

3 Invited Talks

I4 Relaxation Analysis of Porous Media at High Magnetic Field Strengths: the Influence of Internal Gradients

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It is well known that internal magnetic field gradients, caused by susceptibility differences at solid-liquid interfaces, alter transverse relaxation times observed in liquid-saturated porous media. As such, CPMG measurements provide only an effective $T_{2,\text{eff}}$ relaxation time determined by molecular diffusion, rather than the true T_2 relaxation time determined by solid-liquid interactions. In order to overcome the influence of internal gradients, NMR data can be acquired at low magnet field strengths. Of course, the definition of low field needs to be quantified in order to optimise experimental parameters, and a simple calculation for estimating the maximum magnetic field strength is presented. However, the use of low magnetic fields is not a universal solution: this can be disadvantageous in some circumstances, where suitable magnets are unavailable, or if chemical sensitivity is required. It is known that internal gradients increase with magnetic field strength, and so it is important to understand the role of these gradients in high field NMR measurements.

The strength of the internal gradients will determine the diffusion behaviour observed, and three significant diffusion regimes need to be considered when measuring $T_{2,\text{eff}}$ relaxation times in porous media: the motional averaging regime is governed by pore size; the short time regime is governed by the CPMG echo spacing; and the pre-asymptotic localization regime is governed by the magnetic field profile in individual pores. By measuring $T_{2,\text{eff}}$ across a range of magnetic field strengths, it is possible to observe the diffusion behaviour in different regimes. Here, we demonstrate techniques for examining distributions of effective internal gradient g_{eff} and diffusion behaviour. For example, it is possible to observe exchange between regions of different gradient strength using two-dimensional T_2 - T_2 measurements. This method is demonstrated in brine saturated reservoir rock plugs.

It is also possible to deconvolve the contributions from diffusion and surface relaxation, allowing the true T_2 relaxation time to be obtained from measurements of $T_{2,\text{eff}}$ acquired in the presence of internal gradients. This is of importance when measuring the ratio T_1/T_2 as a function of magnetic field strength in order to determine surface mobility of adsorbed species. According to theoretical predictions, both T_1 and T_2 relaxation times should increase with magnetic field

strength; this is observed for T_1 but not $T_{2,\text{eff}}$. However, the true T_2 relaxation time does indeed increase, as demonstrated in packed beds of glass spheres. As such, correct T_1/T_2 ratios can be obtained even using high field spectrometers that would have been deemed inappropriate previously for the study of liquid-saturated porous media. The determination of corrected T_2 relaxation time distributions are discussed in the light of results from heterogeneous catalyst supports.

I5 The Use of Internal Magnetic Field to Characterize Porous Media

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When a porous material is placed inside a magnet, the magnetic field inside the pore space is naturally inhomogeneous due to the susceptibility contrast. Such internal field is ubiquitous in materials and intimately related to the packing structure of the grains and can be used as a fingerprint of the material. This talk will outline several magnetic resonance imaging (NMR and MRI) techniques, the underlying diffusion physics to quantify the internal field, spatial correlation, and their application in the study of pore structure of rocks and biological tissues.

I6 Intracellular Confinement of Magnetic Nanoparticles by Living Cells: Impact for Imaging and Therapeutic Applications

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Magnetic labelling of living cells creates opportunities for numerous imaging and therapeutic applications such as cell manipulation, magnetically-induced hyperthermia or MRI cell tracking. The unique advantage of magnetic-based methods is to activate or monitor cell behavior by a remote stimulus, namely the magnetic field. Cell labelling methods using superparamagnetic nanoparticles have been developed, showing no adverse effect on cell proliferation and functionalities, while conferring magnetic properties to various cell types. Magnetic nanoparticles are internalized by living cells within intracellular compartments, which confine the nanoparticles at high concentration.

The ability of iron oxide nanoparticles to create MRI contrast or to generate heat under alternating field is governed by the dynamical behavior of their magnetic moment. The dynamics results both from Brownian motion of the particles and from internal fluctuations of the magnetic moment within the nanocrystal (Néel dynamics). Intrinsic properties of nanoparticles, such as their size, their magnetization and their magnetic anisotropy, are the relevant parameters governing the dynamics. However environmental characteristics such as the local viscosity or the way nanoparticles are organized within intracellular compartments, also affect their behavior.

We will present the effect of cellular environment on nanoparticle properties, stressing the role of interparticles magnetic interactions created by intracellular confinement.

Intracellular confinement will be shown to influence the MRI contrast properties of nanoparticles, their detectability as well as their efficiency as heating mediators.

I7 Magnetic Resonance Imaging for Petroleum Reservoir Core Analysis

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Despite laudable efforts to diversify the world energy supply, the industrialized world will remain dependent on petroleum for economic development and prosperity for many decades. Despite the importance of petroleum resources however, typical reservoir recovery rates are often no better than 40%. Increasing these recovery rates requires detailed scientific knowledge of the fluid behavior in reservoir rocks. In addition, new reservoir exploration and development around the world is increasingly occurring in marginal reservoirs where the fluid or rock matrix properties are challenging, or in inhospitable environments such as the far north or offshore. In each case detailed knowledge of the fluid and matrix properties aid decision-making such as how to develop the reservoir, or indeed whether the reservoir is economic to develop at all.

In each of the two cases outlined above magnetic resonance imaging is able to decisively contribute to improved scientific knowledge of the fluid and matrix properties. MRI has the unique ability to analytically determine fluid content non-invasively as functions of space and time. MRI methods for core analysis include SPRITE fluid density imaging and new T_2 mapping spin echo methods. The use of these methods for laboratory core analysis and evaluation of enhanced oil recovery strategies will be described.

I8 Phase State and Dynamics of Fluids in Mesoporous Solids

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Mesoporous solids represent an important class of materials widely used in different applications in various fields including chemical engineering, material science and pharmaceuticals. In particular, mesoporous hosts attract special attention due to their fascinating match of transport, geometrical and chemical properties[1]. By tailoring pore structure in these materials, their properties may be efficiently tuned to meet specific application-oriented purposes. Therefore, fundamental understanding of the correlations between the geometrical features of mesoporous solids, the phase state of confined therein fluids and their transport properties is an important factor for routing synthesis of novel

host systems and their optimal use in practical applications.

In this contribution, recent advances related to establishing of such interrelations in mesoporous materials using nuclear magnetic resonance will be reviewed. Among different topics, diffusion behavior of fluids during gas-liquid [2], solid-liquid [3] transitions, transition to the supercritical state [4] and kinetic effects accompanying hysteretic phase transitions in disordered matrices [5-6] will be discussed. In particular, it will be shown that molecular diffusivity may serve as a sensitive microscopic parameter of the system thermodynamic state.

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19 Experience of Large-Scale NMR Measurements in Porous Media *Anatoly Legchenko¹, Jena-Michel Vouillamoz¹*

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The proton Magnetic Resonance Sounding (MRS) is a geophysical technique that allows non-invasive investigations of water-saturated rocks. The method is based on the Nuclear Magnetic Resonance (NMR) phenomenon in the Earth's magnetic field. The measuring setup consists of a wire loop on the surface that is energized by one or two pulses of oscillating current. The frequency of the current is set equal to the Larmor frequency in the geomagnetic field that varies between 800 and 2800 Hz around the world. After the pulse is cut off, the free induction decay (FID) and/or the spin echo (SE) signals from groundwater could be measured. MRS results are averaged over the investigated volume that depends on the loop size and typically varies from $20 \times 20 \times 20$ to $100 \times 100 \times 100 \text{ m}^3$.

MRS performance depends on the magnitude of the natural geomagnetic field, the electrical conductivity of rocks, the electromagnetic noise and other factors. For example, the maximum depth of groundwater detection for currently avail-

able equipment can vary from 45 to 170 m depending on measurement conditions, although an average depth of investigation is generally considered to be about 100 m.

Our recent results show that combination of FID and SE allows rendering the MRS less dependent on the geological conditions. Because of different scales, use of rock samples for calibration of the MRS estimate of the water content is difficult or impossible. Thus, for interpretation of experimental data we use a mathematical model that allows computing the theoretical signal generated by groundwater. The processing of MRS data can provide the depth, thickness and water content of investigated aquifers. The existing models are simplified and real experimental conditions of the MRS experiment may not obey the approximations that were made in the mathematical models and MRS is not always able to provide robust estimates of the MRS water content. For improving estimate MRS results we use calibration based on borehole pumping test data. Based on the water content and the relaxation time provided by MRS it is possible to estimate the aquifer's hydrodynamic properties. In this aim, experience gained through NMR logging has been applied to MRS data interpretation. Presented discussion of the advantages and disadvantages of the MRS, the accuracy of the MRS results and of the practical limitations of the method allows better understanding of this geophysical technique.

I10 Halbach Arrays for NMR and MRI

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During the last decade several magnet designs based on a Halbach arrays has been proposed for desktop NMR instruments. Compared to conventional C-shaped magnets, Halbach arrays accommodate larger samples inside the magnet bore and thanks to their jokeless design they are relatively small and light. In theory, the magnetic field generated by an infinitely long cylindrical Halbach array is perfectly uniform over the whole magnet bore. However, due to variations of the polarization of the magnet pieces used in the assembly, the magnetic field found in real magnets is strongly inhomogeneous. The field variation is such that only a small fraction of the bore can be excited. This is the reason why previously published magnets have been used for relaxation measurements while MRI and high-resolution spectroscopy are excluded. To cope with this problem, Halbach magnets have been scaled up, or the samples simply reduced, but then Halbach arrays became in practice as bulky and heavy as state of the art C-shaped magnets. Further drawbacks of the Halbach design are the complexity of the design and its associated manufacturing cost and the impossibility of placing high permeability materials, like iron pole shoes, in the inner bore of the magnet. Pole shoes smooth out the fast spatial variations of the magnetic field due to the local inhomogeneity of the magnet pieces leaving

mostly first and second order terms what can efficiently be corrected by simple electrical shim coils.

We have recently presented a robust method for correcting strong field inhomogeneities of the order of several thousands of ppm like the ones found in the stray field of single-sided magnets. The method is based on the displacement of magnet pieces specially designed in order to allow the generation of field variations orthogonal in space such as the spherical harmonics. The first implementation of the method was to generate a spot of highly homogeneous field (fraction of ppm) outside the magnet for single-sided ^1H spectroscopy. Later, the method was extended to correct the field inhomogeneities of a Halbach magnet for MRI. In that case, a second Halbach array made of movable pieces was placed in the bore of an existing Halbach to efficiently generate first and second order shim terms. Finally, the method was refined by incorporating the movable pieces into the main magnet design and extending the correcting shim terms to higher orders [1]. Here we present the implementation of this approach to design and build Halbach magnets generating homogeneous field for the several purposes, like, for example, miniature magnets for high-resolution spectroscopy, low field/low weight magnets for T_2 relaxometry of large samples, and desktop MRI systems.

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I11 Application of Hyperpolarized Xenon-129 NMR to Single File Diffusion and Exchange Dynamics in Nanoporous Materials

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Supramolecular materials often exhibit porosity over a wide range of length scales and with diverse pore space architectures. Particularly intriguing are crystalline solids exhibiting one-dimensional pores, which afford a high adsorption capacity with size selectivity and uni-dimensional diffusion properties. For basic studies of molecular diffusion in one-dimension, the material should have well-defined, defect-free channels with tuneable and monodisperse diameters. Here, hyperpolarized xenon-129 NMR techniques are presented for studying diffusion and Xe exchange in nanotubes formed by molecular wheel compounds. A large family of molecular wheels has been reported in the literature over the past two decades, typically with a single-strand topology with respect to the metal ions. Particularly beneficial synthetically has been the use of a central template whose size and nature determine the size (metal nuclearity) of the resulting wheel that forms around it. However, such central templates prevent the crystal from exhibiting nanoporosity. In contrast, recent work replacing the MeO^- groups of $\text{Fe}_{10}(\text{OMe})_{20}(\text{O}_2\text{CMe})_{10}$, and the corresponding $\text{Ga}_{10}(\text{OMe})_{20}(\text{O}_2\text{CMe})_{10}$ (abbreviated Ga_{10}) analogue, with 1,3-propanediolate

(pd²⁻) has provided a non-template means to change the wheel size, as in [M₁₈(pd)₁₂(pdH)₁₂(O₂CMe)₆(NO₃)₆](NO₃)₆ (M₁₈; M = Fe or Ga) [1]. In fact, both the M₁₀ and M₁₈ wheels have empty central cavities, and in the crystal they thus stack to form supramolecular nanotubular channels of monodisperse diameters. This talk will focus on the application and development of hyperpolarized ¹²⁹Xe NMR [2-5] methods to study diffusive transport and gas exchange in molecular wheel nanotubes of different channel sizes. The availability of two different wheel sizes provides the opportunity to study unidirectional diffusion as a function of the central cavity diameter. Evidence of single file diffusion of Xe atoms in the Ga₁₀ crystals is consistent with the relative size of the Xe atom with respect to the channel diameter. Furthermore, the diffusion of gas atoms between the nanochannels and the bulk gas phase was observed by continuous and interrupted-flow hyperpolarized ¹²⁹Xe 2D exchange NMR. The results presented here illustrate how hyperpolarized NMR can characterize molecular transport in materials with one-dimensional pore structures.

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I12 Pulmonary Physiology with Hyperpolarized ¹²⁹Xe

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The purpose of the lung is gas exchange; O₂ diffuses from alveolar gas spaces to blood and CO₂ diffuses in the reverse direction. Efficient gas exchange occurs because of the large alveolar surface area (~ 100 m²) and thin tissue barrier (< 1 μm) separating alveolar gas and capillary blood. Reduction of surface area or thickening of the tissue barrier layer reduce the diffusing capacity of the lung. To diagnose and determination of treatment efficacy in pulmonary disease, methods are needed to noninvasively measure sub-components of lung physiology. To that end, we describe here a magnetic resonance method to evaluate three parameters: alveolar surface area per unit volume (*S/V*) which decreases in emphysematous disease; septal thickness, which increases in interstitial disease; and capillary transit time, which is a function of pulmonary hypertension and vascular health.

Because of a large chemical shift between ¹²⁹Xe in gas and tissue/blood, it is straightforward to measure the septal uptake of ¹²⁹Xe in tissue and blood (dis-

solved phase). After selective saturation of the dissolved phase magnetization (M_{Xe}), we observe the recovery of M_{Xe} . We call this method Chemical Shift Saturation Recovery (CSSR). Initially, M_{Xe} increases diffusively as \sqrt{t} with a proportionality constant of S/V [1]. After ~ 100 ms, the septa begin to saturate with ^{129}Xe and the time dependence of the xenon septal uptake begins to level off to a plateau, the value of which is proportional to the septal thickness. Because of blood flow, however, M_{Xe} does not plateau and continues to increase at long times. Fits of human xenon septal uptake curves to a 1D analytical model of this process provides estimates of S/V , septal thickness and capillary transit time [2].

We obtained whole lung results using the CSSR method in 4 healthy subjects, 2 subjects with mild to moderate COPD, and 2 subjects with mild to moderate interstitial lung disease (ILD). The COPD subjects showed a remarkable reduction (more than a factor of 4) in S/V compared to the normal subjects whereas the two ILD subjects showed an increase in septal thickness compared to our normals of 36 and 97%.

More recent experiments were performed with a modified version of the Xenon Transfer Contrast (XTC) method [3] to obtain 3D regional maps of S/V in a healthy subject [4]. Rather than direct observation of dissolved phase ^{129}Xe magnetization in CSSR, XTC measures the reduction in the gas phase ^{129}Xe magnetization by allowing multiple opportunities for interphase diffusion. We have demonstrated that analytically identical results to CSSR can be obtained with XTC if π pulses are used for the gas exchange sensitization portion of the pulse sequence rather than the traditional $\frac{\pi}{2}$ pulses.

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I13 Detecting Fleeting MRI Signals with Frequency-Modulated Radio Waves

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A fundamentally different approach to MRI is described called SWIFT (sweep imaging with Fourier transformation) [1,2]. SWIFT exploits time-shared RF excitation and signal acquisition, allowing capture of signal from spins with extremely short transverse relaxation time, T_2^* . MR signal is acquired in gaps inserted in a broadband frequency-swept excitation pulse, which results in acquisition delays of only 1–2 microseconds. In SWIFT, 3D k -space is sampled in a radial manner, whereby one projection of the object is acquired in the gaps of each frequency-swept pulse, allowing a repetition time (TR) on the order of the

pulse length (typically 1–3 milliseconds). Thus, SWIFT images can be acquired in scan times similar to and sometimes faster than conventional 3D gradient echo techniques. Because the orientation of consecutive projections varies in a smooth manner (i.e., only small increments in the values of the x , y , z gradients occur from view to view), SWIFT scanning is close to inaudible and is insensitive to gradient timing errors and eddy currents. With its ability to capture signals from ultrashort T_2^* spins, SWIFT promises to expand the role of MRI in areas of research where MRI previously played no or negligible role. Broad-band frequency-swept excitation and extremely short acquisition delay make it possible to preserve signals from spins experiencing large frequency shifts due to magnetic susceptibility effects. For example, superparamagnetic-labeled nanoparticles (e.g., SPIOs), which cause signal voids in images acquired with a conventional gradient echo sequence, give rise to positive contrast (bright spots) in SWIFT images [3]. Early experience suggests SWIFT can play a role in materials science and porous media research. One conceivable advantage will be for capturing signals in heterogeneous porous media with strong surface relaxivities (e.g., due to abundant iron or manganese) [4].

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I14 Diffusion in White Matter

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Diffusion magnetic resonance imaging permits non-invasive probing of tissue microstructure and function and provides invaluable information in brain diagnostics. Conventional methods are based on a simplified picture of Gaussian diffusion of water molecules in brain tissue characteristic of the isotropic non-confined liquids. However, more detailed experiments show that water in brain tissue tends to exhibit essential deviations from patterns of the Gaussian diffusion. The propagation of water molecules in the brain and in biological tissue, in general, is affected by multiple factors such as compartmentalization, restric-

tions and anisotropy imposed by the cellular microstructure [1,2] which can be modelled, quite in general, as a composite porous medium [3,4]. Interfacial interactions with the cell membranes («bound water») and exchange tend to further complicate the measured response. Due to the heterogeneity and complexity of the tissue microstructure, a differentiation between the various contributions to the average NMR signal in *in vivo* studies represents a difficult task. Our aim is to develop the advanced approaches capable of capturing more detailed information on the propagation mechanisms and underlying tissue microstructure in comparison to conventional methods. In this work, we will present a diffusion study of the brain based on the detailed analysis of the attenuation patterns in the extended range of the diffusion-encoding gradients. Experimental data are based on the *in vivo* studies of healthy volunteers and on the measurements of artificially constructed anisotropic «phantoms». The discussion will be supported by results of random-walk Monte Carlo simulations [5] in the well-defined model systems relevant for the structural organisation of white matter.

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I15 Linking Soil Science with NMR Relaxometry: Potential and New Challenges

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¹H-NMR-Relaxometry is being increasingly applied in soil science due to its potential for helping to understand water uptake into the soil matrix and processes occurring at the solid-liquid interface at soil particle surfaces. This contribution discusses current applications of proton NMR relaxometry in the context of soil science and identifies its potential and current research gaps. NMR relaxometry is a sensitive, informative and promising method to study pore size distribution in soils as well as many kinds of soil physicochemical processes, among which are wetting, swelling or changes in macromolecular status. It is further a very helpful method to study interactions between molecules in soil organic matter and can serve to study the state of binding of water or organic chemicals to soil organic matter. Relaxation times determined by NMR relaxometry are sensitive to various factors that play a role in soil-water interaction which is both an advantage and shortcoming of the method: NMR relaxometry can be applied to numerous investigations in soil science, but at the same time interpretation of the results is challenging in such complex and heterogeneous systems like soils.

I16 High-Throughput Low Resolution NMR Methods to Analysis of Agri-Food Products

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We have recently proposed a low resolution NMR method termed continuous wave-free precession (CWFP) to enhance signal-to-noise ratio in quantitative analysis, measuring flow, longitudinal (T_1) and transverse relaxation time (T_2) measurements in a single experiment, and thermal diffusivity measurements in a few seconds. We have been using this sequence for on-line and non-destructive measurements of agri-food products based on a low resolution NMR spectrometer. The on-line spectrometer is based on a CAT 100 NMR transceiver, Tecmag, a 30 cm bore, 2.1 T superconducting Oxford magnet and in a homemade polycarbonate conveyor belt, driven by a Parker step motor.

The CWFP regime is attained when a train of short pulses, with period T_p small as compared to T_2^* is applied to a liquid or heterogeneous sample. This causes the amplitude of the transverse magnetization just preceding pulse to be equal to the amplitude following the pulse. Since the condition $T_p < T_2^*$ implies that dephasing of isochromats in each interval T_p is relatively small, a continuous wave periodic signal with practically constant amplitude, displaying n nodes within each T_p interval, is obtained. Therefore, the CWFP signal can be observed continuously for arbitrary long periods of time while a stream of samples is conveyed to the NMR receive/transmit coil. The CWFP sequence has the potential to measure the oil content in more than 20.000 samples per hour or to measure the intramuscular fat content in more than 500 beef portions/hour.

Using the same on-line spectrometer and CPMG pulse sequence we have been measuring the oil quality in intact seeds. The CPMG decay processed by chemometric methods was able to determine the oil quality in intact seeds by its fatty composition, cetane number, iodine value and kinematic viscosity with a correlation coefficient $r > 0.9$. The automated NMR system has the potential to analyze more than 1000 samples per hour. The CPMG sequence has also been used to detected mechanical injuries in fruits such as banana, pears.

I17 Characterisation of Heterogeneous System by PFG-NMR

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In heterogeneous media, as food stuff or rock cores saturated with crude oil and/or brine, the use of pulsed field gradients is an essential for resolving the NMR response from the different components. In addition one may use the diffusion measurements themselves to extract information about the environment in which the diffusing molecules are confined.

Ever since Mitra et al. (Physical Review B 47 (1993)) introduced the short observation time expansion of the observed diffusion coefficient, resolving the

surface to volume ratio (S/V) from the surface relaxivity (ρ) we have focused on developing applications where this model has been used. This short observation time model is unique as it resolves the surface to volume ratio from the surface relaxivity, and thus makes it possible to either measure the S/V directly or combine it with relaxation time measurements to extract pore size distributions in rock core plugs or droplet size distributions in emulsions.

In our work with developing methods for characterising emulsions, a major obstacle has been the settling time for the system to regain the thermal equilibrium along the external magnetic field (~ 5 times T_1) between each scan. Instead of letting the magnetisation reach thermal equilibrium before each scan, we apply a combination of RF-pulses and magnetic field gradients which aim at spoiling any magnetisation in any direction. Then, using a waiting time equal to T_1 after the spoiling, we have already regained 63% of the magnetisation 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. As a consequence 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.

The acquisition time is an important issue when you for example are to analyse biological tissue, a biopsy, during surgery. By using the spoiler approach we reveal information that may assist the surgeon to decide the best approach for the surgery of a patient.