

CHALLENGES IN NMR MAGNETOMETRY

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Abstract – After reviewing the basic principles of Nuclear Magnetic Resonance (NMR) magnetometers, we will describe the current state-of-the-art in commercially available instrumentation, capable of measuring and mapping static magnetic fields of up to 30 T or even higher, and attaining precisions of one part per billion (ppb). We will then review the most important remaining constraints of the technique: inhomogeneous fields, operation at low temperatures, rapidly varying fields, and weak fields.

Keywords: NMR, magnetometers, overview, challenges, trends

1. INTRODUCTION

NMR magnetometers hold a special place in magnetometry, since they provide an absolute, practically drift-free measurement of the flux density magnitude B . In addition, with an appropriate choice of NMR sample material, their precision is unsurpassed, close to 1 part per billion (ppb) in strong, uniform fields.

Despite these undeniable benefits, NMR magnetometers are and remain a specialty item. They are used principally to calibrate other magnetometers, to map specialty magnets with strong and highly uniform fields, and for other applications requiring extreme resolution.

A new generation of commercial NMR magnetometers, introduced in 2014, brings order-of-magnitude improvements in almost every key performance parameter, lifting many existing constraints.

But even these modern instruments are far from being general-purpose magnetometers. The key practical constraints concern utilization in inhomogeneous fields, operation at low temperatures, measurement of rapidly varying fields, and measurement of weak fields.

We will start by briefly reviewing the physics of NMR and the key elements of an NMR magnetometer. We will then describe the characteristics and capabilities of existing commercial NMR magnetometers, and contrast that with a new-generation system introduced in 2014. Finally, we will pass in review the key remaining challenges, enumerate the proposed approaches for a solution, and assess the feasibility of these proposals.

2. ELEMENTS OF AN NMR MAGNETOMETER

The physics of NMR is well known and even extensively vulgarized – see for example [1]. The phenomenon involves the interaction of the magnetic moment of a nucleus \mathbf{M} with an external magnetic field \mathbf{B}_0 (see Fig. 1). By judicious application of an excitation field \mathbf{B}_1 , oscillating at the NMR resonant frequency, \mathbf{M} can be forced to flip its orientation relative to \mathbf{B}_0 .

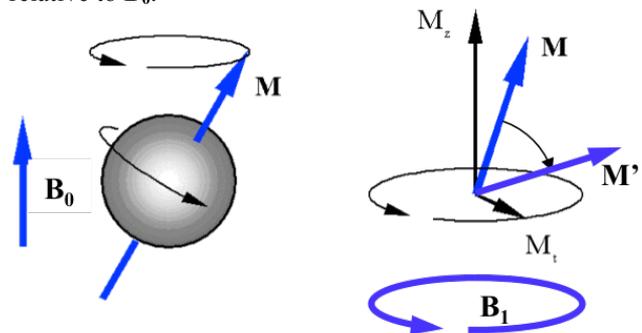


Fig. 1. A nucleus with charge and spin produces a magnetic moment \mathbf{M} . An external, static magnetic field \mathbf{B}_0 causes this magnetic moment to precess at a characteristic frequency known as the Larmor frequency. A rotating excitation field \mathbf{B}_1 , normal to \mathbf{B}_0 , will change the tilt angle of \mathbf{M} relative to \mathbf{B}_0 , as long as \mathbf{B}_1 oscillates at the Larmor frequency (the resonance condition).

An NMR magnetometer functions by measuring the NMR resonant frequency [2]. This frequency depends only on the vector magnitudes B_0 and M ; since M is fixed for a given type of nucleus, it is a direct measure of B_0 . The relation is linear; the proportionality constant is called the gyromagnetic ratio, γ , which varies from one type of nucleus to the next. For example, for the hydrogen nucleus (proton), $\gamma \approx 42.6$ MHz/T, whereas for deuterium, $\gamma \approx 6.54$ MHz/T.

An NMR magnetometer incorporates the following elements:

- **NMR sample:** The sample material must have a nuclear spin; many common isotopes, such as ^{12}C or ^{16}O , have zero spin and are transparent to NMR. The material must also exhibit a sharp resonance; in a molecule, the NMR resonance is broadened by interactions with the other nuclei and electrons. Finally, the nuclei must “relax” to their initial, spin-aligned state in a “reasonable” amount of time: too short a relaxation time prevents us from detecting the resonance, but too long renders repeated

measurements more difficult. The most readily available sample material is water (NMR resonance of ^1H , or proton).

- **B_1 excitation coil:** The B_1 coil must be more or less perpendicular to the field being measured. Unlike Hall magnetometers, imperfect alignment does not change the measurement result; it simply reduces the effective B_1 , causing some loss of sensitivity.
- **RF generator:** The key parameters are bandwidth (≈ 1 MHz to 1 GHz for ^1H), stability (\approx ppb/day), and suppression of spurious frequencies ($\ll -80$ dB). Producing such a generator economically is one of the major challenges in designing an NMR magnetometer.
- **Detector:** Various techniques exist to detect the NMR resonance:
 - **Inductive bridge:** a pick-up coil perpendicular to the B_1 coil detects when, at resonance, spins are rotated by 90° .
 - **Marginal oscillator:** the B_1 coil is part of a marginally stable oscillator. At resonance, the NMR sample absorbs energy, acting like a resistance, thus lowering the Q and reducing the oscillation amplitude.
 - **Envelope / peak detector:** because of the same energy absorption, the driving oscillation on the B_1 coil dips slightly at resonance.
 - **Pulsed-wave:** the sample is excited with a short pulse applied to the B_1 coil; then, in a second step, the B_1 coil is used to detect the Larmor precession during the relaxation time.
- **Modulator:** All but the pulsed-wave technique require some sort of modulation, to detect a change when crossing the resonance. The most obvious solution is to modulate the frequency, but it is often more practical to add a small coil to modulate B_0 , taking care to synchronize the measurement with the modulation zero crossing.

3. THE CURRENT STATE OF THE ART

The NMR magnetometer with by far the world's largest installed base today is the Precision Teslameter PT2025, built by our company, Metrolab (See Fig. 2). Using an envelope / peak detector, B_0 modulation, and analogue feedback circuitry to automatically tune to the NMR resonant frequency, the PT2025 achieves a relative precision of 0.1 ppm and absolute accuracy of 5 ppm.



Fig. 2. The NMR Precision Teslameter PT2025 is built around a voltage-to-frequency converter with a fundamental range of 30-90 MHz and divided down by up to four levels of frequency dividers. Probes with proton samples (rubber) range up to 2.1 T, probes with deuterium samples (heavy water) up to 13.7 T.

The NMR magnetometer with the second largest installed base is a specialty system for mapping Magnetic Resonance Imaging (MRI) magnets, Metrolab's Magnetic Field Camera MFC3045. This instrument supports simultaneous measurement of up to 32 proton probes (see Fig. 3). The probes provide a relatively narrow measurement range, typically $\pm 2\%$ of the nominal field, 0.2 to 7 T. The MFC3045 is built around a Direct Digital Synthesizer (DDS) RF generator with frequency modulation, plus an envelope / peak detector for each probe. It achieves a relative precision of 0.01 ppm and absolute accuracy of 5 ppm.



Fig. 3. MFC3048 Probe Array for the Magnetic Field Camera MFC3045 multi-probe NMR mapping system. The geometry of the array is custom-designed for the magnet to be mapped, typically a half-moon, 160 to 500 mm in diameter, with the probes arranged around the edge.

Recently, Metrolab has introduced a new-generation NMR magnetometer, the Precision Teslameter PT2026 [3], destined to eventually replace the PT2025 as well as the MFC3045 (see Fig. 4). Featuring a pulsed transmit / receive detector and Digital Signal Processor (DSP), the PT2026 achieves precision comparable to the MFC3045, but over a wide measurement range, like the PT2025. An RF generator ranging up to 1 GHz supports proton probes up to over 20 T.



Fig. 4. Besides an extended range and improved precision, the NMR Precision Teslameter PT2026 provides numerous functional improvements over its predecessors, such as flexible probe ranges, fast search for NMR resonance, and improved performance in inhomogeneous fields.

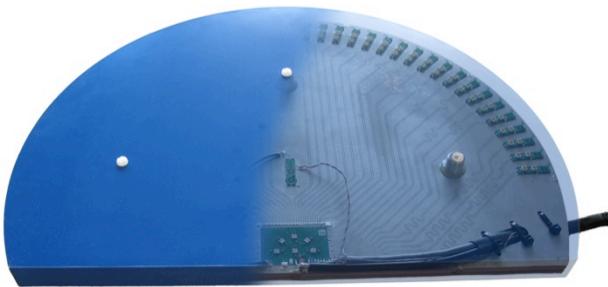


Fig. 5. Probe Array for the 11.7 T full-body MRI scanner being developed by the joint French-German Iseult project [4]. It features 40 measurement points at 500 MHz on a 475 mm diameter semi-circle, plus a wide-range probe in the middle. The RF switches at the bottom are the only active components; unlike current-generation Probe Arrays, each measurement point requires just a coil and two trim caps.

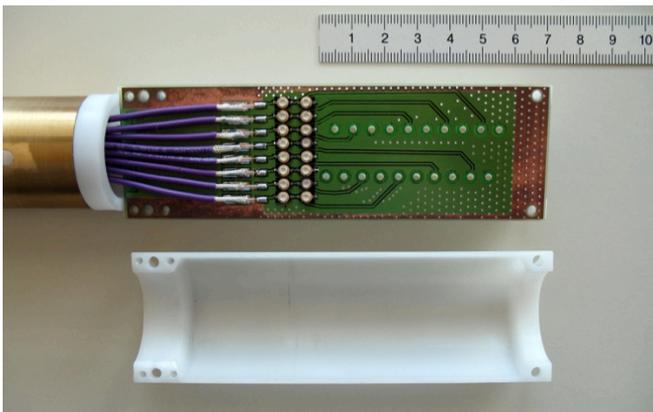


Figure 5. Experimental Probe Array for 300 MHz (7 T) and 400 MHz (9.4 T) vertical small-bore NMR spectroscopy magnets. The 16 active probes are arranged on a 13.2 mm x 37.5 mm rectangle, interleaved left and right to maximize their vertical spacing. Dummy probes at the top and bottom of each row minimize inconsistencies due to paramagnetic effects. A complete map with 32 angular positions takes less than 5 minutes.

In addition to the single-probe system shown, prototype multi-probe systems based on the PT2026 have been tested (see Fig. 5 and Fig. 6). Compared to the MFC3045, these provide a higher field range, support small-bore magnets, and offer the possibility of placing a wide-range probe on a probe array, thus combining the functionalities of the PT2025 and MFC2045.

4. REMAINING CHALLENGES

4.1 Field uniformity

The greatest limitation of NMR magnetometers is that the field to be measured must be uniform. If not, the opposite ends of the sample resonate at different frequencies, which broadens the spectral response and, through destructive interference, reduces its amplitude.

It is relatively simple to rethink the signal processing to accept a broadened spectrum. However, for highly inhomogeneous fields, the only way to avoid losing the signal is to reduce the sample size, which reduces the signal/noise ratio (SNR). Somehow, this SNR must be recovered. Some possible ways to do so are discussed in Subsection 4.4; but they all introduce complications and compromises.

Side-by-side comparisons show that the PT2026 tolerates more than twice the field inhomogeneity than the PT2025; although impressive, this is a modest improvement compared to the order-of-magnitude leaps achieved for most other parameters. We expect that progress on this front will continue to be difficult, and that field inhomogeneity will continue to be the key limitation of NMR magnetometers.

4.2 Cryogenic operation

Another challenge for NMR magnetometers are low temperatures. As superconducting magnets capable of generating very intense and very uniform magnetic fields become more common, manufacturers of such magnets are demanding cryogenic NMR probes.

Unfortunately, the transverse relaxation time T_2 , which determines the length of the “ring-down” of the NMR resonant response, is dramatically shorter in solid NMR sample materials than in liquid ones; for example, whereas T_2 of water is several seconds, T_2 of ice is on the order of a microsecond [5]. In addition, the active electronics of an NMR probe does not function at cryogenic temperatures.

However, the literature does describe appropriate sample materials [6], and the PT2026 allows the passive probe head to be separated from the active electronics by several meters of coaxial cable. Thus we expect that commercially available cryogenic NMR probes are not very far off.

4.3 Measurement rate

NMR magnetometers are traditionally slow, optimized for extremely precise measurements of static fields. For example, the PT2025 performs one measurement per second.

Although the PT2026 provides better than an order of magnitude improvement in this respect as well, much higher

measurement bandwidths should be possible, since the NMR physics imposes no constraints in this respect.

In fact, the literature already describes measurements of field perturbations in an MRI system in the kHz range [7]. Although the described system uses very sophisticated – and expensive – measurement and analysis techniques, far removed from traditional NMR magnetometers, it is clear that the measurement bandwidth can be dramatically improved.

4.4 Weak magnetic fields

Last but not least, NMR magnetometers are best adapted for strong magnetic fields. In weak fields, the spin flips induced by B_1 are drowned out by thermally induced random spin flips. For example, the bottom of the PT2025's measurement range is 43 mT; especially Hall calibration systems would like to have NMR reference measurements much closer to zero.

There are several proven approaches to this problem:

- **Larger sample:** provides more nuclei and thus a better SNR. However, the large probe size is a great practical hindrance, and is in fact counterproductive in inhomogeneous fields.
- **Electron-Spin Resonance (ESR):** very similar to NMR, except based on electron spin instead of nuclear spin, with a gyromagnetic ratio in the GHz/T instead of the MHz/T. Currently known ESR probe materials are chemically unstable and/or have wide resonance widths, making them unsuitable for an industrial instrument.
- **Pre-polarization:** improve the SNR by aligning the spins in a strong magnet before measuring the resonance in the weak field. Requires physically transporting the sample material – for example water – from the polarization magnet to the B_1 coil.
- **Higher pick-up sensitivity:** replace the coil with a more sensitive pick-up, such as a superconducting coil or Superconducting Quantum Interference Device (SQUID).

In the past, Metrolab has shipped PT2025 probes with large samples and with ESR samples; neither proved to be entirely satisfactory. We continue to search for innovative ESR sample materials. High-sensitivity pickups may be a promising long-term solution, but the technological complexity is daunting.

Pre-polarization in a flowing-liquid system appears to be the most promising approach. NMR magnetometers capable of measuring down to the earth's field (~50 μ T) have been on the market in the past [8], and Metrolab have also built prototype systems. A fully industrialized and robust NMR magnetometer for measuring weak fields can be expected to appear on the market in the intermediate term.

4. CONCLUSIONS

Because they provide an absolute, drift-free and extremely precise measurement of the flux density, NMR magnetometers are and remain a cornerstone of magnetometry. Recent attempts to even further improve the precision, to increase the measurement range, and to generally reduce the technique's limitations have been spectacularly successful. We foresee this evolution will continue, in particular with cryogenic probes, high measurement bandwidths, and low-field capability. Limitations due to inhomogeneous fields will be pushed back, but will remain the primary constraint to more widespread use of NMR magnetometers.

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