnetic field gradients of arbitrary shape. This we call the spoiler recovery sequence.

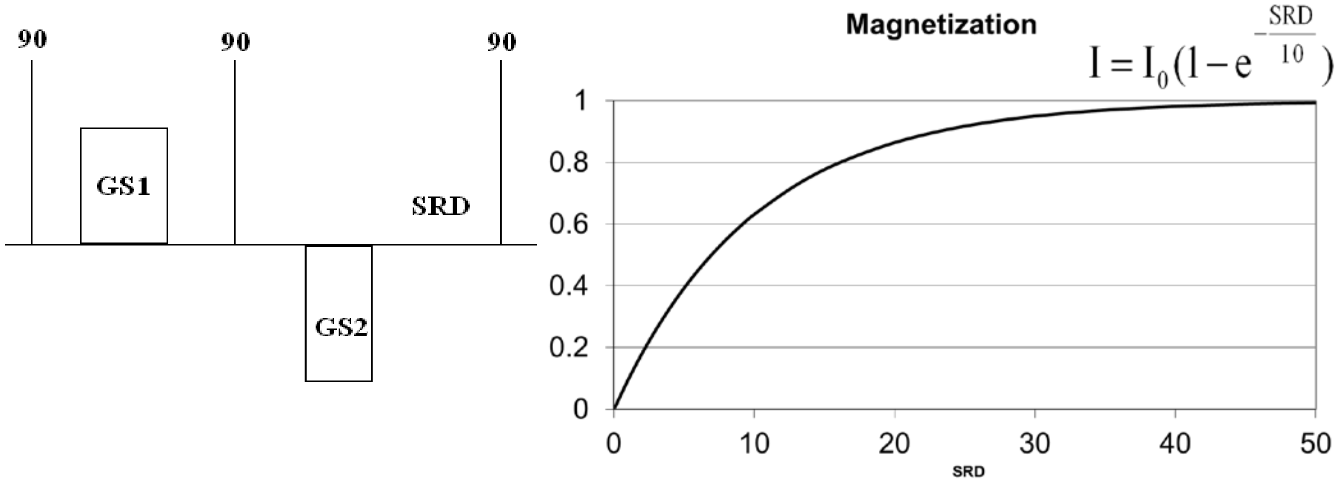

Figure 2.1 The spoiler recovery sequence and a plot of the magnetization after a variable delay SRD.

Figure 2.1 shows how the spoiler recovery pulse sequence and how the recovery path back to thermal equilibrium will be for the magnetization. GS1 and GS2 are chosen such that any coherence transfer pathway arising from the two first 90 degree RF-pulses does not contribute to any significant echo signal after application of the third 90 degree RF-pulse which is the excitation pulse. Thus the phases of the two spoiler gradient pulses must not be equal as given in equation 2.1

$$\gamma\, GS1 \int_0^{\delta_{GS1}} z_1(t)\, dt \neq \gamma\, GS2 \int_0^{\delta_{GS2}} z_2(t)\, dt \qquad (2.1)$$

Where δ_{G1} and δ_{G2} are the durations of the spoiler gradient pulses, $Z_{1,2}\,(t)$ are the molecular positions at the time of the two gradient pulses, and γ is the gyromagnetic ratio. To make the two accumulated phases very different we choose the gradients to bipolar, of different length, and the gradient area of GS2 to be larger than the gradient area of GS1. If there initially was any magnetization along any direction it should have been dephased by the application of the spoiler recovery sequence. To acquire noise only during the SRD interval it is important to choose the GS1 and GS2 values as described above.

3. Experimental

Here we present a set of sequences that uses the spoiler recovery sequence to reduce the acquisition time by approximately 80 % or more, without any significant loss of signal to noise. The low resolutions measurements were performed on a 0.25 Tesla Maran DRX permanent magnet bench top instrument with 40 mm proton probe and magnetic field gradients up to 1.2 T/m (gradient coils mounted on the pole shoes). The high resolution measurements were performed on a Bruker 500 MHz Avance III instrument with 5 mm diffusion probe with actively shielded magnetic field gradients up to 18 T/m. Samples used were:

- Pure water (both at 0.3 and 11.7 Tesla)
- Doped water in H_2O/D_2O (at 11.7 Tesla) used to speed up experimental time when measuring diffusion as a function of RD/T_1 (figure 6 in section 4.2)
- 2mM Lysozyme in H_2O/D_2O 90/10 (11.7 Tesla)
- Two asphaltene solutions (11.7 Tesla): The solutions were prepared by dissolving asphaltenes extracted from a crude oil sample in toluene-D_8 (99.6 atom %D, Aldrich) at a concentration of 1.0 wt% and then magnetically stirred overnight. The second asphaltene solution (0.01 wt%) was prepared by diluting the previous one with toluene-D_8.

4. Results and discussion

4.1 The SR combined with the 11 interval bipolar PFGSE

In figure 4.1 we have put the spoiler recovery sequence in front of the 11-interval PFGSE [12], and the sequence was tested on pure water on the 0.25 Tesla permanent magnet system with SRD equal to 5 times T_1 (the ordinary approach) and SRD = 0.5 seconds. Number of scans was 4 plus one dummy scan, and the gradient strength was ramped 20 times.

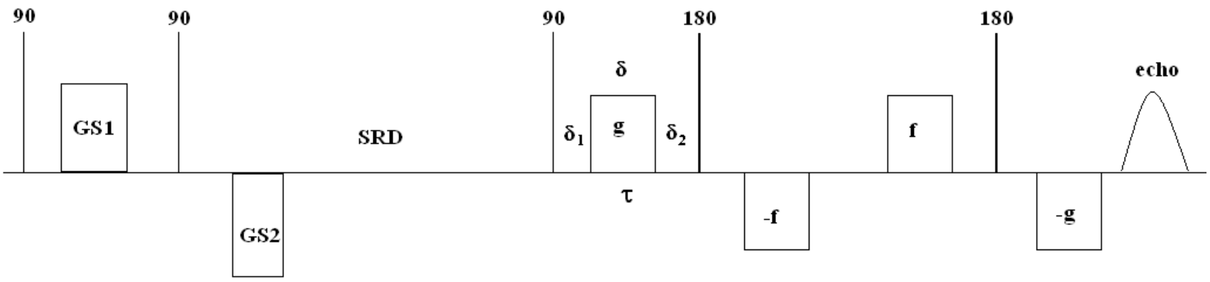

Figure 4.1 The combined spoiler recovery 11-interval PFGSE sequence

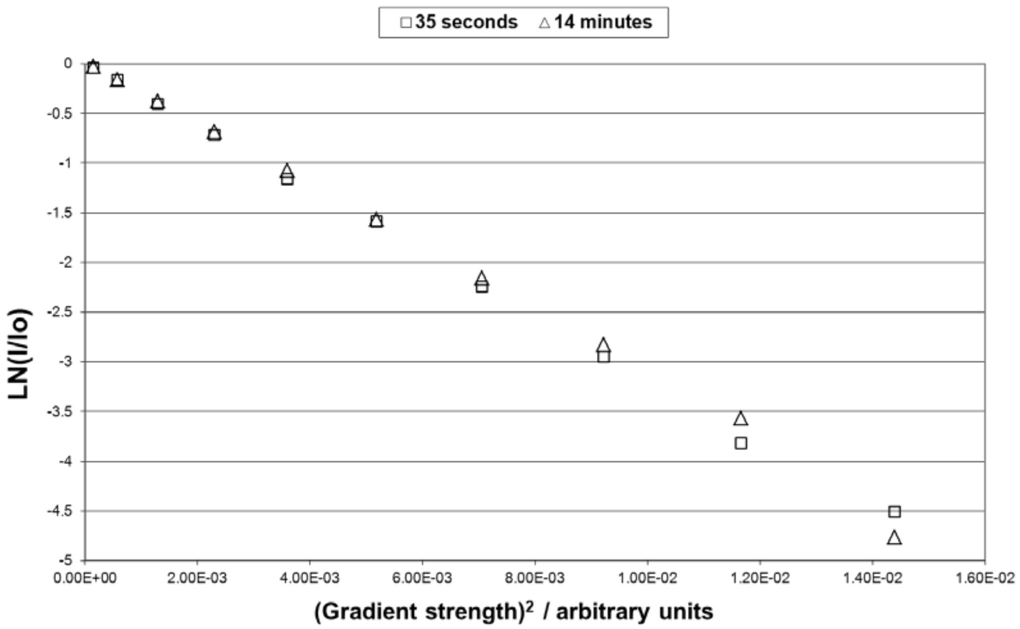

Figure 4.2 Comparison of the 11-interval PFGSE with the spoiler recovery (total experimental time of 35 seconds) and without the spoiler recovery (total experimental time of 14 minutes) on pure water.

As can be seen from figure 4.2 there is no discrepancy between the two methods for acquiring the attenuation due to diffusion, and the logarithm of the decay is linear down to the noise value. Thus within the same signal to noise region, the spoiler recovery approach takes only 35 seconds while the ordinary method that allows the signal to recover 5 times T_1 takes 14 minutes. This is the major advantage using the spoiler recovery technique as compared to the ordinary saturation recovery technique. Question then remains to whether this is just accidental or we truly remove any unwanted signal using the spoiler-recovery regardless of recycle delay and operating magnetic field, from low field (~0.25 Tesla) to high field (~10 Tesla). Especially important is to check whether radiation damping may have any influence on the results at higher magnetic field [13].

4.2 The SR combined with the 13 interval bipolar PFGSTE

In figures 4.4-4.7 we show results from using the 13-interval PFGSTE [14] with spoiler recovery (figure 4.3) using a 500 MHz Avance III instrument. Again the logarithm of the attenuation is linear regardless of recycle delay between each scan on pure water, and the measured diffusion coefficient is thus a true diffusivity. Conclusion is that there are no indications that the use of the spoiler recovery sequence at higher applied magnetic fields should not work as expected. However, for very sensitive systems with low signal to noise for the component of interest, there might be interference with higher order coherence transfer pathways. Even though we may reduce the (recycle delay)/ T_1 down to practically 0 we still need some time to let a signal recover after spoiling it and some time to record the FID. Thus in practice the time between each scan (including the pulse sequence) will not be much lower than 0.1 times T_1.

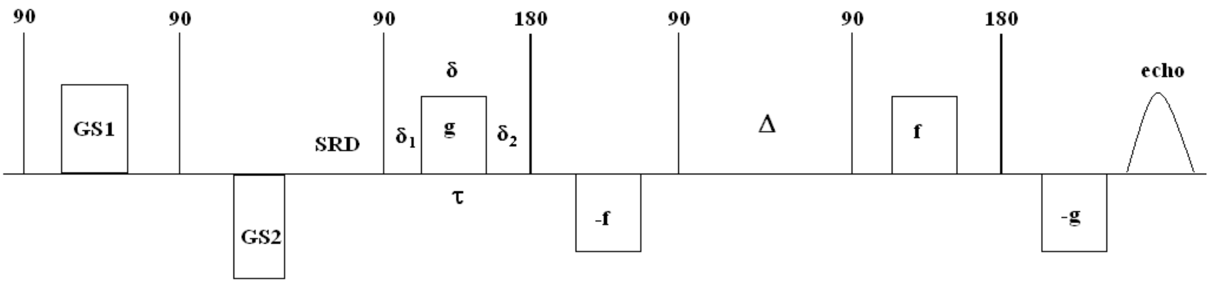

Figure 4.3 The combined spoiler recovery 13-interval PFGSTE sequence

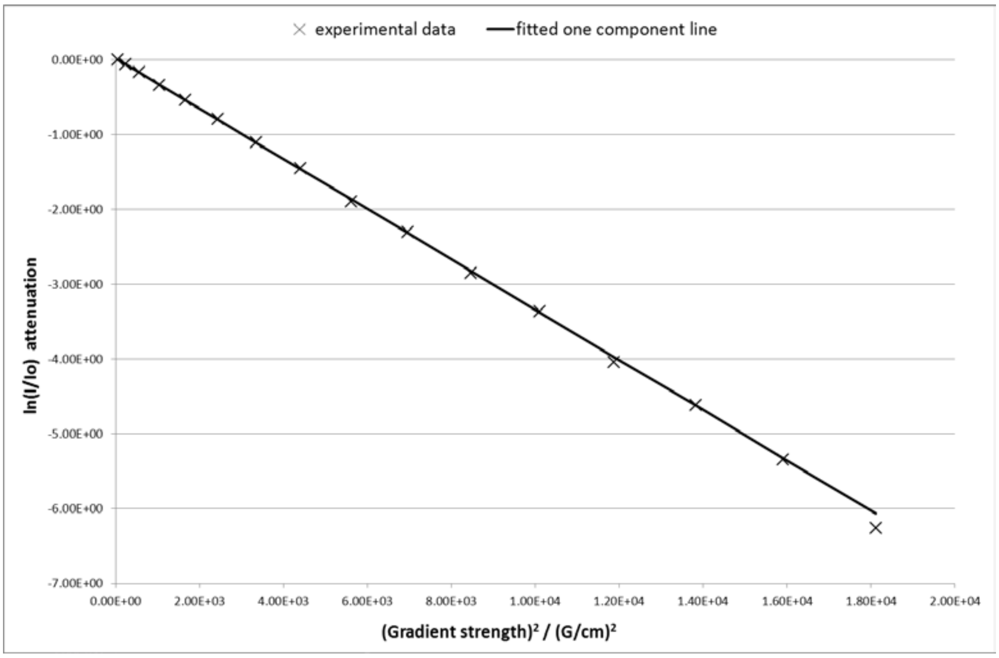

Figure 4.4 Application of the combined spoiler recovery 13-interval PFGSTE on pure water at 11.7 Tesla.

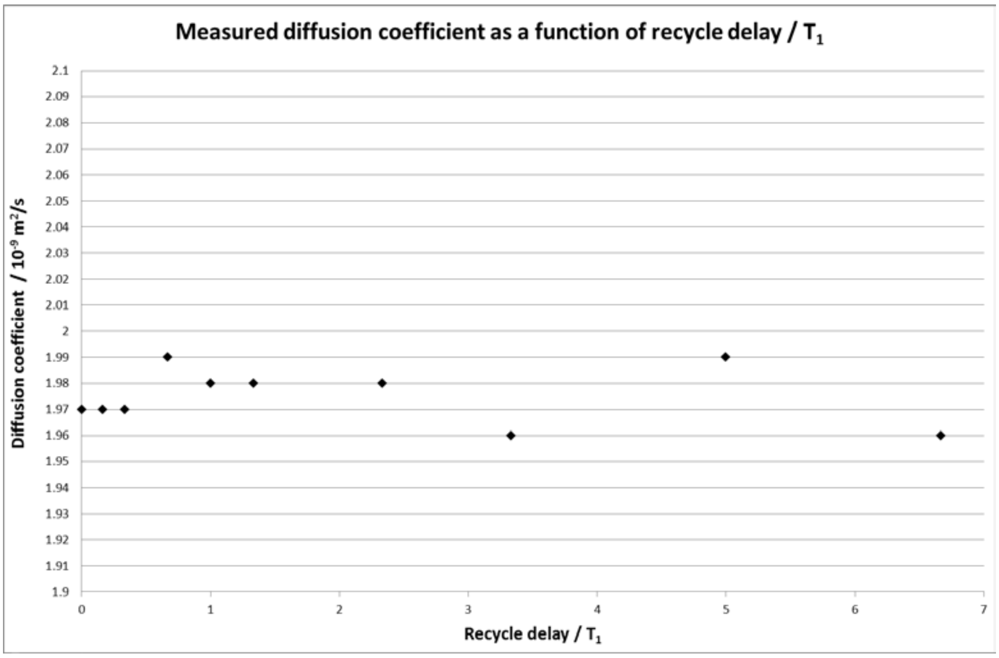

Figure 4.5 Varying the recycle delay on a doped water sample (T_1~300 ms) using the spoiler recovery 13-interval PFGSTE.

The spoiler recovery was tested on a well know system for verifying the method, a solution of 2 mM lysozymes in H_2O/D_2O. Applying the spoiler recovery sequence we reduce the acquisition time by approximately 80% as compared to the ordinary sequence with 5 times T_1 as the recycle delay. In figure 4.6 we have displayed the attenuation from the highest peak at 0.68 ppm, and the diffusion coefficient from this alphatic region was found to be 1.11 10^{-10} m^2/s. This is comparable to the value found by others [15].

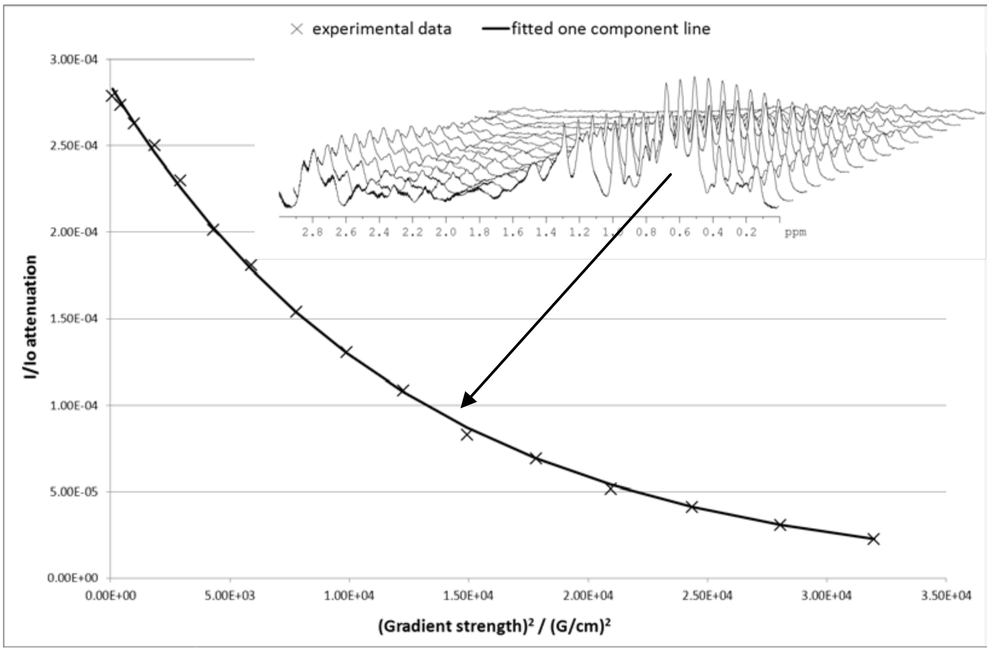

Figure 4.6 The spoiler recovery 13-interval PFGSTE applied on lysozyme sample.

The last results presented using the 11.7 Tesla are on asphaltene diluted into two concentrations, 1.0 wt % and 0.01 wt % (figure 4.7). Due to the low concentration a large number of scans have been necessary in order to achieve proper signal to noise. Using the conventional approach we would need 18 hours to run the diffusion experiment on the 0.01 wt % sample. With the spoiler recovery method the experiment was run in approximately 4 hours, resulting in the same signal to noise ratio. By fitting the NMR signal decay from the two samples we found an approximately mono exponential decay for the 1.0 wt % sample while there was a clear indication of a bimodal decay at the lowest concentration of asphaltenes. The approximately single component diffusion value for the most concentrated sample was 2.2 10^{-10} m^2/s. For the most diluted sample we get a nice two-component behavior with one fast diffusing component (73% of signal) at 1.6 10^{-9} m^2/s and one slow diffusion component (27% of signal) at 1.7 10^{-10} m^2/s. This indicates that the asphaltenes are aggregated at the highest concentration [16] while there is a mixture of states at lowest concentration which is assumed to be close to the Critical Nano Aggregate Concentration (CNAC) [17]. It is not the task here to interpret why the slow diffusion component has a lower mobility than in the more concentrated sample, but it may not be unlikely that the smaller clusters break up before the larger ones, leaving us with some larger clusters in the more diluted sample.

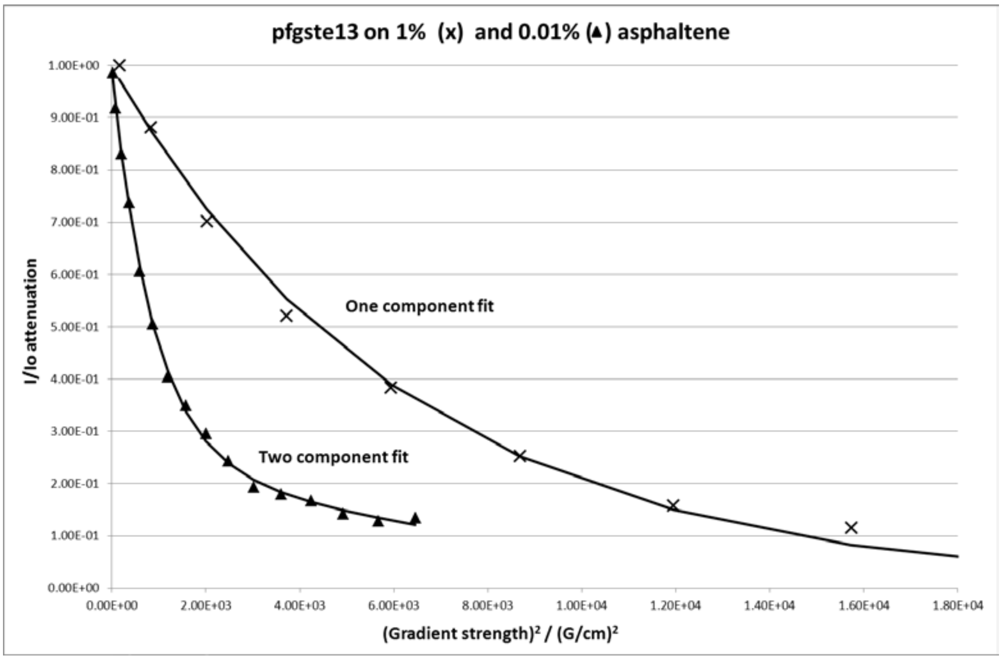

Figure 4.7 The spoiler recovery 13-interval PFGSTE applied on asphaltene samples

Conclusion

The spoiler recovery sequence has shown to be an important tool for reducing the total acquisition time for an NMR experiment. This reduction in time moves some of the applications shown here from the category of being of purely academic interest to be potential quality control applications.

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