Inductively-Coupled Microcoils and Solution Flow for Increased NMR Sensitivity

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To circumvent the sensitivity problems inherent to slow return of magnetization to equilibrium in liquid-state NMR we present a 3D-printed NMR device based on a mini bubble-pump associated with fluidics and micro-detection that can be installed in every commercial liquid-state NMR probehead. It is based on the use of a closed-loop circuit of the solution near the NMR magnetic center, which presents two main advantages: i) pre-polarization is achieved for the whole solution volume, ii) this volume can be reduced to tens of microliters.

This device (dubbed WIFI-NMRS) is inserted from the top of the NMR magnet, as would be the case for any liquid sample. A gas flow driven by a programmable syringe pump actuates a mini bubble-pump which leads to circulation of the liquid sample. A part of this circuit crosses the NMR detection region consisting of a micro-solenoid. A brass rod fixed on the upper part of the insert and ended by a Vernier placed on top of the magnet enables angular positioning of the micro-coil (Figure 1). The NMR insert has the shape of an NMR tube with its spinner, in order to be easily positioned inside the probehead. Only the diameter of the lower part varies to be adjusted to the commercial probehead (from 5 to 20 mm). Optimization of the coupling between the two coils is made by manually adjusting the angular position of the insert thanks to the Vernier.

As an example of the performance of the approach for slowly relaxing nuclei, magnetic resonance spectroscopy and imaging experiments have been performed with various samples and nuclei (^{13}C, but also ^{7}Li, ^{89}Y etc.). The approach of using a circular flow has also a great interest for the continuous monitoring of chemical reactions, and particularly those involving modification of quaternary carbons. The flow motion homogenizes the reactant mixture, and as detection of poorly relaxing nuclei is facilitated, more quantitative results are obtained.

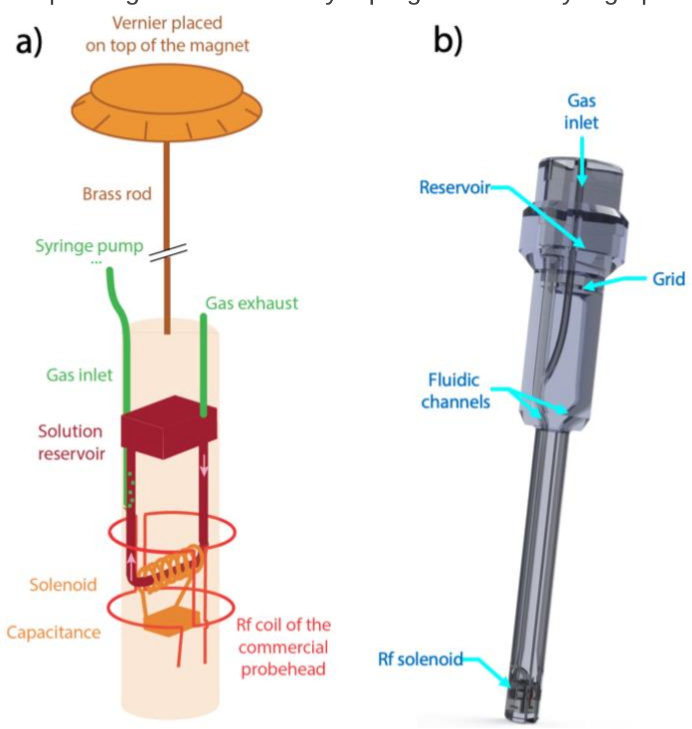

Figure 1. *a) Principle of the WIFI-NMRS device b) 3D rendering of the NMR insert (8mm-version).*

The inductive devices also benefit from all the capabilities of the host probe, allowing heteronuclear experiments even with a mono-tuned microcoil: ^{1}H decoupling (Figure 2), X-^{1}H experiments. Furthermore, the coupling of the microcoil to one of the host probe channels creates two resonant frequencies which can be modulated to extend the probe capabilities, either to reach frequencies unattainable with the host probe alone, or to use both of these resonance frequencies to study two different nuclei with the optimized detection allowed by the microcoil. To increase the signal-to-noise ratio one step further, this system can also be used to efficiently dispense gaseous species such as hyperpolarized xenon and parahydrogen to the solution.
Finally since the quality factor depends on the host probe, the device will be very even more powerful when used in conjunction with cryoprobes.

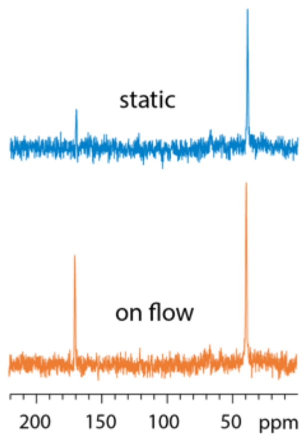

Figure 2. *^{1}H-decoupled ^{13}C NMR spectra on a sample of ^{15}N-^{13}C-enriched glycine*

Reference. G. Carret, T. Berthelot, P. Berthault, Analytical Chemistry **90** (2018) 11169–11173, DOI: 10.1021/acs.analchem.8b01775

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