

# Oral Contribution Abstracts

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## Oral Contribution Abstracts

O-04

### FLUORINE TRACERS FOR THE IDENTIFICATION OF MOLECULAR INTERACTION WITH POROUS ASPHALTENE AGGREGATES IN CRUDE OIL

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The relation of NMR relaxation times and diffusion coefficients with overall viscosity and molecular size in a typical fluid composition has been established for bulk oils [1-3]. A major obstacle for the task of compositional analysis remains, however, the widely unknown role of molecular shape and chemistry, most importantly aromaticity, on the NMR relaxation behaviour. This is particularly important in asphaltene-containing oils where the relaxation of soluble compounds (maltenes) is significantly affected by interactions with radical-containing asphaltenes [4]. However, aromatic and aliphatic maltenes are expected to interact differently with asphaltene aggregates [5], and size-dependent residence time variations within the porous aggregates become important [6]. While fundamental studies have attempted to provide a molecular dynamics description of relaxation times that take advantage of data obtained at variable magnetic fields [7], they still suffer from a lack of distinction of dynamics between molecules of various architecture, and the generally broad relaxation times distribution in natural oils.

In this study, we have applied <sup>19</sup>F containing tracer molecules at low concentrations to natural oils of different asphaltene content, and investigated the tracer's relaxation time ratio  $T_1/T_2$  and the field dependence of relaxation times,  $T_1(\Omega)$ . This strategy has the advantage of specifically determining the behaviour of different tracers, where molecular weight and aromaticity are considered as variables. One main finding of this study is the significant increase of  $T_1/T_2$  for aromatics in the presence of asphaltenes compared to alkanes. The results are interpreted in terms of selective maltene-asphaltene interaction based on frequency dependent relaxation results. The strong contrast of relaxation times allows for a simplified quantification of either asphaltene concentration or aromaticity of maltenes in natural oils.

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O-05

### MEASUREMENT AND MODELING OF SUPER-DISPERSION IN UNSATURATED POROUS MEDIA USING NMR PROPAGATORS

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Dispersion in porous media has been studied for a long time from breakthrough curves using a tracer. In contrast, the NMR propagator technique brings a crucial new information: the dependence of dispersion with time. Dispersion is non Gaussian if the variance of the molecule displacements does not grow linearly with time,  $\sigma^2 \propto t^\alpha$  (for super-dispersion  $\alpha > 1$ ). We present NMR experiments performed in grain packs in saturated and unsaturated conditions [1], and samples representative of a variety of structure encountered in natural porous media. In a homogeneous 30 mm grain pack and  $10 < Pe < 35$ , we observed weak super dispersion in saturated conditions ( $\alpha = 1.17$ ) and gradually strong super-dispersion as the water saturation decreases (up to  $\alpha = 1.5$ ) during steady-state oil-water two phase flow. In saturated conditions, the corresponding longitudinal propagators and breakthrough curves are Gaussian or nearly Gaussian, whereas in two phase conditions, the longitudinal propagators are non symmetric and the breakthrough curves show a tail at long time.

We built a general model (SMIM) specifically designed for the interpretation of NMR velocimetry data [2]. Extending the well known concept of Mobile/ Immobile tracer particles applied in dispersion theory, we describe the immobile periods by independent random arrests of finite average, and combine it with the possibility of unexpectedly long but rare displacements (Levy process). From the derived analytical expressions of the NMR signals fitted to the recorded data, we can determine a generalized dispersion coefficient and the stability exponent of the Levy process. Hence, we can quantify the observed super-dispersion effect. We also analyzed the observations using a pore network model in order to compute the long time behaviour of NMR propagators, not accessible from the experiments [3]. Although the pore network does not reproduce the small scale features of the porous structure, very good agreement was obtained with the NMR data.

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O-06

### BIG ANALYTICS FOR DE-CONVOLUTING SIZE AND CHEMICAL DISPERSITY EFFECTS – A SYSTEMS APPROACH TO COLLOID AND INTERFACE SCIENCE

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Colloid and interface research has contributed very significantly to science due to a strong nexus between theory

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and experiments. The research has resulted in models for predicting the effect of nano-, micro- and macro interfaces on the behaviour of colloidal materials. Unfortunately, the models are often limited to simple materials, mono-disperse and chemically homogeneous particles for instance. As we look forward surface and size dispersity factors represent grand challenges for developing models that can predict behaviour for “real life” materials.

Our hypothesis is that there is new information to be extracted from the right combination of surface spectroscopy techniques utilising multidimensional data - *big analytics*. In addition to hypothesis driven research we should therefore develop methods for *letting the data speak for itself*<sup>1</sup>. The objective is to de-convolute the various factors that contribute to the performance of colloidal systems in e.g., energy conversion and storage, pharmaceutical formulation performance and minerals processing.

Multi-dimensional NMR techniques, recent advances in other correlative spectroscopic techniques<sup>2</sup> together with mathematical and statistical approaches in the field of systems biology<sup>3-7</sup> makes us propose a *systems approach* to colloid and interface science. The strategy again relies on a strong nexus between theory and experiments and in this seminar we describe the experimental part of the strategy for de-convoluting dispersity factors and their effects on the performance of different sized colloidal particles with varying degrees of surface modification.

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### O-07

#### **T<sub>1</sub> MMRI STUDY OF THE DIFFUSION AND EQUILIBRIUM DISTRIBUTION OF A $\mu$ MRI CONTRAST AGENT IN A POLYELECTROLYTE SOLUTION; A MODEL FOR CARTILAGE.**

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A loss of glycosaminoglycans (GAGs) is an early sign of osteoarthritis. GAGs are highly negatively charged and build up the fixed charge density (FCD) in cartilage. In order to detect early signs of degeneration, a non-destructive method has been developed that gives spatial resolution of FCD in cartilage<sup>[1]</sup>. The method uses <sup>1</sup>H MRI together with a contrast agent, Gd(DTPA)<sup>2-</sup>, which is a paramagnetic, negatively charged complex that affects the T<sub>1</sub> relaxation in the tissue. The assumption is that Gd(DTPA)<sup>2-</sup> will distribute in inverse relation to the GAG concentration and by measuring the T<sub>1</sub> in cartilage one can determine the Gd(DTPA)<sup>2-</sup> concentration, which is then used to obtain the FCD from ideal Donnan theory<sup>[1]</sup>. However, for an accurate FCD quantification some questions remain to be answered. For instance, how is the diffusion of Gd(DTPA)<sup>2-</sup> affected by the status of the cartilage. Moreover, the use of

ideal Donnan analysis has been debated. Experimentally one has found that the method outlined above gives a factor of ~2 smaller value of FCD compared to <sup>23</sup>Na MRI measurements of cartilage<sup>[1,2]</sup>.

For a physical chemist, cartilage is a complex porous system of biological macromolecules. We have developed a model system for  $\mu$ MRI studies that capture the important physics of cartilage in order to investigate the diffusion and the equilibrium distribution of Gd(DTPA)<sup>2-</sup> in cartilage. The system is based on a polyelectrolyte solution that is separated by a semipermeable membrane from a salt solution. The FCD of the polyelectrolyte solution can be varied systematically. In the experiment, Gd(DTPA)<sup>2-</sup> is added to the salt solution and then T<sub>1</sub> is measured simultaneously with spatial resolution in the two solutions at different times when the ion diffuse into the polyelectrolyte solution. The ideal Donnan analysis can then be tested by comparing the known FCD in the solution and the calculated FCD from Gd(DTPA)<sup>2-</sup> concentration profiles and computer simulations<sup>[3]</sup>.

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### O-08

#### **SENSITIVE DETECTION OF AXONAL INJURY USING DOUBLE PULSED FIELD GRADIENT MRI**

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**Introduction:** Sensitive measurements of changes in tissue microstructure in the nervous system can improve the detection and diagnosis of pathology. Following mechanical, chemical, or metabolic insults<sup>1</sup> axons exhibit a beaded morphology, but Diffusion Weighted MRI (DWI) methods like DTI are not sensitive or specific enough to characterize the underlying pathology. Methods like Double Pulsed Field Gradient (d-PFG) MR<sup>2,3</sup>, which provide microstructural information, such as average cell size, cell shape, and microscopic anisotropy, may be able to detect these microscopic changes. In these studies d-PFG MRI was used to characterize beading in a nerve injury model.

**Material & Methods:** Fixed samples of rat sciatic nerve subjected to axial tension sufficient to induce beading were used as a model of acute axonal injury. A 7T vertical bore scanner with a micro-2.5 gradient set (Bruker Biospin) was

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used. D-PFG filtered MRI sequences were applied. Bead diameters and length size distribution were obtained by fitting the data to a mathematical model, with beads characterized as combinations of spheres and infinite cylinders<sup>4</sup>.

**Results & Discussion:** The beaded sciatic nerves displayed a clear difference in the d-PFG measurements compared to control nerves. In control nerves, fitting yielded a distribution of axonal diameters measured perpendicular to the nerves and low restriction parallel to the nerves in agreement with straight, parallel nerve morphology. In the injured nerves, on the other hand, fitting yielded two unique distributions for the diameter perpendicular to the nerves and high restriction parallel to the nerves, reflecting the beaded morphology. Preliminary histological data agree with those findings.

**Conclusion:** d-PFG MRI shows promise for characterizing tissue microstructural features in acute axonal injury such as stroke, traumatic brain or spinal cord injury. Methods like d-PFG MRI have the potential to more accurately characterize tissue microstructure and enable *in situ* and *in vivo* detection of specific pathologies.

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### O-09

#### CHANGES IN ANOMALOUS DIFFUSION DURING AGING IN THE RAT BRAIN

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In diffusion-weighted MRI studies of the brain, the classical model assumes Brownian motion with Gaussian statistics, which predicts a monoexponential signal decay. However, reports describe signal decays that are better fit by a stretched exponential, particularly in the white matter [1,2]. In this study we modeled diffusion in neural tissue using the continuous time random walk [3,4]. Consequently, the characteristic diffusion decay is represented by the one-parameter Mittag-Leffler function,  $E_{\alpha}(-Dq^{\beta}\Delta^{\alpha})$ , which captures the governing statistics in terms of the asymptotic power law decays of the waiting times ( $1/t^{1+\alpha}$ ) and jump distances ( $1/x^{1+\beta}$ ) [4]. We then used entropy as a measure of the anomalous behavior of the probability density function. Diffusion-weighted MRI experiments were performed on healthy fixed rat brains (adolescent and adult) using an imaging spectrometer operating at 17.6 T with b-values arrayed up to 25,000 s/mm<sup>2</sup>. We examined the signal decay by varying the gradient strength,  $q$ , for a mixing time,  $\Delta=17.5$  ms. In brain white matter we observed decreasing values for both  $\alpha$  and  $\beta$  with increasing age, which implies more anomalous diffusion with tissue microstructure development. These changes were also reflected in the entropy map which exhibited high contrast with maturation. The results demonstrate that the Mittag-Leffler and entropy parameters captured new information regarding subdiffusion.

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### O-10

#### NANOPARTICLE DIFFUSOMETRY IN BIOPOLYMER GELS

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In biopolymer gels, entangled networks span the solvent, yielding viscous and elastic materials. These gels are used for the structuring of foods and fast-moving consumer goods, but are also utilized as substrates for the release of active molecules and as separation and barrier media.

On the sub-micron-scale, gels are heterogeneous and form very open, meso-porous structures. Whereas small molecules generally diffuse freely through these structures, nanometer-size diffusive particles “probe” the obstructions and can therefore be used to quantify their structural and dynamical features.

Models are available that predict the diffusion coefficient of the particles from the structural parameters of the network [1]. This allows us to derive parameters such as mesh size and polymer strand thickness from the particles’ long-time diffusion coefficient. On the short time scale, a distribution in particle displacements reflects network heterogeneity. Recently, even the dynamical features of flexible polymer networks were modeled and the time-dependency of the mean displacement of embedded nanoparticles was predicted [2]. Using this model, “nano-rheological” information about the polymer network is obtained.

We see a strong potential to use PFG NMR to assess diffusive behavior of nanoparticles in polymer matrices, because the technique can be used to determine both the time-dependent average displacement propagator and the diffusive spectrum.

For this purpose, we have developed nanoparticles that are spherical, monodisperse and labeled with <sup>19</sup>F-groups for background-free observations by NMR. These particles have star-like polymer (dendrimer) or poly-ion cores and polyethylene glycol (PEG) coronas to prevent sticking to the matrix. We first compare <sup>1</sup>H and <sup>19</sup>F frequency and time domain PFG NMR nanoparticle diffusometry at different field strengths and discuss the different approaches in terms of sensitivity and resolution. We also describe the differences in average displacement propagators of particles in more flexible, homogeneous systems and more rigid, heterogeneous gels. Finally, we present some initial work on the determination of the diffusive spectrum of nanoparticles in polymer gels.

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### O-12

#### COHERENT DYNAMICAL RECOUPLING OF DIFFUSION-DRIVEN DECOHERENCE IN MAGNETIC RESONANCE

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Dynamical decoupling (DD), a generalization of the original NMR spin-echo sequences, is becoming increasingly relevant as a tool for reducing decoherence in quantum systems. Such sequences apply non-equidistant refocusing pulses for optimizing the coupling of systems and environmental fluctuations, characterized by a given noise spectrum. One such sequence, dubbed Selective Dynamical Recoupling (SDR) [1] allows one to coherently reintroduce certain interactions such as those driven by weak fluctuations arising from chemical exchange or J-couplings. The fully-refocused, constant-time nature of SDR also allows one to filter out “intrinsic”  $T_1$  and  $T_2$  weightings, as well as pulse errors acting as additional sources of decoherence. Here, we will explore such features as driven by diffusion decoherence effects. In particular, we show that these concepts can be exploited to selectively recouple diffusion processes in restricted spaces. The ensuing method provides a novel tool to measure restriction lengths in confined porous systems such as capillaries, pores or cells [2]. Alternatively, using Non-uniform Oscillating-Gradient Spin-Echo (NOGSE) sequences [3], these concepts are transcended to MR imaging, and implemented towards mapping compartment sizes in ex-vivo pig spinal cords and mouse brains. The effects of size distributions on these maps are also briefly analyzed. We show also that unrestricted diffusion-driven SDR can be exploited to address the decoherence effects arising from the frequency fluctuations imposed by internal gradients [4]. As a result of this, SDR presents a unique way of probing and characterizing these internal magnetic field gradients. This has important implications in studies of structured systems, including porous media and live tissues, where the internal gradients may serve as fingerprints for the system’s composition or structure. The potential of this approach is demonstrated with the generation of a novel source of MRI contrast, based on the background gradients active in ex-vivo mouse brains.

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### O-13

#### SINGLE-SHOT DIFFUSION MEASUREMENTS USING 2ND ORDER MAGNETIC FIELDS FOR PARALLEL ACQUISITION OF Q-SPACE

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Acquisition of displacement space with NMR, the conjugate of q-space, has many applications including diffusion, dispersion, velocimetry, tortuosity, and surface to volume

ratio measurements in porous media. Normally, acquisition of q-space data requires a series of scans over which current pulsed through a gradient coil producing a constant magnetic field gradient is varied to step through q-space. Using a second order magnetic field coil in conjunction with imaging techniques, we have developed PGSE and PGSTE sequences which allow parallel acquisition of q-space using a single echo.

The use of a second order magnetic field results in a spatially dependent gradient, and when applied as a diffusion gradient in a PGSE or PGSTE sequence, results in the encoding of q-space into real space. With the aid of a read gradient to image real space upon echo formation, using a thin slice selection, we are able to map the read image from real space onto q-space. As the Fourier transform of q-space is the propagator, this makes the acquisition of the echo itself a direct propagator measurement.

This technique for parallel acquisition of q-space may be used in conjunction with the pulse sequence DiffTrain [1] to acquire values of the time dependent apparent diffusion coefficient  $D^*(t)$  at multiple times in a single shot experiment. Using our method, each stimulated echo in DiffTrain may be transformed into a diffusion measurement for a different diffusion encoding time. Using the short time behaviour and asymptotic long time behaviour of  $D^*(t)$  to determine the surface to volume ratio and tortuosity of the porous medium [2], we may, for the first time, measure these properties using a single excitation pulse. We present a proof of concept of the parallel q-space acquisition using the PGSE and DiffTrain techniques for free diffusion, showing much promise for implementation with restricted diffusion.

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### O-14

#### NMR DETECTION OF ACOUSTIC WAVES IN FLUID-SATURATED ROCKS

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The ability to measure the mobility of a fluid in a pore matrix (such as oil in rock) without the need to actually extract the fluid would be of great benefit. Mobility is understood as the ratio of the permeability to viscosity and experiments finding this quantity typically rely on measurements of flowing fluids and are conducted either downhole or in the laboratory by measuring pressure and flow rate as fluids are extracted. NMR provides a tool that would eliminate the need for this flow. By using an acoustic source to force an oscillation of the fluid and encoding molecular motion with pulsed field gradients oscillating at the same frequency, the depth of penetration of can be measured by the accumulation of phase in the NMR signal [1]. This is a direct application of MR elastography [2], but is applied to longitudinal, rather than transverse acoustic motion.

Here we show laboratory verification of this method and discuss possibilities of implementation in the oil industry in downhole NMR logging and uphole core analysis.

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### O-16

#### HYDRODYNAMICS MEDIATES STRUCTURE DURING ABIOTIC GROWTH OF A CALCITE PRECIPITATE BARRIER: A COMBINED MRI/CT STUDY

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Strategies for sealing the geologic environment surrounding carbon capture and storage applications are a necessary precaution against leakage potential, and calcite ( $\text{CaCO}_3$ ) precipitation offers a means of cementation for pore spaces and fractures that is resistant to supercritical  $\text{CO}_2$ . One approach to  $\text{CaCO}_3$  deposition involves abiotic reaction of aqueous  $\text{Ca}^{2+}$  and  $\text{Na}_2\text{CO}_3$  [1,2], which constitutes a problem in reactive transport controlled by dispersive mixing in a porous medium. The opacity of porous media has restricted most studies to simulations, bulk measurements, and experiments in 2-D flow cells [2-4], but non-invasive MRI techniques offer a means of imaging precipitate structure and measurement of flow/dispersion in 3-D geometries [5,6]. MR studies of bacterially-induced precipitation have been reported, but we present new data on hydrodynamics and precipitate structure in the abiotic case.

Reaction of equimolar  $\text{Ca}^{2+}$  and  $\text{Na}_2\text{CO}_3$  solutions was carried out in a flow cell designed for use in a Bruker 300 MHz system. The modified, glass HPLC column contained borosilicate glass microspheres (180-212  $\mu\text{m}$ ), and reagents were injected concentrically via the bottom endcap to produce a vertical, radially symmetric flow. With constant total volumetric flow rate (395 ml/hr), the effect of varying the inner and outer flow rates was studied using a PGSE-MRI sequence in a 64x32x1 mm slice through the column center. Images revealed reduction in spin density, dispersion, and velocity from pore-clogging near the interface between the two solutions. The morphology of the precipitate barrier depends on the relative flow rates, being thinner and more clearly defined for equal inner/outer flow. Quantitative, in-situ MRI dispersion measurements were complemented with post-reaction, high-resolution X-ray CT structural images, together yielding information essential to inform hydrodynamic models of calcite cementation processes.

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### O-17

#### NMR STUDY OF THE EVOLUTION OF PALISADIC AND SPONGY PARENCHYMA IN OILSEED RAPE LEAVES THROUGH SENESCENCE

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Low field NMR has been used to study water distribution and status in leaves at the subcellular level [1]. It has been recently used [2] to detect structural changes associated with senescence process in oilseed rape leaves. An interpretation of the multi-exponential signal of leaf tissue taking into account both cellular compartmentation and heterogeneities at tissue level has been proposed. This study revealed a process of cell enlargement and hydration, specifically in the palisadic parenchyma while senescing.

The aim of the present study was to demonstrate that specific evolution of palisadic and spongy leaf parenchyma during senescence can be related to changes in vacuole-related NMR signal component. In fact, transverse relaxation times ( $T_2$ ) of young and mature oilseed rape leaves were characterized by three water-associated components; the highest  $T_2$  component assigned to vacuole [2] representing about three-quarters of the total water. In senescing leaves, this  $T_2$  component split into two components, still representing close amount of the total water. The estimation using light micrographs of the vacuolar volume of cells from both spongy and palisadic parenchyma showed a similar evolution between the highest  $T_2$  NMR signal components and the estimated vacuolar volume of each parenchyma. The observed split was associated to cell enlargement and combined with increasing hydration resulted in the specific increase in  $T_2$  [3] of vacuole of cells from palisadic parenchyma.

Comparison of NMR results with leaf physiological parameters (chlorophyll, starch and water contents), used as indicators of leaf development, showed that the split of the vacuole-associated NMR signal component describes a specific developmental status.

The results will be discussed in view of possibilities to study plant functioning and to develop method for plant phenotyping.

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### O-18

#### THE EFFECT OF FERROCYANIDE IONS ON SODIUM CHLORIDE CRYSTALLIZATION IN SALT MIXTURES: A NMR STUDY

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The use of crystallization inhibitors such as ferrocyanide has been proposed as a potential preventive treatment method against salt damage of historical monuments. It has been extensively tested for crystallization of single salts, where it has shown to be effective. However, in practice there are always mixtures of salts present. Therefore, before using inhibitors in practice, there is a strong need to explore their effect on salt mixtures [1, 2]. A main obstacle is the measurement of the individual salt content in a mix as to determine the ternary phase diagram. We have developed a NMR setup in which we are able to measure quasi-simultaneously Na, Li and H, giving the possibility to determine measure both the Na and Li concentration. We have also incorporated a digital microscope, giving the possibility to perform time lapse microscopy of the crystallization. This gives the possibility to connect the measured concentration with the point of crystallization.

In this research, we studied the effect of ferrocyanide ions on NaCl crystallization in single salt and in salt mixtures of NaCl - KCl and NaCl - LiCl. A series of micro droplet drying experiments were undertaken. For a NaCl solution droplet, in the presence of inhibitor, a significantly higher supersaturation, in the order of 10 M, prior to the onset of crystallization and a change in crystal morphology were observed. On the other hand, for the salt mixtures NaCl - KCl and NaCl - LiCl, the NaCl supersaturation was much lower in the presence of inhibitor than for the single salt. However, a significant change in the crystal morphology was seen in the presence of inhibitor for these salt mixtures.

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### O-19

#### MAGNETIC RESONANCE PORE IMAGING: OVERCOMING THE RESOLUTION LIMIT OF MRI FOR CLOSED PORE SYSTEMS

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The structure of porous materials is important in many areas of basic and applied science. Various Nuclear Magnetic Resonance (NMR) techniques are applied to study porous media on different length scales. Among them diffusive-diffraction Pulsed Gradient Spin Echo (PGSE) NMR is able to resolve features of the pore space on the micrometer scale<sup>1</sup>. However, this technique only measures the modulus square of the structure factor, which yields the pore density correlation function upon Fourier transformation.

In this contribution, we present experimental evidence that it is possible to obtain the full structure factor with a recently suggested modification<sup>2</sup> of the PGSE NMR experiment. Our adaptation which we call Magnetic Resonance Pore Imaging (MRPI)<sup>3</sup> creates a hybrid between Magnetic Resonance Imaging (MRI) and PGSE NMR. This allowed us to obtain two-dimensional average pore images with an unprecedented resolution as compared to conventional MRI. Special emphasis

will be given to the design and manufacturing of suitable calibration samples with pores of well defined micro-structure and orientation. Based on these advances we demonstrate that MRPI integrates well with proven concepts of MRI and offers great potential to characterize even heterogeneous porous structures by mapping the MRPI signal on MRI images. Furthermore, we discuss the experimental implementation of MRPI (based on a CPMG like pulse sequence) and the use of Phase Incremented Echo Train Acquisition (PIETA)<sup>4</sup> to study the various contributing coherence pathways to the MRPI signal.

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### O-20

#### IMAGING MICROSCOPIC ANISOTROPY AND ORDER PARAMETER USING DIFFUSION NMR WITH MAGIC-ANGLE SPINNING OF THE Q-VECTOR

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In diffusion tensor imaging, DTI, the fractional anisotropy, FA, is given by the eigenvalues of the diffusion tensor in each voxel. FA is influenced by the microscopic anisotropy of the structures inside the voxel as well as the relative order of the microscopic domains. FA maps of the brain can show the integrity of white brain matter as long as the axons are aligned. However, FA will decrease if the fibers are crossing even though the integrity of the axons is unchanged [1].

The microscopic anisotropy can be detected with the newly presented diffusion NMR sequence, *q*-MAS, where the *q*-vector is rotated at the magic angle, giving the mean diffusivity of the water, without the influence of the orientational order of the micro-domains [2]. In analogy with the FA parameter, the microscopic fractional anisotropy,  $\mu$ FA, can be quantified by using the *q*-MAS in combination with DTI. The  $\mu$ FA is obtained by quantifying the difference in variance between the probability distribution of diffusion coefficients from the DTI experiment and the *q*-MAS experiment relative to the mean diffusivity.

In liquid crystals, the order parameter, OP, is used to describe orientational order of molecules [3]. Here we use OP to describe the orientational order of the micro-domains inside the imaging voxel. For completely ordered micro-domains the OP would be 1, and for randomly ordered domains the OP would be 0.

In the FA maps obtained with the normal DTI, FA depends on both the  $\mu$ FA as well as on the OP of the micro-domains. Here we present a method to resolve and quantify these two contributions to the FA, and map them as individual parameters. We will show proof-of-principle experiments done on liquid crystals including time resolved experiments, which allow observing the parameter changes during equilibration of the liquid crystal.

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### O-21

#### SAMPLE, HARDWARE, AND SEQUENCE LIMITATIONS FOR PURE VELOCITY PFG MEASUREMENTS IN POROUS SYSTEMS

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The present work tackles the problem of using pulsed field gradient (PFG) experiments to measure pure velocity probability density functions in restricted flows. This need was recently expressed by the rheology community in order to study the penetration of non-Newtonian fluids in porous systems [1]. The question of how the strongly non-linear behaviour of shear-thinning and/or yield stress fluids impacts the macroscale relation between flow rate and pressure gradient is indeed strongly debated [2]. It is believed that a direct assessment of velocity fields in the pore space may bring valuable information in this matter.

Studies require low flow rates (few 10 $\mu$ m/s), and molecular diffusion is prone to result in an unacceptable blurring of velocity distributions. It is then important to know how such blurring can be or not avoided taking into account the various experimental conditions such as fluid properties (composition, diffusion coefficient, NMR relaxation times), flow rate, pore size, and hardware characteristics (raising time and maximal strength of the gradient system).

Taking as typical fluids a colloidal suspension with a continuous water phase, and a water-in-oil emulsion with disconnected droplets, we establish synthetic theoretical predictions on the influence of each of the various constraints on the optimized setting of sequence parameters and on measuring possibilities [3]. In particular, we show that for given working conditions, measurement feasibility and sequence tuning can be discussed in a graphical way.

Interestingly, optimised sequence for emulsion systems often deviate from the narrow pulse paradigm. We also get for a given fluid, flow rate and NMR hardware a quantitative estimate of the minimum pore size compatible with pure velocity assessment. Fluid composition turns out an essential parameter. On the contrary, limitations owing to available gradient strength are of concern for only very specific situations.

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### O-22

#### TRANSITION OF STAGE I TO STAGE II EVAPORATION REGIME IN THE TOPMOST SOIL: HIGH RESOLUTION NMR IMAGING, PROFILING AND NUMERICAL SIMULATION

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Since bare soils can be considered as a porous medium, evaporation from the surface to the atmospheric boundary layer mainly depends on the liquid continuity inside the soil. Below critical moisture liquid continuity to the surface (Stage I) ceases and water transport is mainly governed by vapor diffusion inside the medium through an increasing dry surface layer (Stage II). This surface layer constitutes an effective barrier for further evaporation and may have a considerable impact on water balance at the unvegetated earth surface. The aim of our study was to investigate moisture changes in the topmost soil layer during evaporation by means of NMR imaging and a unilateral NMR sensor for assessing its later usage for field measurements because quantitative imaging of moisture content in natural soils is challenging due to the inherent fast  $T_2$  times of clay/silt mixtures. An initially saturated column consisting of medium sand was exposed to evaporation under isothermal conditions over a period of 67 days. Moisture profiles were investigated at certain time points using a spin echo multi slice (SEMS) as well as a single point imaging sequence (SPI3D) for high field (4.7 T vertical bore). Additionally, the  $T_2$  distribution function over time was monitored using CPMG. In parallel, an open unilateral sensor was used to achieve moisture profiles via CPMG detection. Our results show a uniform decrease in moisture over a first period of 47 days until the onset of Stage II what could be monitored by SEMS, SPI as well as the unilateral NMR sensor. Thereafter, a dry surface layer developed and a heterogeneous drying front receded into the soil, coincided with the vanishing of the slowly decaying mode in the  $T_2$  relaxation time distribution functions ( $\approx$  200 ms). To assess our results we compared and cross-validated these observations against simulated moisture profiles using a coupled liquid, vapor and heat flow model, which exceeds the limitation of the conventional Richards' equation. Both, the measured profiles for Stage I and II and the onset of stage II are well predicted by the simulations.

### O-24

#### NMR SHIELDING OF HELIUM-3 IN THE MICROPORES OF ZEOLITES

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Recently the direct measurements of nuclear magnetic shielding were proposed for gaseous and liquid chemicals [1]. It was shown that experimental NMR studies can be simplified if the resonance frequency of a sample is monitored jointly with a deuterium lock system. In such a case there is no need to apply any additional reference of chemical shifts, or even use the chemical shifts, because the lock  $^2\text{H}$  NMR signal of deuterated solvent simultaneously serves as the reference standard of shielding. All the measurements of shielding for

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various magnetic nuclei are calibrated to the shielding of an isolated helium-3 atom [2]. As shown for hydrogen and its deuterium isotopomers [3] the above method delivers accurate values for nuclear magnetic shielding and permits one to study tiny effects of intermolecular interactions [4]. In the present work we have applied the measurements of <sup>3</sup>He shielding in order to observe helium-3 gas in the micropores of Linde type zeolites KA, NaA and CaA under pressure up to 300 bar. We have observed distinct effects of molecular interactions between helium gas and zeolite powders but these effects are mostly due to the change of bulk susceptibility and therefore they are much weaker than suggested before [5]. On the other hand we can confirm that the use of helium-3 as a probe is promising because it allows one to study the smallest micropores in zeolites and the measurements of magnetic shielding provide more precise results than NMR chemical shifts.

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### O-25

#### INVESTIGATION OF MOLECULAR MOTION OF CO<sub>2</sub> IN THE MOF Zn<sub>2</sub>(BDC)<sub>2</sub>(DABCO) BY <sup>13</sup>C NMR AND MD

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Zn<sub>2</sub>(bdc)<sub>2</sub>(dabco) is crystalline metal-organic framework (MOF) [1], in which Zn metal centers are interconnected via organic linkers forming a three dimensional microporous network. The pore structure consists of parallel one-dimensional channels interconnected by small windows. The windows which an adsorbed molecule has to pass when diffusing in channel direction are formed by 4 bdc linkers, the smaller windows perpendicular to the channel direction are formed by 2 bdc and 2 dabco linkers. The material shows ability to quickly adsorb CO<sub>2</sub>.

NMR spectroscopy using <sup>13</sup>C enriched CO<sub>2</sub> showed significant anisotropic broadening of the resonance line which is caused by chemical shift anisotropy. This effect is caused by host-guest interaction between the MOF lattice and the adsorbed CO<sub>2</sub>. It was observed previously for liquids or gases confined in other microporous materials [2, 3]. The measured width of the adsorbed CO<sub>2</sub> resonance in Zn<sub>2</sub>(bdc)<sub>2</sub>(dabco) is about 50 ppm at room temperature and, therefore, significantly smaller than in solid CO<sub>2</sub> (330 ppm). This already indicates a residual mobility in the adsorbed phase. Molecular Dynamics simulation show anisotropic motion within the channels.

The CO<sub>2</sub> interacting with the adsorption sites is preferentially oriented in channel direction. This is the origin for the residual chemical shift anisotropy.

However, the observed lineshape deviates from Pake-pattern. Obviously, there is a second type of motion on microsecond timescale which leads to modulations of the CO<sub>2</sub> preferential orientation expected from MD simulation in the crystal structure. Diffusion measurements by <sup>13</sup>C PFG NMR showed a high mobility in the order of 10<sup>-9</sup> m<sup>2</sup> s<sup>-1</sup>. The corresponding displacements to the motion are in the order of a few microns. Thus, our interpretation of the observed deviation from Pake-pattern is exchange between channels with different orientations.

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### O-26

#### NMR RELAXOMETRY OF METAL-ORGANIC FRAMEWORKS FOR SURFACE AREA SCREENING

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Metal-organic frameworks are porous crystalline solids consisting of networks of metal clusters or ions connected by organic linkers through coordination bonds. The effectively infinite number of metal-ligand combinations and the modular nature of framework synthesis make high-throughput synthesis an effective optimization tool, but subsequent characterization of frameworks presents a bottleneck to this workflow. Herein, we describe a robust screening technique which correlates the surface area of metal-organic frameworks to the T<sub>2</sub> relaxation behavior of imbibed solvent at low field (13 MHz).

Samples of solvent-imbibed metal-organic frameworks can be approximated as having two pore size regimes: nanometer-sized pores belonging to the inherent structure of the framework (pore-confined) and micron-sized voids between the individual crystallites (inter-particle). In small-pore (<1 nm) frameworks, exchange between these two populations remains slow compared to the T<sub>2</sub> of the pore-confined solvent, which allows for a direct porosity analysis of the T<sub>2</sub> spectrum obtained from Laplace inversions[1]. Increasing the framework pore-size (>1 nm) leads to corresponding increases in exchange rate and the T<sub>2</sub> of confined solvent, as confirmed by T<sub>2</sub> relaxation exchange (REXSY) experiments[2]. Since comparable rates of relaxation and exchange preclude the direct analysis of Laplace inversions, two- and three-site kinetic models were applied to extract porosity from relaxation decays, improving the accuracy and utility of the screening technique.

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### O-27

#### DIESEL PARTICULATE FILTERS: INVESTIGATING THEIR MANUFACTURE AND OPERATION USING MAGNETIC RESONANCE TECHNIQUES

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Diesel particulate filters (DPF) are an important and relatively new addition to the armoury of devices available to treat internal combustion engine exhaust emissions [1]. The traditional role of the DPF is to remove harmful particulate matter (PM) from diesel exhausts. However, their application is now being widened by the addition of catalysts to address other important pollutants in the exhaust, and to gasoline exhaust emissions. When designing and manufacturing a catalysed DPF (CDPF) it is essential that the catalyst is applied to the porous ceramic (cordierite, silicon carbide, aluminium titanate) DPF substrate in such a way that the gas flow and low back pressure characteristics of the filter are maintained, while the catalytic function is also at an optimum. To achieve this on an industrial scale requires an in depth understanding of the manufacturing process. Here we show how nuclear magnetic resonance techniques can be used to shed light on a range of phenomenon in the manufacture and operation of DPFs and CDPFs.

Initially we show how NMR can be used to study the drying process, which is one of the final stages in the manufacturing process. Non-ideal drying can result in the macroscopic redistribution of the catalyst resulting in a non-optimised catalyst [2], and drying is also an extremely energy intensive process. Therefore a better understanding of the drying mechanism is required for optimal drying cycles to be designed. A range of magnetic resonance techniques have been used to investigate the drying process for CDPFs: MRI has been used to provide spatially resolved measurements of the moisture content on the scale of the monolith as a whole, and NMR relaxometry to provide information on the microscale.

In the second part we will present the use of MR velocimetry to visualise and understand the hydrodynamics of the exhaust gas in the operation of a DPF. This information can eventually be used to enable the design of improved DPF systems.

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### O-28

#### IMPLEMENTATION OF ULTRA-SHORT ECHO TIME MAGNETIC RESONANCE IMAGING IN SHORT $T_2$ AND $T_2^*$ SYSTEMS

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Porous media are often difficult to image due to the many interfaces between the solid matrix and fluid in the pore space giving rise to strong internal gradients, hence short  $T_2^*$  (<1 ms). Further, porous materials such as rubber, catalyst support, and wood have short  $T_2$  relaxation times as well (~1 ms). Ultrashort echo time (UTE) imaging has been used previously to observe short  $T_2^*$  samples in medical imaging<sup>1</sup> and in this work UTE imaging will be introduced in conjunction with compressed sensing (CS) to enable imaging of porous material with a reduced acquisition time.

UTE imaging in the medical field is typically used to image materials such as cartilage and cortical bone.<sup>2</sup> UTE uses a half-Gaussian pulse for slice excitation in which the slice gradient and rf excitation are switched off together. Images are then acquired using a radial acquisition. Two excitations are required for each line in k-space to ensure accurate slice selection. UTE permits a reduction in echo time down to the order of 10  $\mu$ s.

The principle of UTE is simple, however limitations of slew rate on the gradients mean that the gradients cannot switch off instantaneously. Instead, Variable Rate Selective Excitation (VERSE) is used to ramp the gradient and rf pulse off simultaneously.<sup>3</sup> The timing and power of both the rf and gradient used for slice selection must be carefully balanced.<sup>4</sup> In this work, we describe the implementation of UTE in detail including measurements of the gradient and rf pulses to maximize the accuracy of the slice selection. Further, we use CS to reduce the number of radial spokes, and hence reduce the total acquisition time. We demonstrate the advantages of UTE by imaging a range of samples including rubber and cork.

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### O-29

#### INVESTIGATIONS OF CTAB REVERSE MICELLES USING DIFFUSION NMR AND MOLECULAR DYNAMICS

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Reverse micelles (RMs), formed in water-in-oil microemulsions, consist of a layer of surfactant molecules that surround a water droplet in an organic continuous phase. RMs have a broad range of applications, such as the formation of nanoparticles<sup>1</sup>, drug delivery carriers<sup>2</sup> and reactors for chemical and enzymatic reactions<sup>3</sup> and consequently, there is significant interest in their microstructure, size and chemical properties.

We are interested in RMs formed with cetyltrimethylammonium

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bromide (CTAB), these require a co-surfactant which provides an additional parameter by which the size, shape and interface rigidity of the RM can be controlled<sup>1</sup>. CTAB is of interest as a surfactant because the headgroup provides a good model for the lipid phosphatidylcholine<sup>4</sup> found in cell membranes.

NMR measurements of diffusion have been employed on the CTAB/hexane/pentanol/water system to characterise the microstructure and determine the role of the co-surfactant, pentanol, in RM formation. At short diffusion times, the pentanol has two diffusion coefficients for pentanol in the interface and in the continuous phase. Exchange was investigated as a function of diffusion time, and the proportion of pentanol in the two phases can be determined. This exchange of pentanol is well known<sup>5</sup>, however exchange of the surfactant, CTAB, is observed which has not previously been reported.

The distribution of pentanol and its exchange behaviour between interface and continuous phase was further investigated using molecular dynamic (MD) simulations. These MD simulations, supplement the experimental findings by providing information on the shape, which shows the reverse micelle has an oblate shape, rather than the previously assumed spherical.

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### O-30

#### TOWARDS ONLINE ANALYSIS OF SUBSEA PROCESS STREAMS USING LOW-FIELD NMR

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Sub-sea separation (the remote splitting of oilfield product fluid phases (oil, water, condensate, gas) in sub-sea production systems) has the potential to unlock significant hydrocarbon resources offshore, but this potential is limited by the available remote metrology systems for measuring both the multiphase flow entering the separation process and the quality of the separated phases, specifically the discharge water. Here we begin to explore the use of low field bench-top NMR to measure such quantities. In terms of multi-phase flow metering, we present preliminary results featuring remote detection of a turbulent flow stream using the Earth's magnetic field and a mobile upstream permanent magnet. The consequential data (NMR signal intensity as a function of separation distance) is well described by an appropriate model as a range of flow-rates featuring no free parameters. In terms of the use of low-field NMR to determine the oil contamination of discharge water, we compare with current established technology (i.e. IR spectrometry). Using a commercially sensitive process featuring solid phase adsorbents and solvent extraction we are

able to reliably detect below 20 ppm (oil contamination) using a 1T permanent Halbach magnet (Magritek). An automated process has been developed and is critical to the success of any such measurement protocols.

### O-32

#### DRYING AND FILM FORMATION IN POLYMER DISPERSIONS - NOVEL INSIGHTS FROM PARALLEL PROFILE NMR AND GRAVIMETRIC EXPERIMENTS

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Drying and film formation of polymer dispersions is an essential process for optimal performance of water-based paints and coatings. Over the last decades, a wide range of experimental techniques as well as theoretical tools were applied to the study of film formation (for a review see [1]). In recent years, a range of studies using STRAFI or profiling NMR for the study of film formation have been published [2].

Many of the available experimental studies on film formation are single-techniques studies. Furthermore, it is often difficult to compare drying conditions in different experimental setups. We have recently set up a parallel system consisting of a computerized analytical balance and a profile NMR setup equipped with identical drying chambers [3]. The analysis of gravimetric and NMR data indicates a strongly non-linear relationship between NMR signal and water content in the film that can only be described under the assumption of a strong change in the water relaxation mechanism occurring during the drying process.

This change in relaxation times can be explained by an immobilization of the initially rotating polymer particles that occurs at a critical packing density of the polymer particles. Comparing the critical water contents observed in polymer dispersions with and without added film-formation agents, the inhibition of particle rotation in dispersions with film formation agents occurs at higher water contents which is in good agreement with the expected plastification and swelling of the polymer particles in presence of the film formation agent.

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### O-33

#### COMPACT NMR SPETROSCOPY

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The first chemical-shift resolved NMR spectrum has been measured in 1951 at Varian from ethanol with a 0.76 T electromagnet at 0.1 ppm resolution [1]. Today NMR spectra are measured routinely at 31 times higher field (23.5 T) with an accordingly wider frequency range for the chemical shift and about 1000 times higher sensitivity. Why then would <sup>1</sup>H NMR at fields as low as 1 T be of interest? The lecture tries

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to answer this question with several examples from materials and chemical analysis with permanent magnets, whose field strength is effectively limited to values below 2 T. The examples include nondestructive testing, reaction monitoring in real time and chemical analysis for quality control [2,3]. While the trend to smaller and more powerful NMR analyzers is documented with the recent advent of desktop spectrometers, it is left to speculation how small NMR spectrometers may become and what use they may have [4,5].

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### O-34

#### DXT<sub>2</sub> CORRELATION USING THE INHOMOGENEITY OF SINGLE SIDED NMR DEVICES

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Single sided NMR devices have become a very powerful tool in order to perform low field NMR diffusion and relaxation analysis. These analysis are very useful in the industry environment when evaluating the quality and quantity of Hydrogen based materials, besides distinguishing the content proportions of different phases in the samples. Several techniques have been developed over the last decade in order to take advantage of the characteristics of these devices, increasing their applicability to many different fields<sup>1-4</sup>.

In order to determine diffusion coefficients of fluids in different environments, this work uses a pulse sequence combining spin echo and CPMG experiments (SGSE-CPMG)<sup>5</sup>, where the first echo time is varied in each subsequent measurement to record two-dimensional data sets. Furthermore, three different strategies to process the 2D signal decay are discussed, each of which having its own advantages and niche of application. In particular, special care has been taken to correct for the influence of  $T_2$  in the first echo, separating it from the signal decay due to diffusion.

This technique can be used to determine the proportional content of fluid mixtures as well as explore fluid diffusion in porous host systems using single sided NMR devices. The experiments were performed using the Kea2 spectrometer<sup>6</sup> and the Mobile Lateral Explorer (MOLE)<sup>7</sup>.

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### O-36

#### EMULSION CHARACTERIZATION USING LOW FIELD NMR

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Emulsions are dispersed multiphase systems, where one liquid is dispersed in another liquid in the form of droplets with radii of the order of micrometres. Most emulsions are thermodynamically unstable and will separate into their constituent phases given sufficient time. As they have a significant industrial importance (food, agriculture, oil and gas), the properties of an emulsion need to be well understood. The droplet size distribution is the main characteristic of such systems, which will give insight to other relevant functionalities (e.g., viscosity, stability, and turbidity). Hence an ability to experimentally determine this size distribution is essential [1, 2].

Application of NMR techniques for emulsion characterization has provided many unique and valuable insights. Here we present recent developments using bench-top low field NMR applied to sizing of water-in-crude oil emulsions. Using different bench-top NMR equipment and a combination of NMR relaxometry, diffusion and spectroscopy we will report on the following developments:

Automation of emulsion droplet sizing and its use to probe various emulsion breaking strategies.

The impact of flow on the emulsion droplet sizing and the extraction of quantitative dispersion data to characterise enhanced emulsion droplet collisions under flow.

The use of emulsion droplet sizing to quantify the microstructural changes that occur following the transition of the droplets into cyclopentane hydrate particles.

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### O-37

#### UNDERSTANDING TRANSPORT FROM MOLECULAR TO MICRON SCALES IN NANOPOROUS POLYMER MEMBRANES

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Nanoporous polymer membranes conduct mobile species (ions, water, alcohols, gases) according to a hierarchy of structural morphologies that span sub-nm to ~ 10 micron in length scale. In order to comprehensively understand such materials, our group combines multiple types of NMR dynamics and transport measurements (spectroscopy, diffusometry, relaxometry, imaging) with structural information from scattering and microscopy as well as with theories of porous media, electrolytic transport, and oriented matter. Using this correlated knowledge and novel NMR strategies, we seek to give informed feedback on the design of polymer membranes used in efficient water purification, batteries, fuel cells, and myriad liquid and gas separations.

In this presentation, we will discuss relations between multi-scale polymer alignment (<sup>2</sup>H and <sup>23</sup>Na spectroscopy), local dynamics and structural heterogeneity ( $T_1$  and  $T_2$ ), and transport (PFG) in nanoporous polymers.<sup>1</sup> We have also investigated the sub-nm-scale intermolecular interactions that influence transport by exploring the quantitative physical meaning of PFG-NMR activation energy measurements and applying this to polymer electrolyte membranes (PEMs)<sup>2</sup> We will focus on recent studies that allow quantitative separation of the two major effects that govern transport in polymer membranes: 1) local intermolecular energetics<sup>2</sup> and 2) polymer morphology<sup>1,3</sup> (e.g., tortuosity, and dimensions and symmetries of local channel networks) on 1 nm - 10 micron scales. We will discuss such morphology-transport correlations in two polymer membrane systems – the archetypal PEM Nafion,<sup>1,2</sup> and blend membranes composed of a polyelectrolyte and a neutral fluoropolymer.<sup>3</sup> These combined dynamical, structural, and transport studies allow for unprecedented understanding of soft matter systems and provide critical information toward advanced membrane design.

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### O-38

#### NMR OF NATURAL GAS IN NANO-POROUS MEDIA

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The understanding of the adsorption-desorption of natural gas in nano-porous media is vital for unraveling the dynamics of natural gas in unconventional shale reservoirs. As more than 50% of the natural gas in shale could be in adsorbed form, methods to enhance its release are vital for production. In this presentation we provide a fundamental understanding of gas dynamics in nano-porous media using high field NMR spectroscopy and relaxometry techniques. This is enabled by the construction of a high pressure laboratory setup capable of pressurizing methane gas to over 20 Kpsi inside a 9T NMR magnet. We show how high field NMR can provide a direct measure of the Gas in Place (GiP) at downhole conditions,

resulting in direct deliverable for petrophysical evaluations. By performing experiments as a function of pressure we demonstrate how Gibbs excess isotherms for both adsorption and desorption can be constructed for methane gas in the porous Vycor glass, enabling the total GiP to be converted into free and adsorbed gas fractions. Furthermore, these experiments provide the hydrogen index or the net density of the gas in the pore space which is vital for petrophysics. We also show how high field NMR spectroscopy can help aid this analysis by identifying the different gas species in the porous media.

Methane gas in nano-porous material also provides an ideal test-bed for revealing the intricacies of the different Inverse Laplace based multidimensional NMR methods invented in the last decade. This is because the relaxation Hamiltonian is dominated by spin rotation for the bulk gas and dipolar interactions for the confined gas. The resultant long spin lattice relaxation times, combined with short and separable spin-spin relaxation times in addition to the high diffusion coefficients provide the ideal conditions for 2D relaxation exchange spectroscopic methods like  $T_2$ - $T_2$  and  $T_1\rho$ - $T_2$ . Furthermore using pressure as an additional control we show how different relaxation and diffusion modes can be excited in these experiments. Finally, we discuss the methodology that needs to be adopted to make these experiments successful in gas shales where susceptibility effects hinder separation of free gas from those in organic nanopores.

### O-40

#### PARAHYDROGEN ENHANCED NMR STUDIES OF HYDROGENATION REACTION DYNAMICS ON OXIDE-SUPPORTED IR NANOPARTICLES

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Parahydrogen induced polarization (PHIP) is an NMR sensitivity enhancement scheme which utilizes chemical hydrogenation to derive observable nuclear spin hyperpolarization from the pure singlet spin order of parahydrogen [1,2]. In the decades following the 1987 discovery of PHIP using Wilkinson's catalyst it was believed that supported metals would be ineffective as PHIP catalysts, despite their high activity for alkene hydrogenation. According to the widely accepted Horvut-Polanyi mechanism, dihydrogen is activated by chemisorption as H atoms. It was thought that spin-correlation of para-H<sub>2</sub> would be lost on the surface due to rapid H-atom diffusion. Nevertheless, PHIP has been observed using several types of oxide-supported metal nanoparticles [3]. In addition to potential biomolecular imaging applications, PHIP provides a unique probe of hydrogenation catalysis because of its selectivity to the pair-wise dihydrogen addition pathway.

Here we describe a specialized hydrogenation reactor for PHIP experiments with gas/solid heterogeneous catalysts. The flow reactor operates in a temperature-controlled furnace installed in the fringe field of a 9.4 T NMR magnet. Mass flow controllers regulate mixing and flow of reactants (para-H<sub>2</sub> or normal-H<sub>2</sub> and the alkene substrate). Hyperpolarized alkane

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products are delivered from the reactor to the NMR probe via PFA tubing. Key advantages of our reactor design include superior temperature control and thermometry, access to higher temperatures (important for catalyst activation), and attainment of ALTADENA conditions. The net alignment of product multiplets resulting from hydrogenation at low field avoids the destructive interference inherent to product formation in the PASADENA regime at high field. We focus on results obtained with Ir nanoparticles supported on various oxides. By comparing the NMR spectra obtained using normal-H<sub>2</sub> and para-H<sub>2</sub>, contributions from random or pairwise addition can be isolated and the corresponding reaction orders and activation energies for each process may be deduced.

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### O-41

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A microwave resonator with 2 GHz (S-Band) resonance frequency was designed, simulated and constructed for Dynamic Nuclear Polarization (DNP) experiments at 73mT. The device is based on the Alderman-Grant resonator [1], is compatible with 3mm NMR tubes and can be used with transverse and axial magnets with a minimum bore diameter of 20mm. The structure provides good separation of the microwave electric and magnetic fields, allowing for comparatively large sample volumes with only small dielectric heating effects.

Experiments are shown, investigating the electron spin saturation efficiency and sample heating effects. A first application is demonstrated, combining the S-Band DNP setup with a commercial Fast Field Cycling relaxometer. DNP-enhanced <sup>1</sup>H and <sup>13</sup>C fast-field-cycling relaxation dispersion measurements are demonstrated. Furthermore, DNP measurements at 10 GHz for polymer melts with BDPA radical and preliminary DNP experiments with crude oil samples are shown.

The results show that the Alderman-Grant resonator design is suitable for DNP experiments at S-Band microwave frequencies and, being scalable in size and resonance frequency, represents a versatile approach towards DNP-enhanced measurements for a range of NMR experiments at low and moderate magnetic fields. Applications of DNP for samples with various dynamic timescales are envisaged.

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### O-42

### HYPERPOLARIZATION OF NUCLEAR SPINS IN HETEROGENEOUS HYDROGENATIONS AND BEYOND

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Applications of magnetic resonance to porous media often suffer from insufficient sensitivity, particularly the MRI studies and studies addressing gases in the pores or molecules and processes on the surface of pore space. This can be overcome through the development of hyperpolarization techniques including parahydrogen-induced polarization (PHIP). Our recent studies successfully demonstrated that PHIP effects are observable in heterogeneous hydrogenation reactions catalyzed by various solid catalysts [1]. This development provides new possibilities including the production of catalyst-free hyperpolarized liquids, access to a much broader range of hyperpolarized gases, the possibility to produce hyperpolarized fluids in a continuous (as opposed to batch) mode, and the use of PHIP as a hypersensitive technique for the mechanistic studies of a number of industrially important catalytic reactions which require molecular hydrogen.

At the same time, the hyperpolarization techniques have significant limitations as well. In particular, the lifetime of hyperpolarization is limited once it is produced. As demonstrated recently, this can be remedied through the use of the so-called long-lived spin states. Another problem specific to PHIP in heterogeneous hydrogenations catalyzed by metals is the dissociative chemisorption of parahydrogen on metal surfaces which limits the observed signal enhancements. The use of nuclear spin isomers of molecules other than H<sub>2</sub> can potentially provide practical solutions to these problems. We have designed and experimentally demonstrated an approach which utilizes chemical synthesis for the enrichment of nuclear spin isomers of ethylene in the gas phase [2]. The degree of enrichment and the quantities of enriched ethylene produced are sufficient for the use of these long-lived spin states for signal enhancement in NMR and MRI. All these developments will be demonstrated with practical examples.

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### O-43

### VARIABLE-ANGLE SPINNING OF THE Q-VECTOR IN DIFFUSION MRI

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A wide range of porous materials, from lyotropic liquid crystals to brain tissue, contain anisotropic pores with varying sizes, eccentricities, and degrees of alignment on mesoscopic length scales. A complete characterization of the material requires estimation of all these parameters, but unfortunately their effects on the detected MRI signal are hopelessly entangled when using standard diffusion MRI methods. Building on the formal analogy between the chemical shift and diffusion

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anisotropy tensors, we have recently shown that solid-state NMR techniques, such as magic-angle spinning, can be fruitfully adapted to diffusion MRI [1]. In its simplest form, magic-angle spinning of the  $q$ -vector allows for estimation of the distribution of isotropic diffusivities free from the confounding influence of anisotropy. Drawing inspiration from variable-angle [2] and switched-angle [3] spinning in solid-state NMR, we here propose the corresponding diffusion MRI methods for separating and correlating the isotropic and anisotropic diffusion components. Intuitively, one would like to convert the acquired data to a multi-dimensional distribution of apparent diffusivities using a general inverse Laplace transform algorithm [4], and subsequently extract the desired microstructural parameters by inspection of the resulting distribution. Regrettably, this general data inversion approach is extremely sensitive to experimental noise and the details of how the distribution is regularized, thus rendering the results too ambiguous to be practically useful. Consequently, we instead design data acquisition protocols where pre-defined hypotheses about the sample microstructure can be tested directly in the acquisition domain. Proof-of-principle experiments are carried out on colloidal model systems that can be conveniently tailored to give the desired diffusion properties. By using numerically optimized gradient waveforms giving sufficient diffusion-weighting even on hardware with limited gradient capabilities [5], we pave the way for future implementation within the context of clinical MRI.

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### O-44

#### **DISTINGUISHING EFFECTS FROM FLUID TYPE, PORE SIZE AND MORE IN HETEROGENEOUS SAMPLES: THE DIFFUSION TIME CORRELATION EXPERIMENT**

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Diffusion measurements are a key tool in low field NMR to determine pore size [1], and fluid composition [2]. However, distinguishing their respective contributions from traditional measurements of diffusion spectra is not always possible without prior knowledge of the saturating fluid, given heterogeneities in the pore geometry and fluid composition. I will discuss how these and other effects can be unambiguously distinguished with correlated diffusion measurements (d-PFG) with novel sampling and analysis schemes.

In particular, I will detail the diffusion time correlation experiment (DTC), which utilizes the time dependence unique to restricted diffusion to unambiguously differentiate effects from fluid composition and pore size. The DTC experiment exploits the interaction of the first and second PFG encoding gradient at small mixing times to correlate diffusion over two different lengths of time. Unrestricted diffusion is then unambiguously identified as an off diagonal signal. This approach is in contrast to prior diffusion correlation techniques [3]: instead of viewing

the d-PFG as two successive s-PFG encodings it takes the symmetric and anti-symmetric gradient waveforms as the principle encoding vectors for a new perspective and method for the traditional d-PFG experiment.

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### O-45

#### **HALF A DOZEN WAYS TO COMPUTE RESTRICTED DIFFUSION PROPAGATORS: ARE SOME BETTER THAN OTHERS?**

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Restricted diffusion is a well-established tool for NMR structural characterisation of sedimentary rocks, biological tissues and other multicompartments systems [1, 2]. Their morphology can be inferred from NMR diffusion-diffraction plots or the time-dependence of the apparent diffusion coefficient. These provide, respectively, the characteristic pore size and the degree of obstruction to diffusion presented by walls or cell membranes. Diffusion NMR signal attenuation can be computed from the restricted diffusion propagator, which describes the distribution of diffusing particles for a given starting position and diffusion time.

We present two novel techniques for efficient evaluation of restricted diffusion propagators for use in NMR porous-media characterisation. The first is the Lattice Path Count (LPC) [3]. Its physical essence is that the restricted diffusion propagator connecting points A and B in time  $t$  is proportional to the number of distinct length- $t$  paths from A to B. By using a discrete lattice, the number of such paths can be counted exactly. The use of arbitrary-length integers enables implementation of LPC for large lattices.

The second technique is the Markov transition matrix (MTM) [4]. The matrix represents the probabilities of jumps between every pair of lattice nodes within a single timestep. The propagator for an arbitrary diffusion time can be calculated as the appropriate matrix power. For periodic geometries, the transition matrix needs to be defined only for a single unit cell. This makes the physical size of the system amenable to simulation is almost unlimited, rendering MTM ideally suited for periodic systems.

LPC and MTM perform favourably compared to Monte Carlo sampling, yielding highly accurate and almost noiseless restricted diffusion propagators. Both new methods are applicable to complicated pore-space geometries with no analytic solution. We discuss the new methods in the context of NMR techniques for characterisation of materials and tissues.

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## Oral Contribution Abstracts

O-46

### NMR DIFFUSOMETRY THROUGH THE EYE OF ELECTROSTATICS

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Given a system of freely diffusing particles, the Echo decay retrieved by a diffusion NMR experiment is linear on a logarithmic scale. If the diffusing particles are confined to a restricted geometry the Echo decay will no longer be linear. An interesting question has been to figure out what geometrical information can be retrieved from this deviation of the Echo decay (see e.g. [1]). Today several models are used to describe a non-linear Echo decay: Multi-exponential models, the stretched exponential model, and power expansion of the Gaussian model [2], to mention a few. It has however been difficult to evaluate the validity of these different models with respect to the geometrical impact (see e.g. [3]).

It has recently been shown that there exists an intimate relationship between the theory of Electrostatics and the theory of Diffusion [4-6]. Quite surprisingly, this relationship reflect precisely how the Echo Decay, is affected by a confining geometry. In this talk we will explore this relationship between Electrostatics, Diffusion and NMR and show how this gives a new interpretation of NMR Diffusometry in terms of an influence from the surrounding geometry. We will demonstrate the strength of this approach by evaluating the use of the different models mentioned above. The talk will be accompanied by exemplary geometries and different experimental setups.

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O-47

### PARAMAGNETIC MECHANISM OF NMR RELAXATION OF FLUIDS IN SILICATES

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In the fast diffusion limit, in which  $1/T_{1,2} = 1/T_{1,2,b} + \rho_{1,2}S/V$ , where  $T_{1,2}$  is the longitudinal or the transverse relaxation time of the fluid,  $S$  – pore surface area,  $V$  – pore volume and  $\rho_{1,2}$  –longitudinal and transverse relaxivities, the rapid relaxation of the fluid is thought to be the result of the influence of paramagnetic centers on the surface of the pore [1]. In such porous media as glass beads paramagnetism is present in the form of bulk iron impurities [2] and surface radicals [3].

Homogenous glass beads with diameters ranging from 57

µm up to 436 µm, and quartz sand filled with water and hydrocarbons have been studied by NMR, EPR and an electron microscope.

In both porous media the ratio  $T_1/T_2$  has been found to be equal to 1 for water and near 20 for hydrocarbons. The element analysis of the glass beads has shown no paramagnetic admixtures on their surface. Each of the EPR spectra of the glass beads contains a  $Fe^{3+}$  admixtures peak in 158 G ( $g = 4.24$ , constant intensity) [2] and an oxygen-associated hole centers peak in 3364.5 G ( $g = 1.999$ , variable intensity) [3]. Since the intensity of the latter peak increases with decreasing pore size, the peak can be attributed to the glass structure irregularities ( $\equiv Si\cdot$ ,  $\equiv SiO\cdot$ ,  $\equiv SiOO\cdot$ ) at the pore surface. It has been shown that the molar ratio of Fe to  $SiO_2$  is  $10^{-4}$ , and 1 – 10 % of the  $SiO_2$  surface molecules exhibit paramagnetism. To conclude, the surface relaxation in silicates is explained by the glass surface defects, rather than iron admixtures.

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O-48

### GAS-GAS ( $CO_2$ - $CH_4$ ) DISPERSION MEASUREMENTS USING LOW-FIELD MRI

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Enhanced gas recovery (EGR) is an emerging technology where  $CO_2$  is injected into natural gas reservoirs as a means of maintaining the pressure of the reservoir and to enhance the natural gas recovery, with the additional benefit of  $CO_2$  sequestration within the reservoir. It is essential for reservoir models to be developed that have accurate values for the Dispersion Coefficient of supercritical  $CO_2$  into  $CH_4$  within the reservoir rock as  $CO_2$  is a significant asset contaminant. Research is currently being done to measure this important Dispersion parameter within rock cores (both sandstone and carbonates) using core-flooding systems and infrared spectroscopy (IR) to obtain breakthrough curves [1, 2]. Erroneous entrance and exit effects using these non-spatially resolved techniques can be significant (on the order of 25% of the total dispersivity). Using spatially resolved breakthrough curves using time resolved 1D MRI profiles, we can avoid the end effects and obtain a more accurate value for the Dispersion Coefficient within the porous media. We demonstrate this result using a model porous medium (mono-dispersed glass beads) in a PEEK cell capable of holding high gas pressures (up to 80 bar) in a 12.9 MHz NMR rock core analyser (Oxford Instruments) and compare the results with IR measurements on the outlet stream (breakthrough curve) during the same experiments. We consequently are able to quantify the erroneous contribution of mixing due to entry and exit effects.

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accepted.

### O-49

#### OVERCOMING NEW CHALLENGES OF NMR SHALE CHARACTERISATION

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Increased worldwide energy demand and declining conventional petroleum resource discoveries has led to increased attention to hydrocarbons located in shale resources. NMR relaxometry has great interest for shale characterization as traditional core analysis methods often fail because the small pores sizes and low permeability of shales hinders flow. NMR does not suffer similar difficulties because it is non-invasive, however, analysis of the results is significantly more complicated than for conventional reservoirs. Several of the new challenges to interpretation of relaxometry measurements that have not been recognised by the industry are presented. Unlike conventional sandstones and carbonates, shales may contain substantial quantities of organic matter and clays. These can contain considerable amounts of hydrogen in solid or semi-solid form, which may be measured in addition to the fluid-filled porosity by the standard low field relaxometry methods used by the petroleum industry. Relaxation mechanisms in conventional reservoirs tend to be dominated by paramagnetic impurities whereas homonuclear dipolar coupling appears to be the main mechanism in organic matter, making the results highly temperature dependent. Spin diffusion measurements indicate there is significant exchange of magnetization between mobile and immobile phases in shale samples.

To overcome these challenges, new pulse sequences must be developed beyond the basic  $T_1$  and  $T_2$  relaxation measurements commonly used by the petroleum industry. The low permeability and small pores sizes in shales confounds diffusion methods for constituent determination. Instead,  $T_1$ - $T_2$  correlations have been applied to attempt identification. To aid in constituent determination, we present a new pulse sequence, the  $T_1$ - $T_2$  solid echo correlation. The solid echo will refocus dephasing from homonuclear dipolar coupling where the standard spin echo method will not. Both  $T_1$ - $T_2$  methods were applied to oil shales over a range of thermal maturities. The solid echo method produced more stable results between samples. Comparison between the spin and solid echo results enabled identification of kerogen, bitumen and mineral water. Multivariate analysis correlation of the NMR results with FTIR helped confirm the interpretation of the  $T_1$ - $T_2$  solid echo correlation results.

### O-50

#### NON-NEWTONIAN FLUID DYNAMICS IN POROUS MEDIA

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Complex fluids under deformation can exhibit both space and time dependencies, and in combination with the multiple length

scales inherent to porous media, fluid flow behavior is difficult to predict. Nuclear Magnetic Resonance (NMR) Microscopy techniques provide a unique and diverse perspective. Imaging provides micron scale spatial resolution in complex geometries, while time and length scale displacements can be probed using Pulsed Gradient Spin Echo (PGSE) NMR techniques. In this work, PGSE NMR and NMR imaging were used to investigate the dynamics of non-Newtonian fluid flow in porous media, in particular, the flow of micelle solutions. Transport dynamics for a micellar solution of cetyl trimethylammonium p-toluenesulfonate (CTAT) in a model porous media were altered relative to water due to the shear-thickening material properties of the micellar solution. Surfactant systems that self-assemble into micelles are being developed as fracturing fluids due to their viscoelastic fluid properties, making this research relevant to the petroleum industry with the potential to aid advances in hydraulic fracturing techniques.

### O-52

#### HIGH-THROUGHPUT NMR SYSTEM FOR SCREENING OF HAPLOID KERNELS OF MAIZE (CORN)

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One of the modern crop breeding techniques uses doubled haploid plants that contain an identical pair of chromosomes to accelerate the breeding process [1,2]. Rapid haploid identification method is critical for large-scale selection. For example, one of the conventional methods relies on the color of the endosperm and embryo seeds. However, the colors may be affected by donor genotypes and environment. On the other hand, there exists a significant difference between hybrid and haploid seeds generated by high oil inducer, which makes it possible to use oil content inside the kernels to identify the haploid [3].

A high-throughput NMR screening system for maize haploid kernel identification based on oil content is developed to meet the demand of large-scale application of maize haploid breeding and research. The system is comprised of three electronic-mechanical subsystems: 1) Sampler and feeder before the NMR unit, it selects a single kernel, weighs and feeds it into the NMR unit. 2) NMR unit with sample holder to perform NMR, 3) kernel sorter - after the NMR measurement, and the seed is sorted according to the NMR result.

Since the oil T2 in maize is long, CPMG sequence is used to quantify oil content by the signal of an echo time (7.5ms) at a Larmor frequency of 22 MHz. Typically four scans are averaged. The results show that the accuracy of this screening system reaches 92.3% with an average time of screening of 4 seconds per kernel. The automatic screening system can be used in practical application in rapid selection of maize haploid seeds and can also be used to separate the samples of different oil contents.

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### O-53

#### WATER CONTENT AND WATER PHASE TRANSITIONS IN BLACK SPRUCE WOOD MATERIALS

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Wood is a hygroscopic and anisotropic material whose properties are deeply influenced by the presence of water. Wood is also a building material of considerable economic importance to Canada and many other countries around the world. Water exists in wood materials in bound and free water environments. The maximum bound water in the cell walls is termed the fibre saturation point which occurs at around 30% moisture content in most wood materials.

In this work we estimate the bound and free water content of black spruce wood materials by MR lifetime measurements, and by measurements of signal intensity as a function of temperature. The water phase transition for free water is approximately -3 °C in these samples, while the bound water phase transition is approximately -60 °C. Bulk measurements with a desktop instrument, MRI measurements with a superconducting magnet and unilateral magnet measurements are all employed in this study. The experimental goal is a field measurement (handheld unilateral magnet) to determine moisture content of partially dried logs, in particular determination of the moisture content when above the fibre saturation point.