Measurement of the spin-spin relaxation time T2 at very low magnetic field by means of the Fast Field Cycling NMR method

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Objectives and Premises Field Cycling NMR is a reliable and powerful method used so far for measuring the spin-lattice relaxation time T1 at low fields as well as its dependence on the magnetic field strength. Moreover, the Field Cycling NMR is the only technique which allows to extend these measurements down to very low fields, typically close to hearth field or lower. As far as the spin-spin relaxation time T2 is concerned, it was almost impossible till now to exploit the same advantages offered by the technique because of instrumental limits and the lack of data acquisition/evaluation algorithms suitable to face up the intrinsic problems you get with the acquisition of an echo (compared with the acquisition of an FID) in a fast field cycling experiment. In this work we present new instrumental concepts and new NMR methods developed exactly on the objective to overcome these limits and allow the acquisition of complete profiles of T2 (Echo decay) by means of the Spin-Echo FC experiment in the same magnetic field range used for the measurement of a T1 NMRD profile.

The Fast Field Cycling spin-echo experiment

Any NMR signal is in general acceptable in Field Cycling NMR as long as the signal reflects the intensity of M0 at the end of the relaxation period. The NMR types of signals used include all the"classical" ones, such as free induction decays (FID), spin-echoes, envelopes of CPMG spin-echo trains, etc. In order of acquiring information about T2 (or, in general, about the echo decay) at different magnetic fields, the classical Hahn-echo (90x - - 180y - - Acq) sequence can be applied with simple modifications (figure 3). In particular:

1) A high magnetic field Bpol (polarization field) must be initially applied during the polarization period (Tpolarization) in order to build up the initial magnetization M0.

2) During the echo time the magnetic field is switched to the relaxation field Brelax where we want to measure the decay of the echo. The complete echo decay can be traced just by acquiring the amplitude of the echo at different echo time (see fig.1)

The problem

In the experiment of fig1 the shortest echo decay that can be acquired is directly depending on the field switching interval. Nevertheless, the intensity of the detected echo is depending on many physical and instrumental aspects which will not be discussed in the present work. We have to consider that the Fast Field Cycling technique imply the use of low-inductance, air-coil magnets and power supplies capable of switching the field electronically to any desired value in a matter of milliseconds while, at the same time, maintaining the highest field stability and homogeneity required by NMR. Although the typical specification achieved is about 40-60 ppm, the specifications of B0 are not sufficient to run a classical Spin-Echo experiments because amplitude and phase of the echo, are instable and non-reproducible (fig.2) The not very high homogeneity and stability of the magnet system used in Fast Field Cycling Relaxometry was the main problem to face up. Of course the best solution would be to work in a more stable FC magnet system. Anyway this is a very big challenge that would require a very complicated and expensive electronics. The new approach we are proposing is simpler and based on new data acquisition algorithm which in principle could be applied in all NMR experiments which have to be run in an instable magnetic field.

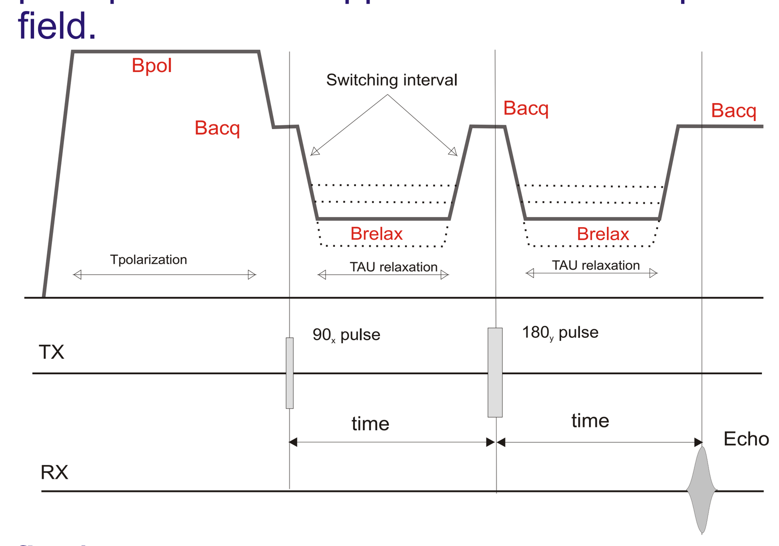


fig. 1
The Fast Field Cycling Spin-Echo experiment

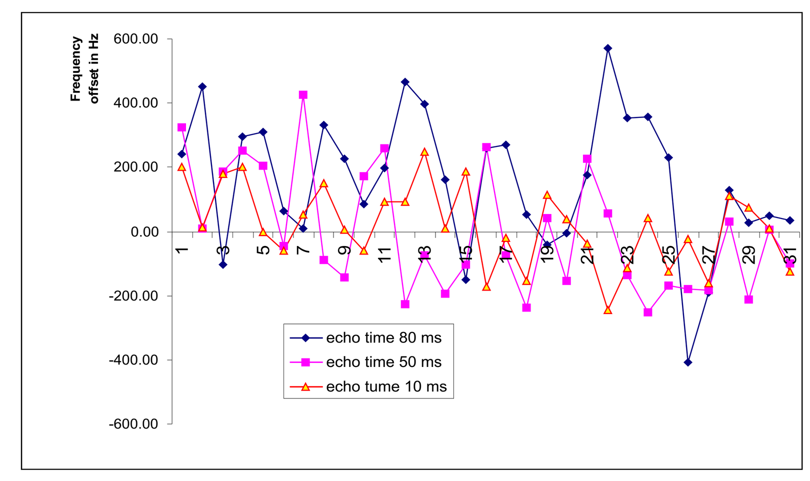


fig. 2 Echo frequency offset measured in 32 identical Spin echo experiments at three different echo time. The total vertical scale is 38 ppm.

Acquisition and accumulation of a Hahn-echo signal in FFC-NMR [1]

To overcome the field stability and reproducibility problems mentioned above (fig 4 and 5), we have implemented a novel data accumulation mode which differ substantially from the usual averaging of the component I and Q of the signal used in NMR. Besides the Cartesian components the NMR data are also acquired in Polar coordinates. Each point of the the signal is averaged in 4 separated set of data I,Q, M (amplitude) and P (phase). The magnitude of signal is insensitive to the field instability effects.

Accumulation of FFC-NMR signals in polar coordinates

In a perfectly stable field, an off-resonance quadrature FID looks like the one shown in **(A)** and is perfectly reproducible. Here the red points indicate the in-phase Cartesian component u and the green ones the out-phase component v, while the black ones denote the computed magnitude m of the complex signal.

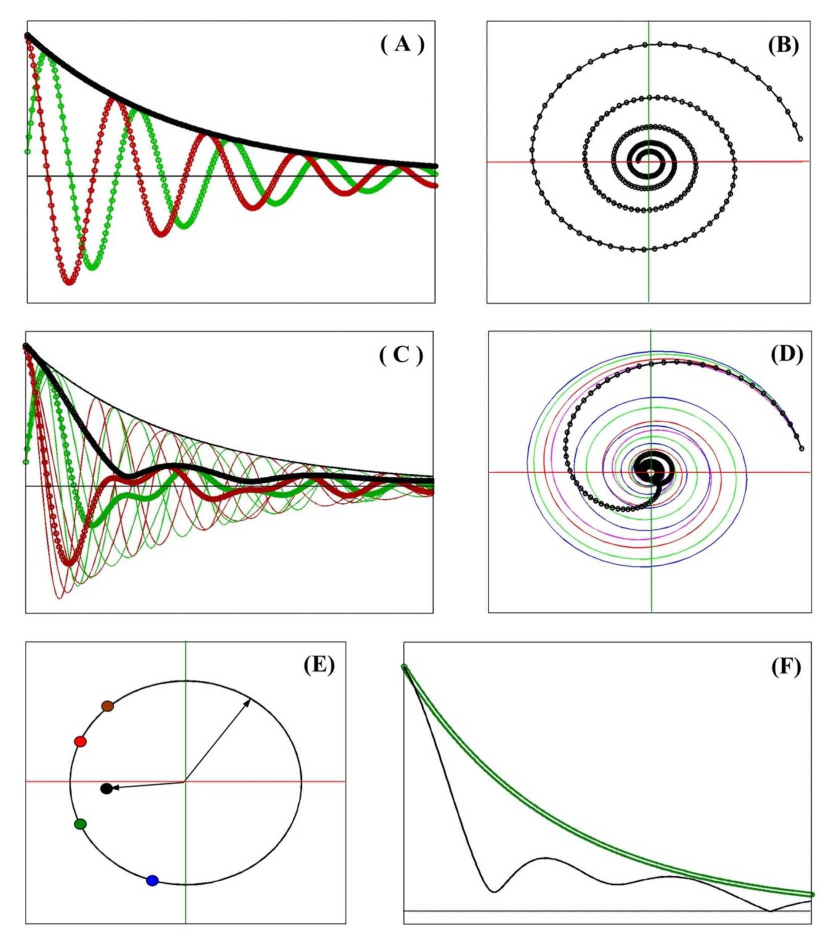
The plot in **(B)** shows the same data in the complex plane (u,v).

When the field is not stable, the echoes are not reproducible and data accumulated in the standard way (i.e., summing up the Cartesian components) are compromised, as shown in **(C).** The corresponding plot **(D)** shows four scans at varying offsets and, in bold, the result of the accumulation.

What happens is best evidenced in **(E)** where the four colored dots show the position of the complex signal point #32 of the four FID's. Since all four points were taken at the same time t after the excitation pulse, they all have the same amplitude but, because of the unstable offsets, a quite different phase. The amplitude, in fact, is insensitive to phase and depends only upon t and T2*. Averaging the Cartesian coordinates of the four points results in a data point represented by the black dot, which is physically almost meaningless.

Averaging separately the polar coordinates (magnitudes and phases) leads to a correct magnitude estimate. This is shown in **(F)** where the thick green line corresponds to the computed averaged amplitudes of the four FID's. The overlaid white line indicates the ideal amplitude decay (the same as the black trace in A), while the bumpy black line is the result of Cartesian-components averaging (the same as the black trace in C). The averaged magnitudes obtained in this way are valid for the whole duration of the FID's which, in liquids, amounts to a precision-improvement factor of up to 100 (with their very short decays, solids are little affected by these effects).

Exploitation of the phase averages is at present hindered by the lack of suitable averaging algorithms for circular distributions (there is work in progress). Overcoming this obstacle, one should be able to recover an accumulated signal with correct amplitude, corresponding to an average and constant offset value.



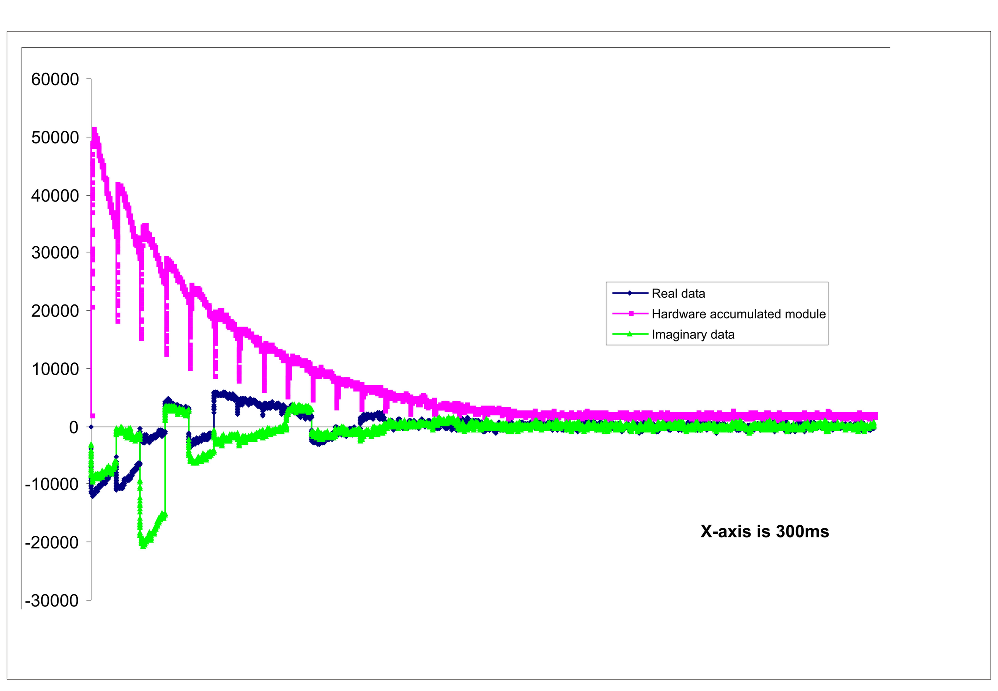


Figure 5.
Echo decay acquired with a Prepolarized Field Cyling Spin Echo. The data represent the amplitude of the echoes at different (echo time). The data are averaged with 16 scans and 32 echo time values. The accumulated real and immaginary data are shown in blu and green. It's evident that the decay of the echoes is destroyed by the field instability when data are accumulated in Cartesian coordinates. On the contrary, the nice decay in the figure represent the accumulated modulus of the same 32 echoes acquired and avereged point by point in polar coordinates.

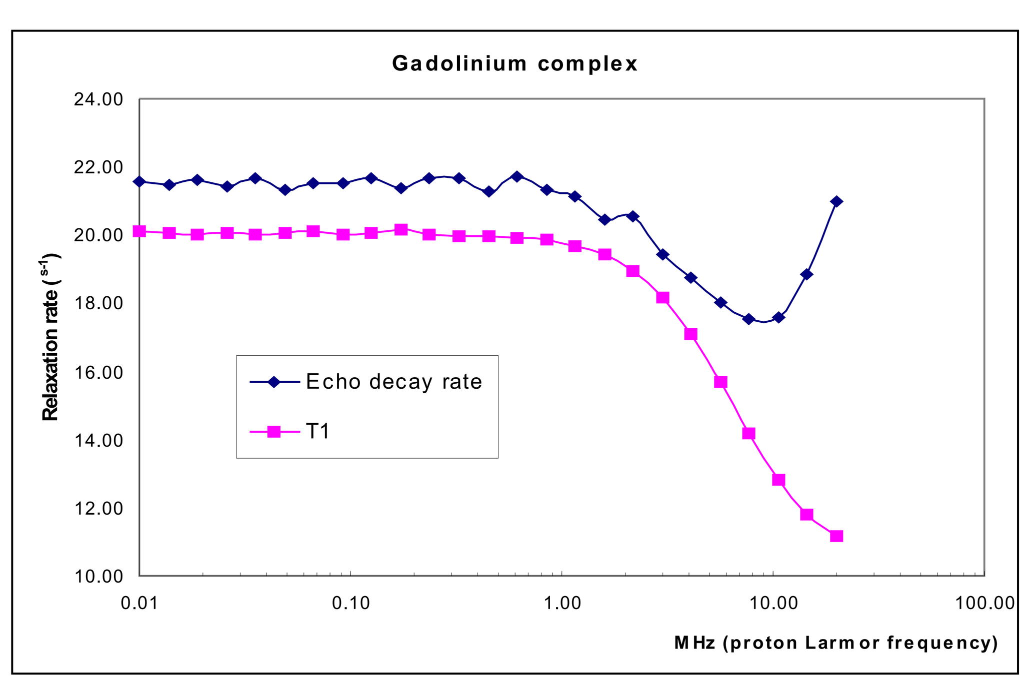


Figure 6.
The figure represents R_1 ($1/T_1$) and the echo-decay rate of a complex of Gadolinium as a function of the magnetic field strenght. In this liquid-like sample. The echo attenuation is dominated by a compromise between T2, G and D. Where D is the diffusion constant and G the intensity of the magnetic field gradient. The echoes were acquired in polar coordinates. The echo decay rates were fitted using the modulus of the echoes as described. The unaspected shape of R2 (blu data) at magnetic field higher than 1MHz is the effect of echo acquisition at different magnetic fields (different thermal conditions) with different homogeneity in presence of diffusion.
In case of modulus accumulation of signal with lower S/N, systematic errors are introduced. These errors can be removed using suitable acquisition procedures as well as proper weighting functions for signal and noise during the accumulation process. These aspects related with accumulation in polar coordinates is not discussed in this poster.

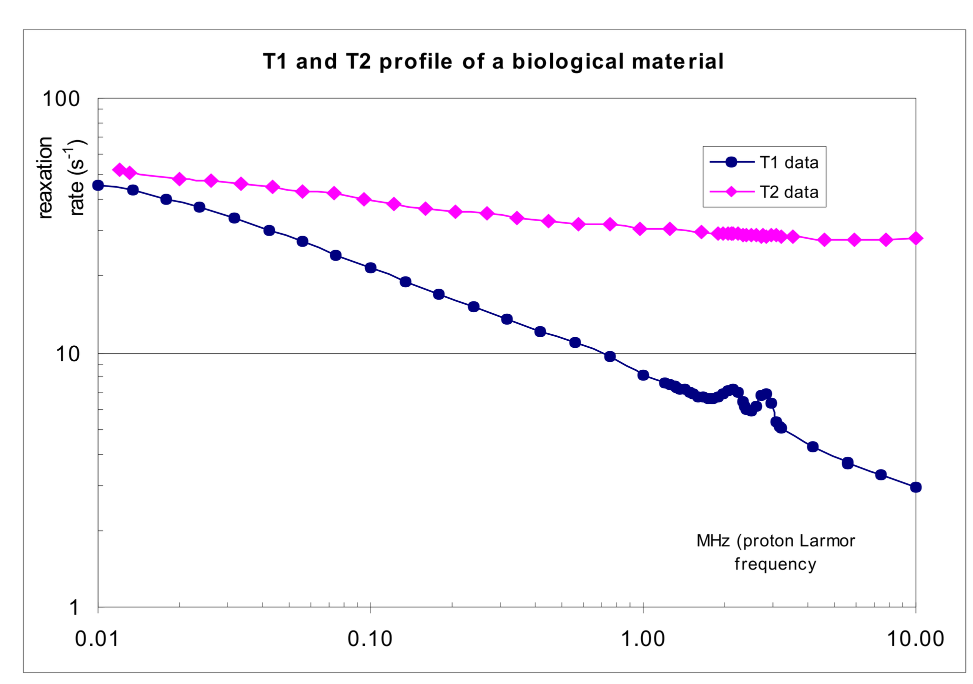


Figure 7.
The graphs represent the T1 and T2 (echo decay) field dependence of a biological material. The data were acquired and evaluated again in the same way of fig.6.
In this solid-like sample we expect that the contribution of diffusion on the decay of the echoes is not prevalent.

Conclusions

We have proposed a novel NMR instrumental method and demonstrated its applicability for the measurements of the echo decay in Fast Field Cycling NMR relaxometry by means of the classical Hahn-Echo experiment.The method wants to be a simple and different approach to overcome the problem of the detection and the accumulation of a NMR signal in presence of field instability. This problem represents the main limitation of the present Fast Field Cycling instrumentation for the measurement of T2 profiles. The interpretation of a echo decay involves all the necessary consideration related with possible contribution of diffusion and field homogeneity . Other possible related with the evolution of M0 in the cycled magnetic field B0 could be present and must understood. More work about all NMR aspects of the experiment, in particular with the liquid-like as well as with the short T2 samples, is necessary. All this will be subject of the next future development of this project. Nevertheless, we believe that the method we are proposing represents a promising approach to measure the field dependence of T2 in many sample in order to understand more about the dynamics of the spin-spin relaxations at low field.

[1] D. Canina, A. Galkin, S. Sykora and G.M. Ferrante
Novel Approaches to Signal Acquisition and Accumulation in FFC-NMR experiments
4th FFC conference Torino 2005