Design and Performance of a Multi-Sample Dissolution Dynamic Nuclear Polarization Setup

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Introduction

The inherent limitation of *in-vivo* MR applications is the low intrinsic sensitivity that can be overcome by hyperpolarization techniques. Ardenkjær-Larsen et al. [1] extended the established solid-state Dynamic Nuclear Polarization (DNP) method by subsequent dissolution of the hyperpolarized sample (dissolution DNP) making it applicable to *in-vivo* MR. All dissolution DNP systems available so far accommodate only a single sample at a time [1,2,3]. Polarizing multiple samples in parallel is not only interesting for time-efficient investigations of the DNP processes and their relation to different experimental and sample parameters, it, moreover, potentially permits repetitive *in-vivo* measurements. The latter aspect becomes important in, e.g., cardiac experiments of repeated ischemia/reperfusion to study conditioning of the *in-vivo* heart. We present the design and performance results of a multi-sample dissolution DNP system with EPR and NMR capabilities for commercial wide-bore magnets.

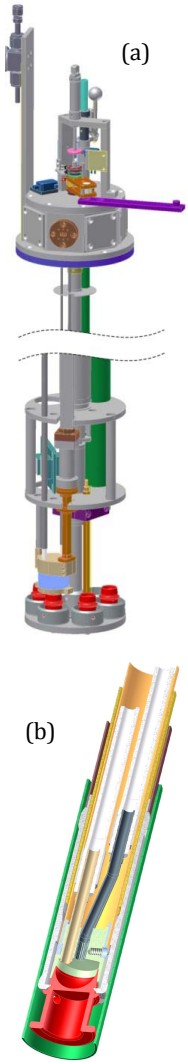

Figure 1 *Design of the DNP probe (a) and the dissolution stick (b).*

Methods

The polarizer is based on designs proposed earlier [1,2,4], extended with multi-sample capability (Figure 1a). The DNP probe can accommodate a maximum of six samples. A revolver-style sample changer enables exchanging the samples at liquid-Helium temperatures. An oversized microwave cavity, designed to concentrate the magnetic field of the microwaves in the sample volume, consists of an NMR saddle coil on the interior and a solenoid EPR coil on the outside. A combination of the two magnetic resonance techniques allows investigations of polarization parameters under DNP conditions.
Through a transfer port, samples can be inserted into the system during any experimental stage at ambient pressure and temperatures above 4.2 K. The core of the dissolution hardware, a sample grabber and an inserted dissolution stick (Figure 1b), is guided through the same port to the samples. The shuttling of the dissolved sample is achieved automatically by means of compressed Helium gas through PTFE tubing to a separate MRI system.

Results

The system has been fully assembled and successfully tested. The system reaches a minimum temperature of 1.3 K at the sample site during single-shot cooling. Down to 4 K, EPR spectra can be acquired by means of the LOD EPR detection method [5,6] (Figure 2a). DNP signal enhancements as a function of microwave power have been measured after 10 minutes build-up at 4.2 K (Figure 2b). The signal decrease for power levels above 30 mW are possibly due to sample heating.
For the maximum ^{13}C polarization measurement, a solution of 16 mM trityl radical in pyruvic acid was polarized at optimum positive DNP conditions. A polarization plateau of 21% is reached with a DNP build-up time constant $\tau = 720$ s (Figure 2c).
A dissolution DNP experiment was conducted by direct ^{13}C polarization at 1.3 K for 70 minutes and subsequent dissolution and shuttling into a 7 T liquid state NMR system. Shuttling was done over a distance of 4 m from bore to bore. The entire shuttling time was 5 s. The maximum magnetization enhancement compared to room temperature at 7 T was measured to be larger than 12 000.

Discussion

In this work, a multi-sample dissolution DNP system compatible with commercial wide-bore magnets has been presented. The multi-sample feature permits streamlined investigations of different sample mixtures at constant DNP conditions. Integrated NMR and EPR capabilities enable monitoring of sample parameters during DNP experiments. The high-Q microwave cavity shows low microwave consumption but leads to sample heating at high microwave power levels. A single large cavity for all samples is considered for future designs. The maximum ^{13}C polarization enhancements measured in the solid-state and dissolved liquids was found to compare well with performances of single-sample DNP system designs described in the literature.

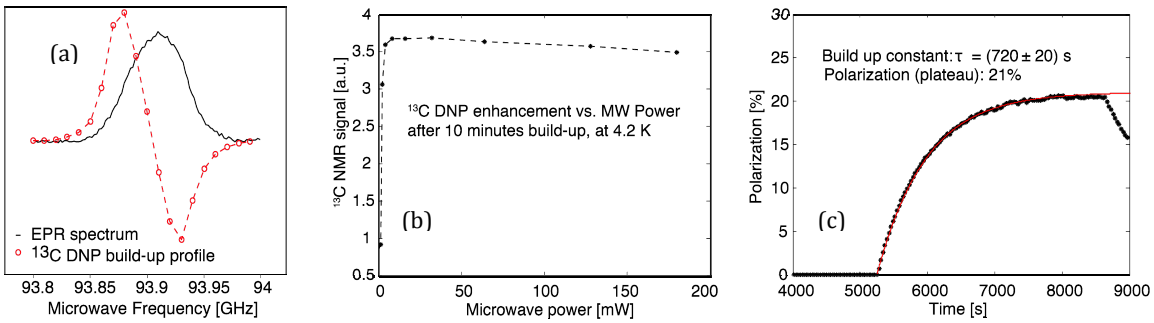

Figure 2 *Sample with 16 mM trityl in 1-^{13}C-pyruvate: the EPR spectrum at 10 K and DNP profile at 3.47 K (a), DNP dependence on microwave power (b), and solid state DNP build-up < 1.6 K (c).*

References:
[1] J. H. Ardenkjær-Larsen, et al. (2003), Proc Natl Acad Sci USA 100, 10158-10163, [2] A. Comment, et al. (2007), Concepts Magn Reson. 31B, 255, [3] Hypersense, Oxford Instruments Molecular Biotools, [4] J. Granwehr, et al. (2007), J Magn Reson. 187, 266, [5] G. Whitfield and A. G. Redfield (1957), Phys Rev. 106, 918, [6] A. Schweiger and R. R. Ernst (1987), J Magn Reson. 77, 512-523