MAGNETIC RESONANCE TECHNIQUES

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Abstract
First the main characteristics of the NMR magnetic measurements, such as accuracy, independence of field direction and zero temperature coefficient are recalled. Then some different magnetic field measuring techniques using NMR, and the conditions to achieve such measurements, are described. Finally, recent NMR applications, used in various domains such as MRI and accelerator-magnet alignment, are described.

1. BASIC NMR REMINDER

1.1 Classical theory

If we consider the proton or nucleus which has kinetic and magnetic moments in an external magnetic field, we have a precessing movement; the spinning mass of the nucleus will act as a gyroscope and the forces between the magnetic moment and the external field tend to align the magnetic moment with the field; the proton will process around the main field direction as shown in Fig. 1.

![Fig. 1 Precession of proton magnetic moment](image)

\[ \gamma = \mu / J = \omega_L / B \]

The precession frequency varies essentially linearly with the field amplitude and is not affected by the temperature of the environment. It is very easy to measure since frequency measurements can be made with a precision of about $10^{-10}$ to $10^{-12}$. This frequency measurement gives the value of the magnetic field modulus, independently of its direction. The field direction has influence only on the signal amplitude.

For a better understanding of this theory, please refer to Abragam’s book mentioned in the Bibliography, at the end of this paper.
1.2 Quantum theory

The levels of energy of the nucleus separate in the field and the energy between the two states is proportional to the field amplitude. In pulsed NMR, when a RF magnetic field pulse is applied for a given time perpendiculary to the main field, the energy levels are pumped to the upper state. When the magnetic field is removed, they will decay giving the frequency corresponding to the difference of energy of the levels. In both cases, we have a relation between the field amplitude and the frequency; this relation is $\gamma$.

![Energy separation in a magnetic field](image)

$\Delta E = h\nu = \mu B / I$  
$\gamma = \mu / hI = \nu / B$

Fig. 2 Energy separation in a magnetic field

1.3 Nuclei commonly used in NMR magnetometers

Different nuclei are used in NMR magnetometry:

*The proton* is mainly used; it is the nucleus for which we have the more precise evaluation of $\gamma$, so it is used as a primary standard. Probably the best measurement of $\gamma$ has been made by NIST (The National Institute for Standards and Technology in US) [1]. In Metrolab magnetometers, we use samples in the form of natural rubber pieces which are easier to handle for probe fabrication.

*Deuterium* is used to measure higher magnetic fields, and we use it in our NMR magnetometer which is derived from the CERN development by Borer and Frémont [2]. For frequencies up to 100 MHz, we can measure magnetic fields up to 14 T. We use the deuterium as heavy water contained in sealed glass ampoules.

*Fluor* is also used as a measuring nucleus in MRI equipments since its $\gamma$ differs by 5% from the proton value, allowing field measurements simultaneous with imaging, with no interference with the imaging system frequency.

*Aluminium powder* is also used, mainly in cryogenic equipments

*He* has also been proposed by Jim Clark from UCLA for use in the LHC.

*Electron Paramagnetic Resonance (EPR)* has also been used in our standard NMR apparatus, to make a probe measuring low fields in the range 5 to 30 gauss, with the same controller and the same frequency range as the standard NMR measurement system.

*Other nuclei* such as Li, Na, Cs etc. can also be used.

A summary of $\gamma$ values can be seen in the following table:
### 1.4 Proton gyromagnetic ratio

The gyromagnetic ratio $\gamma$ of proton has been measured by different means and the official value was given by NIST in 1986. In 1990, a small correction of 1.5 ppm was applied, with a relative uncertainty of 70 ppb. For rubber samples, we recorded a 3 ppm shift in the $\gamma$ value, compared to the official water sample value. Our NMR instruments equipped with rubber samples have therefore been corrected accordingly. For an absolute estimation of uncertainty, we give a conservative value of $\pm 5$ ppm and propose a $\pm 2$ ppm error on the value of the magnetic field measured by our instruments. However, it is very hard to prove this because of the difficulty of transporting a field standard. It is a challenge for the G-2 experiment people in Brookhaven where they need to insure the traceability with the NIST standard up to the precision of $10^{-7}$, since it is a real problem to get magnets as stable in time as in space at this level of precision.

The practical $\gamma$ value used in the Metrolab magnetometer is given in the following table:

<table>
<thead>
<tr>
<th>Source</th>
<th>$\gamma$ value (MHz/T)</th>
<th>Relative uncertainty (ppm)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Codata 1986</td>
<td>42.576 375(13)</td>
<td>0.3</td>
<td>NIST Journal, Vol 92, Nb 2, p 85, March/April 87</td>
</tr>
<tr>
<td>1990 correction</td>
<td>42.576 396(3)</td>
<td>0.07</td>
<td>NIST Journal, Vol 95, Nb 5, p 521, Sept/Oct 90</td>
</tr>
<tr>
<td>Metrolab</td>
<td>42.576 268(3)</td>
<td></td>
<td>Theoretical value : -3 ppm due to para rubber/Brucker 200 MHz spectrometer</td>
</tr>
<tr>
<td>Metrolab</td>
<td>42.576 255</td>
<td></td>
<td>Practical value: -0.3 ppm accepted error due to technical reason</td>
</tr>
</tbody>
</table>

### 2. NMR MAGNETOMETER PRINCIPLE

#### 2.1 Continuous Wave (CW)

##### 2.1.1 Q meter

Our standard NMR magnetometer, developed 20 years ago at CERN by Borer and Frémont [2], uses a water sample in a RF coil placed in the magnetic field, and is low-frequency modulated by an additional pair of modulation coils (see Fig. 3). It is a tuned-coil and capacitor system, fed with continuous RF, using the Q-meter principle for which the peak-to-peak RF level on the coil is detected by a diode system. The signal is very small so it is amplified in an AC amplifier and allows the DC component and its drift problems to be rejected.
The B modulation used is generated by a simple circuit (Fig. 3). The constant frequency RF source is applied by a small coil around the sample. This coil detects the NMR signal only, in contrast to a frequency modulation where the signal can lock on the beating with the external disturbing frequency. Systems with frequency modulation (F modulation) don't need additional modulation coils, leading to simpler probe design. However, some drawbacks may appear such as modulation noise due to the frequency excursion on the tuning curve.

2.1.2 Closed-loop principle

In our standard magnetometer system, we use a Variable Controlled Oscillator (VCO) which is locked on the NMR signal (Fig. 4). When the NMR signal crosses a threshold, it generates a pulse freezing the modulation voltage, proportional to the current in the modulation coils. This voltage is used as an error signal and is sent to the integrator generating the control voltage of the VCO to lock onto the NMR frequency (Fig. 5).
2.1.3 Open-loop principle

We have developed, for MRI magnet measurement, an open-loop principle. It uses a Direct Digital Synthesizer generator (DDS) where frequency is controlled by a computer, and need not be measured a posteriori. This RF is modulated with exactly known parameters. We use, for MRI measurements, probe arrays (up to 30 probes) that can be fed by the same frequency modulated RF signal, so there is no danger of beating between probes (Fig. 6).

The offset from a reference frequency $F_0$ is loaded into a counter for each probe. In each counter, we record the instant the signal appears, going up and down. We take the mean value of these two numbers to get the value of the field (Fig. 7). So, without the need of a multiplexer system, we can measure simultaneously all the values of all probes in a couple of seconds. Then, for each probe, we analyse the mean value and standard deviation, for a number of periods (about 50 for example) with the microcomputer. If we have a gross error, we discard this measure from the mean. The RMS value of the measures also gives information on the confidence level of that measurement. The resolution we achieve with this principle is better than expected, getting below $10^{-7}$. Therefore, we proposed this system for the G-2 experiment in Brookhaven.

2.1.4 Z meter

Another technique, for future magnetometers using higher frequencies, up to 1 GHz, is in development at Metrolab. The principle is not new [3]; it consists of measuring the impedance change in the sample coil. The coil containing the sample is placed at the end of a perfectly adapted coaxial cable; the impedance imbalance at resonance is detected with a hybrid T as in Fig. 8.
When the proton perturbs this balance, there will be a signal that can be detected with a phase detector, and used to produce a feedback signal to control the VCO and lock onto the magnetic field. This principle uses higher modulation frequency, allowing the magnetic field to be tracked more quickly. The use of a lock-in detector also permits a good recovery of weak signals, even with a signal-to-noise ratio lower than 1. The high frequency range also allows protons to be used to measure field amplitude up to 20 T. Probe design is also simplified, since it consists only of an adapted coil placed at the end of a coaxial cable. Using appropriate material, we should be able to make cryogenic probes using this principle.

2.2 Pulsed NMR

The pulsed NMR technique (Fig. 9) is a very clever method for NMR spectroscopy, chemical analysis and analysis of nuclei in molecules [4, 5]. In fact, chemical bondings in molecules split energy levels of nuclei with magnetic moment; so they get different \( J \) values in resonance, displaying a spectrum of frequencies instead of the original frequency of the free nucleus.

To obtain a spectrum, a RF pulse is applied to the sample to tilt the magnetic moment of the nucleus, the tilt of the nucleus spin being determined by the magnitude of the RF pulse. After a given time, the pulse is switched off, and the signal induced by the precessing moments is observed and processed by FFT until they are completely aligned with the external magnetic field (Fig. 10).
2.3 Flowing-liquid principle

The principle has been used in Bratislava by L. Jansak and S. Kvitkovic (and also by J. Tatarczuk in Mainz, Ye Sheng in Wuhan, China, etc...), to measure the field by water transportation. This water transports spin direction, after passage into a polarizing magnet (Fig. 11).

The water proton takes several seconds to align with the field and several seconds to return to a random direction. Once the proton is aligned, water is transported to the field to be measured. A frequency synthesizer emits RF energy which depolarises the nucleus if the frequency matches the resonance. With the auxiliary analyser, only the strength of the signal is observed, not the frequency. When the signal becomes smaller, it indicates that the frequency of the synthesiser is exactly the resonance frequency of the proton.
Fig. 11 Principle of the flowing-water magnetometer

It is a nice process, but slow, manual and difficult to automatize. Yet it allows measurements on very high and very low magnetic fields, even in the order of the magnitude of the earth magnetic field, and on very inhomogeneous fields (by Jansak), which is usually difficult with other NMR methods.

3. MEASURING RANGE AND ACCURACY

3.1 Range

Field measurements can be made, with NMR methods and with the different techniques described above, down to the earth magnetic field (0.05 mT). Current magnet measurements, in MRI and particle accelerators, are in the ranges:
- 0.04 T to 2 T with protons as the sample in the probes
- 2 T to 14 T with deuterium
- 0.5 to 3.2 mT with EPR sample.

3.2 Accuracy

The accuracy we can obtain with the NMR principle can be affected by some parameters, but the gyrometric ratio $\gamma$ is not a source of error in the measurements. Some years ago, Brucker gave an estimation of the temperature coefficient of $\gamma$ inferior to $10^{-7}$ °C. Later, we did some measurements on this effect and essentially found a $T_{c}$ value of zero, between 25°C and 60°C with an uncertainty of $\pm$ 50 ppb/°C. This interpretation can be discussed in the case of the presence of paramagnetic material in the surrounding of the probe, since this can have a magnetic $T_{c}$ different from zero and affect the accuracy.

With a pulsed NMR magnetometer, we can achieve even better accuracy, thanks to the long relaxation time. For example, with a very homogeneous field, it is possible to have an uncertainty of a couple of hertz on a 600 MHz frequency, corresponding to a few ppb.

In the CW NMR magnetometer, currently, for a 1 second measurement, we get a relative accuracy of $\pm$ 0.5 ppm RMS. If we do a mean of several measurements, we can even reach $\pm$ 0.1 ppm for a 10 second measurement duration.

4. MEASURED-FIELD PROPERTY

4.1 In time

The field to be measured must be stable, especially if fields are to be measured with a precision up to 1 ppm. In the Borer system from CERN, we have a tracking speed not exceeding 1% of field variation per second, which is quite slow. With the RF-principle magnetometer, we expect to be able to follow the field more quickly since the modulation frequency is much higher.

4.2 In space

4.2.1 Definition

The magnetic field must also be stable in space. Of course, measurements with an accuracy of 0.1 ppm and if homogeneity is about 1000 ppm / cm, you will see that 0.1 ppm corresponds to a dimension of 1 µm. So, to use NMR magnetometers the field must be homogeneous for two reasons:
(i) probe positioning must be achieved with a spatial position precision proportional to field gradient, which can make impossible positioning with normal means.

(ii) the signal deteriorates in high gradient fields proportionally to the sample dimensions. The effect of the gradient is to spread and weaken the resonance line making it undetectable. So, in a non-homogeneous field, it becomes difficult to detect the NMR signal and to lock onto it.

4.2.2 Example

In our probes, the sample dimension is about 4 mm, giving a base of estimation of maximum gradient. The limit for good measurements is about 1000 ppm/cm for protons and •100 ppm/cm for deuterium. The table below gives the limits of field homogeneity for the standard Metrolab probes.

<table>
<thead>
<tr>
<th>Probe N°</th>
<th>Field range (Tesla)</th>
<th>Probe type</th>
<th>Active volume Ø x L mm</th>
<th>Part of the probe range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>High</td>
</tr>
<tr>
<td>1</td>
<td>0.043 – 0.13</td>
<td>'H</td>
<td>7 x 4.5</td>
<td>600</td>
</tr>
<tr>
<td>2</td>
<td>0.09 – 0.26</td>
<td>'H</td>
<td>5 x 4.5</td>
<td>1200</td>
</tr>
<tr>
<td>3</td>
<td>0.17 – 0.52</td>
<td>'H</td>
<td>4 x 4.5</td>
<td>1200</td>
</tr>
<tr>
<td>4</td>
<td>0.35 – 1.05</td>
<td>'H</td>
<td>4 x 4.5</td>
<td>1500</td>
</tr>
<tr>
<td>5</td>
<td>0.70 – 2.1</td>
<td>'H</td>
<td>4 x 4.5</td>
<td>250</td>
</tr>
<tr>
<td>6</td>
<td>1.5 – 3.4</td>
<td>'H</td>
<td>4 x 4.5</td>
<td>240</td>
</tr>
<tr>
<td>7</td>
<td>3.0 – 6.8</td>
<td>'H</td>
<td>4 x 4.5</td>
<td>300</td>
</tr>
<tr>
<td>8</td>
<td>6 – 13.7</td>
<td>'H</td>
<td>4 x 4.5</td>
<td>50</td>
</tr>
</tbody>
</table>

4.2.3 Local compensation of the field gradient

A method to make measurements in non-homogeneous fields is to use a set of compensating coils, intended to locally compensate the gradient (Fig. 12). The coil set is designed to create a gradient inverse to the local field gradient without modifying the measurement. For this, it is important to place the geometrical centre of the coil set at exactly the centre of the sample of the NMR probe.

Fig. 12 Principle of compensating coils
5. SOME SPECIAL MEASUREMENT CONDITIONS

5.1 On-the-fly measurement of fast ramping magnet

A special use of NMR is as a stand-by system when there are pulses of magnetic field or fast-programmed field variations as in the CERN PS. It gives some reference points in the cycle of the magnetic field. The NMR magnetometer is fed with a given frequency and we wait for the signal to appear when the corresponding value of the field is reached. The difficulty is to manage a proper field variation speed, in order to get a good NMR signal (Fig. 14). Another difficulty is to evaluate the delay between the signal detection and the real NMR resonance. This can be done experimentally and you can get then an accuracy of about 2 ppm.

![Fig. 14 Choice of field measurement points according to the slope](image)

5.2 Measurement of Tokamak magnets

At the Princeton TFTR Tokamak fusion magnet, measurements have been made to control the magnetic alignment of the toroidal coils shown in Figs. 15 and 16. In this arrangement the field is proportional to 1/R, the main radius of the annulus, and it is highly inhomogeneous, so the compensating coils presented previously have been used to allow NMR measurement.

![Fig. 15 Description of geometry](image)  ![Fig. 16 Assembly of the coils](image)
Such measurements have also been successfully made in Cadarache (France) on a similar magnet with the same type of gradient-compensation-coil system. An optical positioning system has been used for this purpose (Fig. 17).

Fig. 17  Field distribution in the toroidal magnet at Cadarache

Fig. 18  SPS magnetic cycle diagram

5.3 Field cycle of the CERN SPS (Fluxmeter measurement backed with NMR)

In order to measure with high precision and good time resolution the field in the CERN SPS cycle (Fig. 18), showing plateaus at 600 gauss (1 second) and 2 T (2 seconds), magnetic measurements have been made [7] by a system (Fig. 19) including:

A Precision Digital Integrator (PDI) recording the complete shape of the cycle, with a high resolution in amplitude and time, but possible slow fluctuations in offset and gain.

Two or three NMR probes controlled by a multiplexer and PT 2025 magnetometer chosen to measure, with NMR precision, at least two points of the cycle, if possible on a plateau. This system gives high precision points to the profile of the magnetic field cycle, allowing the curve recorded by the PDI to be calibrated exactly.
The overall precision obtained is about $10^{-5}$, with 1 µS response time. The comparison of the fixed NMR points to the corresponding output of the PDI, at each cycle of the field, gives a measure of the PDI drift and allows to verify whether this drift is linear and then permits it to be compensated continuously, producing a PDI accuracy of $10^{-5}$. This system has given good results over the last 3 years.

5.4 CERN PS deflection magnet

We have also carried out measurements on the inhomogeneous fields in a magnet of the CERN PS. There is a rule of thumb that says that if you have a long cylindrical-symmetry-gap magnet, you can expect to find an appropriate zone to place an NMR probe in the middle plane of the gap. Closer to the end of the poles, the signal would be poor. If an inner finger is needed in a vacuum chamber, its material must be chosen with extreme care. If you use welded stainless steel, there will be an alteration of the metallurgy in the welding area and ferromagnetic properties may appear, perturbing the homogeneity of the field or even destroying the signal. It seems best to use, for an assembly, stainless steel for machined pieces and brass for welded pieces. For brass however, the material should be tested before use, since some samples show unwanted magnetic properties.

In a CERN PS deflection magnet, such as that shown in Fig. 21, the vacuum chamber occupied the whole homogeneous zone, and an inner finger would have been too expensive. In that case, we had to add iron pieces, aligned with the gap, on both poles, allowing to extend the homogeneous zone and permitting the NMR probe to be placed there.

5.5 Measurements on MRI magnets

This is achieved with probe arrays. These arrays are half-circle shaped and equipped with 12 to about 30 probes, depending on the models (Fig. 22). By turning these arrays
around their diametrical axis, it is possible to achieve, on a spherical surface, a great deal (up to 500) of measurement points in less than 5 minutes. This permits the field of MRI machines to be controlled and shimming of the superconducting magnet.

Fig. 22  Example of a Metrolab 12# probe array

With such a probe array, it is important to have a good calibration from one probe to another. A difference may appear if pieces of paramagnetic material or small electronic components are near the probes. These may slightly distort the flux lines of the magnetic field and then create small discrepancies with adjacent probes. This requires a calibration of each probe array, in a very homogeneous field, and a correction table for each probe of the array. Thus, we achieve a relative accuracy of 0.1 ppm between each probe of an array so that a MRI magnet can be mapped within 0.1 ppm accuracy. For this technique a frequency modulation system, or open-loop principle, described in Section 2.1.3, giving a 2 – 3 Hz precision on a 40 MHz frequency, which corresponds to less than 10^7.

With such equipment, fitted with a good clock, temperature-controlled oscillator and a tightly fixed probe, we can estimate the decay of a superconducting magnet, for 1- or 2-hour intervals to an accuracy of 10^-8 per hour with good confidence.

5.6 Automatic probe calibrator in Saclay

Another common use of NMR measurement is performed in CEA Saclay by M. Tkatchenko and C. Evesque, who have set up an automatic system to calibrate Hall sensors. Several probes are connected to a multiplexer. In this system, one point is at 30 gauss, with an EPR probe, to partially fill the gap towards low fields (< 400 gauss). This development has been achieved in a collaboration between CEA Saclay and Metrolab.

REFERENCES


BIBLIOGRAPHY

A. Abragam, Principles of Nuclear Magnetism, Clarendon, Oxford.