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# NMR magnetometers

A decade of research and development results in a major step forward for nuclear magnetic resonance magnetometers

Among a dozen physical phenomena exploited to measure magnetic field strength, NMR (nuclear magnetic resonance) is by far the most accurate. In addition NMR magnetometers are immune to temperature- or age-related drift. For these reasons they are widely used as a reference for calibrating other magnetometers, such as the common Hall gaussmeter. However due to technological constraints their use beyond calibration has been limited to research and a few industrial applications. This may start to change. Here we review the principles of operation of NMR magnetometers, their benefits and constraints, and recent developments that aim to bring these fantastic instruments into more common use.

## NMR: A discovery destined for greatness

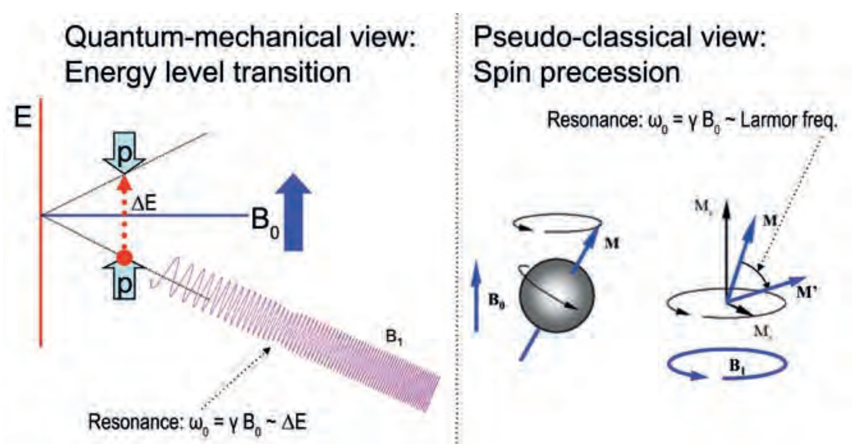
Building on 50 years of physics research, nuclear magnetic resonance (NMR) was experimentally demonstrated in late 1945 by two independent teams led by Felix Bloch at Stanford University and Edward Purcell at Harvard University. Bloch and Purcell received the Nobel Prize in 1952, but industrialisation of NMR had already started in 1948 when Russel Varian, a colleague of Bloch's, founded his company to use NMR for chemical analysis. NMR spectrometers are now an essential tool in chemistry. Similarly magnetic resonance imaging (MRI), first commercialised in 1978, has quickly developed into one of medicine's most important imaging modalities.

Commercial NMR magnetometers became available about the same time as MRI. The principle is straightforward: if a nucleus has spin, it will act like a little compass needle and align itself in a magnetic field. Quantum-mechanically speaking, the nucleus has two energy states: a lower-energy state where the nuclear magnetic moment is aligned with the external field, and a higher-energy state where it is opposed. The gap between these two energy states depends only on the magnitude of the magnetic moment and that of the magnetic field. Since the nuclear magnetic moment is a constant, this energy gap is a perfect measure of magnetic field strength.

As in spectroscopy, injecting just the right amount of energy will cause the nucleus to transition from the lower to the higher energy level. The injected energy is proportional to its frequency, so a magnetic measurement via NMR consists of searching for the frequency – the resonant frequency – that causes the nuclear spins to flip.

The energy is injected by an AC magnetic field (usually called $B_1$), perpendicular to the field being measured ($B_0$). Just as the angular momentum vector of a spinning top precesses around the direction of gravity, the nuclear magnetic moment precesses around $B_0$; resonance occurs when the frequency of $B_1$ exactly matches the precession, or Larmor, frequency. At resonance, $B_1$ rotates the spin away from $B_0$ – even though $B_1$ is generally orders of magnitude smaller than $B_0$.

Figure 1: **Principles of NMR**



### Ingredients for an NMR magnetometer

Practically speaking, an NMR magnetometer has five main 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 the detection of the resonance; too long renders repeated measurements more difficult. The most readily available sample material is water (NMR resonance of $^{1}H$, or a 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 (≈1MHz to 1GHz for $^{1}H$), stability (≈ parts per billion/day), and suppression of spurious frequencies (<≈-80dB). 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:

  • 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 killing the oscillation.

  • Continuous wave (CW): because of the same resistance-like effect, the driving voltage on the $B_1$ coil dips slightly at resonance. An alternate CW technique is the inductive bridge, where a pick-up coil perpendicular to the $B_1$ coil detects when, at resonance, spins are rotated by 90°.

  • Pulsed-wave (PW): the sample is excited with a short, wide-band 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 PW 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 synchronise the measurement with the modulation zero-crossing.

Figure 3 shows the architecture of an actual instrument, Metrolab's Precision Teslameter PT2025. A detailed functional description can be found in the manual; here we just want to point out the five key elements. The Sample, $B_1$ Coil and Detector are all physically located in the probe; the RF Generator consists of a Voltage Controlled Oscillator (VCO) and frequency dividers, located in the main unit; and the Modulator consists of a current generator in the main unit connected to a field modulation coil in the probe. Other important features of this architecture are the tracking loop that automatically adjusts the VCO to stay centred on the resonance, and the auto-tuned variable capacitance, forming a resonant tank circuit with the $B_1$ coil and thus greatly improving the SNR. The basic design dates from 1985 and these instruments now represent the overwhelming majority of the world's installed base of NMR magnetometers.

### Pros and cons

Compared with other magnetometer technologies, NMR has clear benefits. Foremost is the astounding precision and accuracy. The resolution is essentially limited by the stability of the RF generator and the sample's resonance width; for existing instruments such as the PT2025, this is around 0.1 parts per million (ppm). This allows


Figure 2 (above): **The Metrolab Precision Teslameter PT2025**

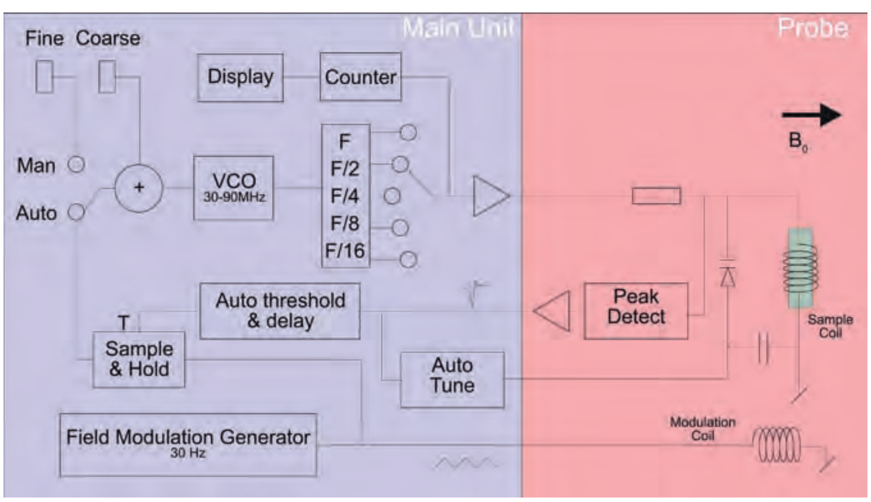



Figure 3 (below): **PT2025 functional block diagram** researchers to measure minute magnetic effects such as the 'training of superconducting filaments'. The absolute accuracy is limited by low-level field distortion caused, for example, by the susceptibility of materials surrounding the NMR sample; for the PT2025 this is around 5ppm, which is more than enough to calibrate other magnetometers.

Finally, NMR is the only way to create a field map with enough resolution to guarantee the uniformity needed for MRI or NMR spectroscopy – NMR magnetometry serving its NMR sister technologies.

NMR is also essentially drift-free. Drift of the RF generator reference clock is important but can be readily maintained at extremely low levels – parts per billion or better. Finally, unlike Hall- or coil/integrator-based magnetometers, NMR measures the total field B regardless of the exact probe orientation.

NMR magnetometers also have limitations. The most important is that they only work in a uniform magnetic field. The reason is simple: the sample has a finite size (≈4mm diameter); a magnetic field gradient causes one end of the sample to resonate at a different frequency from the other; and the higher the gradient, the harder it becomes to determine a unique resonant frequency. Today's limit is a field gradient in the order of 100-1000ppm/cm. Most magnets are very far from this level of field uniformity.

Since NMR is a relatively slow technology – in the order of 10-100ms per measurement – it is of limited use for rapidly varying fields. Finally, the field needs to be relatively strong for the spin-flip energy gap to rise significantly above the room temperature thermal noise. For example the range of PT2025 probes starts at 40mT, or roughly 1,000 times the earth's field. Sadly many interesting and useful applications fall into that three-order-of-magnitude zone.

**Evolution**

NMR magnetometers have evolved considerably since 1985. Many changes simply follow industry trends in terms of electronic components, microprocessors, displays, controls and computer interfaces. However some improvements allow us to push back key limitations, opening the way for more widespread use of NMR magnetometers.

**More is better**

The first major step came in 1992 with the introduction of multi-probe systems for mapping MRI magnets – what eventually became Metrolab's Magnetic Field Camera MFC3045. Up to 32 NMR probes functioning in parallel addressed the need for faster field maps. Other key improvements include the use of a Direct Digital Synthesizer (DDS) as the RF Generator, allowing the use of frequency modulation and eliminating the field modulation coils. Also the auto-tuning circuit with a varactor diode was replaced with a simple trim cap, reducing the measurement range from 300 percent per probe for the PT2025 to around ±2 percent – a perfectly acceptable simplification for MRI magnets, where the target field is exactly known. Finally, the mechanical aspects of the instrument were optimised for MRI production, with robust housing and connectors, remote control, etc.

With this instrument the time to map a magnet was reduced from many hours to around five minutes. Productivity gains add to technical benefits: less magnet drift and fewer human errors, combined with improved positioning precision, meant more self-consistent maps and better convergence of the entire magnet-tuning process. It is fair to say that without the development of multi-probe NMR systems, MRI would not be what it is today.

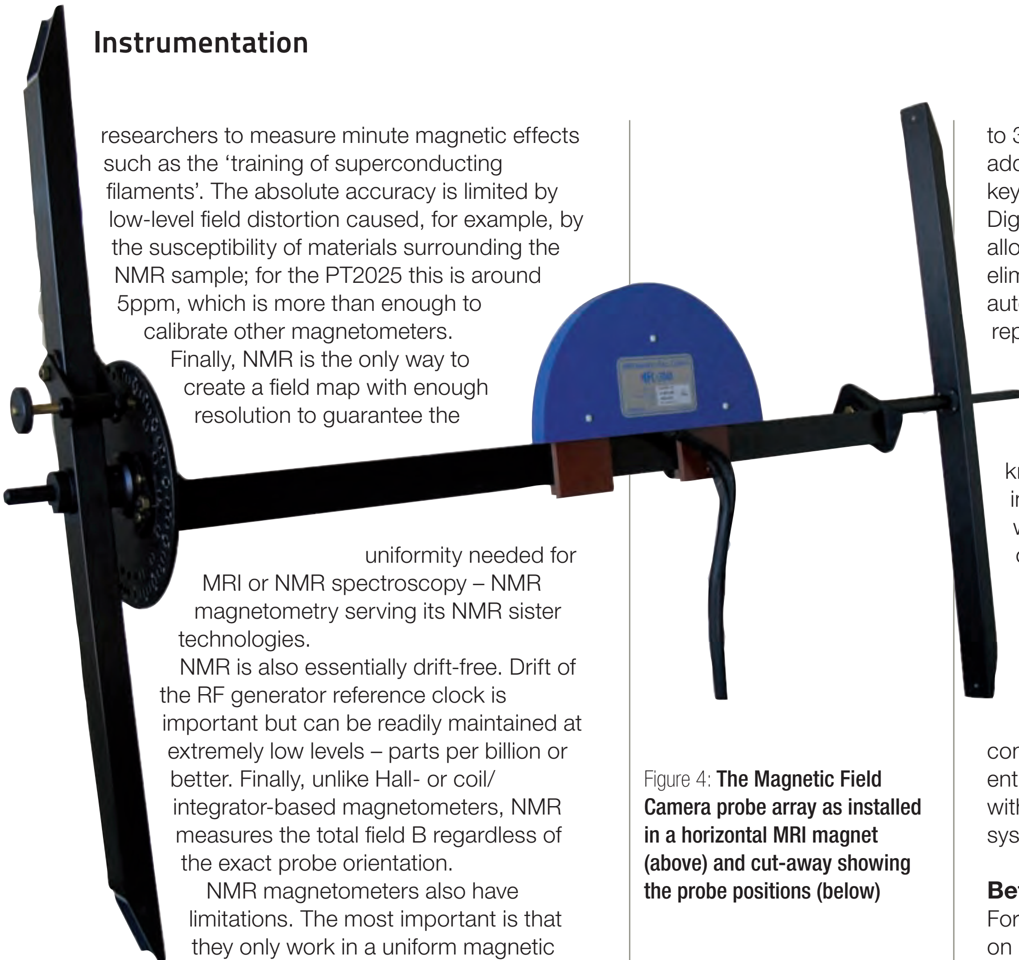



Figure 4: **The Magnetic Field Camera probe array as installed in a horizontal MRI magnet (above) and cut-away showing the probe positions (below)**

**Better is better**

For almost a decade Metrolab has been working on a new-generation, all-digital NMR magnetometer, the PT2026. Actually, as can be seen from Figure 5, the term 'all digital control' would be more accurate. Other important technical improvements include:

- RF Generator: Up to around 1GHz, instead of 90MHz for the PT2025. Absolute frequency control simplifies the architecture and improves stability.
- Detection: Support for either continuous-wave (CW, like PT2025) or pulsed-wave (PW, as shown in Figure 5). Improved performance in poor-SNR environments due to sophisticated digital signal processing.
- Modulation: Field modulation for CW probes, or none for PW probes.
- Multi-probe capability: Up to 512 PW channels,

or 16 times that of the MFC3045.

• Probe tuning: Variable like PT2025, or fixed like MFC3045. For PW probes, dynamic matching improves power transfer.

• Search of NMR resonance: Assisted by a three-axis Hall probe.

What will change from the user's standpoint? For measurements above 2T, delicate heavy water ($^2$H, or deuterium) based probes will be replaced with robust rubber ($^1$H) based probes. The maximum field will go from not quite 14T to over 20T – or practically unlimited if one accepts deuterium probes. The measurement resolution remains around 1Hz but the measurement rate will be an order of magnitude faster. With optional signal averaging, measurement speed can be traded off against resolution; for typical NMR spectroscopy magnets, the resulting resolution starts to approach the parts-per-billion level.

Massively parallel multi-probe systems allow us to conceive fixed, 3D probe arrays rather than rotating 2D probe arrays – resulting in even faster mapping and better positioning accuracy. In addition the new PW probe arrays will share one set of electronics for all the probes, making the actual array simpler and smaller. We have already demonstrated probe arrays that fit into the 40mm bore of a conventional NMR spectrometry magnet – almost an order of magnitude smaller than currently possible.

In addition to maximum field, resolution, speed and multiple probes, the PT2026 promises another key improvement: tolerance of non-uniform fields, where we expect the combination of higher SNR and a DSP to provide close to an order of magnitude improvement. This, combined with usability improvements like fast search assisted by a three-axis Hall probe, will significantly push back the limitations of NMR magnetometers.

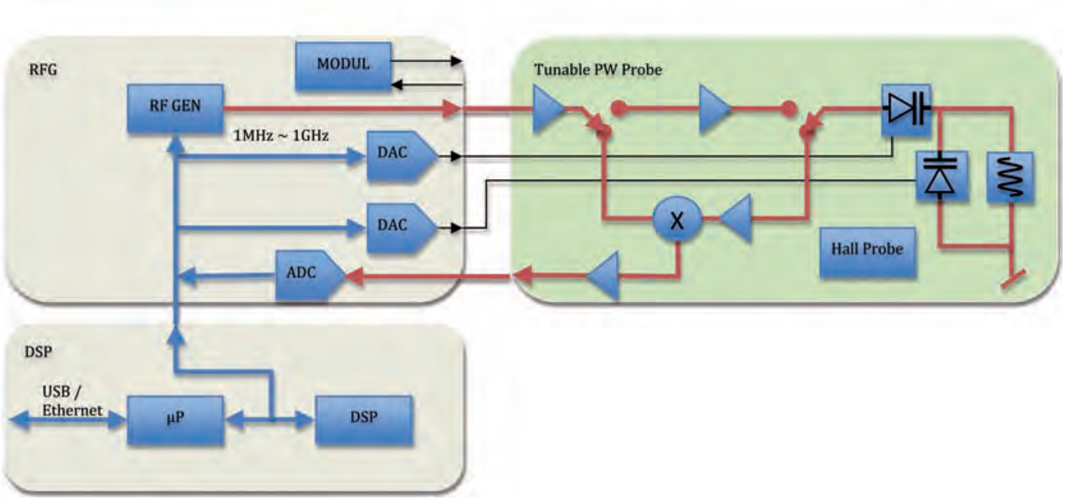
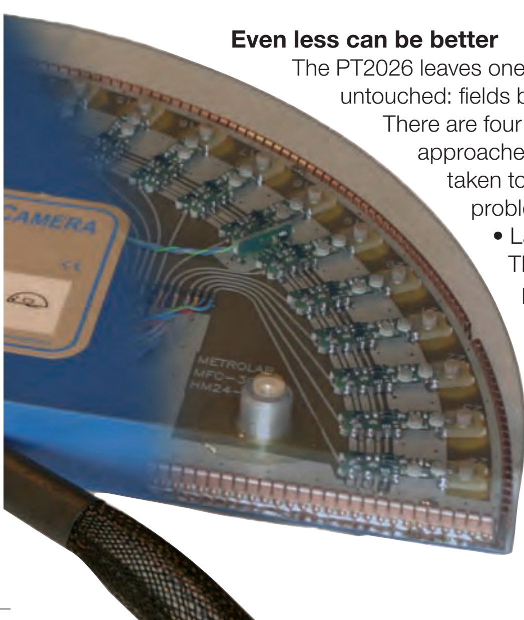



Figure 5: **PT2026 functional block diagram**

### Even less can be better

The PT2026 leaves one major barrier untouched: fields below 40mT. There are four basic approaches that can be taken to address this problem:

• Larger sample: This would provide more nuclei and thus a better SNR, but the large probe size is a considerable practical hindrance.



• Electron-spin resonance (ESR): This is very similar to NMR but 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-polarisation: This would improve the SNR by aligning the spins in a strong magnet before measuring the resonance in the weak field. It requires physically transporting the sample material – for example, water – from the polarisation 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. Metrolab is now pursuing the third option, a flowing water system, specifically for calibrating Hall probes over a wide range of fields (±2T) with a single probe. The company also continues to search for innovative ESR sample materials. High-sensitivity pickups may be a promising long-term solution, but the technological complexity is currently daunting.

Metrolab earned its dominant position in NMR magnetometry by making a delicate piece of laboratory equipment work in the rough-and-tumble manufacturing environment. Its equipment goes from the arctic cold of aircraft holds to the sauna-like Singapore summer, gets dropped by baggage handlers, yanked into place by technicians pulling on the probe cable – and is then expected to deliver parts-per-million accuracy. More than 20 years later such systems are still returned for calibration (and occasionally repair). Metrolab is committed to continuing to push back the limitations as far as physics and good engineering allow. ■