Development of an NMR sensor (magnet and probe) for spectroelectrochemical applications

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Sonia Alves - CRB: 4280/8
To this point in my life, seven people have been mostly responsible for leading me to where I am today, and although it is not possible to list every contribution they have made, I list here the most important ones:

First of all, my mother, Isabel, whose constant words of appreciation and encouragement have allowed me to follow my dreams and passions wherever they may lead. Thank you for all your support, especially in my times of need!

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“Breakthrough innovation occurs when we bring down boundaries and encourage disciplines to learn from each other.”

(Gyan Nagpal)
Resumo

O acoplamento entre a ressonância magnética nuclear e estudos eletroquímicos vem sendo estudado cada vez mais devido à possibilidade de determinar mecanismos de reação e identificação, em tempo real, das espécies eletroformadas e da concentração de reagentes e produtos. O acoplamento entre estas duas técnicas não é simples uma vez que há interferência dos eletrodos da célula eletroquímica no sinal de RMN. Já foi mostrado que é possível monitorar reações eletroquímicas por RMN mas é necessário um grande esforço para poder obter sinais de alta qualidade como por exemplo envolver todos os cabos numa gaiola de Faraday. O presente trabalho de doutorado visou desenvolver um sensor de RMN de média resolução e sonda para melhorar a qualidade do sinal e minimizar o esforço necessário para conseguir analisar sistemas eletroquímicos usando a RMN de média resolução. Em específico, foi desenvolvido, com sucesso, um ímã do tipo H, assim como um modelo novo, denominado de HCM que, devido a problemas com o fornecedor dos magnetos permanentes, infelizmente não atingiu as especificações desejadas de intensidade e homogeneidade de campo magnético. Ainda mais, foi usado com sucesso um probe de RMN fazendo uso de uma bobina secundária para a acompanhar a eletrodeposição de cobre, como exemplo de reação eletroquímica. A bobina secundária aumentou a razão sinal-ruído dos experimentos de RMN e permitiu a obtenção de resultados mais confiáveis do que os obtidos apenas pelos dados eletroquímicos.

Abstract

Coupling between time-domain nuclear magnetic resonance (NMR) and electrochemical studies has been increasingly studied due to the possibility of determining reaction mechanisms and identification, in real-time, of the species formed during the reaction as well as the quantification of reagents and products. Coupling these techniques is not a simple task due to interference that the electrodes of the electrochemical cell produce in the NMR signal. It has been shown that it is possible to monitor electrochemical reactions using NMR but a great effort is needed in order to obtain high quality NMR signals such as using a Faraday cage to envelop all cables connected to the electrochemical cell. The present work aimed to improve the quality of the coupling between these techniques by developing a medium resolution NMR spectrometer to improve the quality of the signal and minimize the effort required to study electrochemical reactions using NMR. Specifically, an H-type magnet was successfully developed, as well as a new type of magnet which we call the HCM magnet that, due to manufacturing problems of the permanent magnets, did not reach the specified magnetic field strength and homogeneity. Furthermore, an NMR probe using an inductively coupled coil was used to follow the test reaction of copper electrodeposition. The secondary coil increased the signal-to-noise ratio of the NMR experiments and enabled them to yield more reliable results than electrochemical data alone.

Key-words: Electrochemistry-NMR coupling. Dipolar magnet. Inductively coupled coil.
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<th>Description</th>
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<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>EC-NMR</td>
<td>Electrochemistry coupled to Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>FID</td>
<td>Free Induction Decay</td>
</tr>
<tr>
<td>CPMG</td>
<td>Carr-Purcell-Meiboom-Gill pulse sequence</td>
</tr>
<tr>
<td>HCM</td>
<td>Hollow Cylindrical Magnet</td>
</tr>
<tr>
<td>RF</td>
<td>Radio Frequency</td>
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<tr>
<td>WE</td>
<td>Working electrode of an electrochemical cell</td>
</tr>
<tr>
<td>AE</td>
<td>Counter (or Auxiliary) electrode of an electrochemical cell</td>
</tr>
<tr>
<td>RE</td>
<td>Reference electrode of an electrochemical cell</td>
</tr>
<tr>
<td>SNR</td>
<td>Signal-to-noise ratio</td>
</tr>
<tr>
<td>PM</td>
<td>Permanent magnet</td>
</tr>
<tr>
<td>$E_{\text{app}}$</td>
<td>Potential applied during the electrochemical experiments, in Volts</td>
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</tbody>
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### List of symbols

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<tr>
<td>$B_0$</td>
<td>Static magnetic field vector, in T.</td>
</tr>
<tr>
<td>$B_1$</td>
<td>Pulsed magnetic field vector, in T.</td>
</tr>
<tr>
<td>$B_r$</td>
<td>Remanent magnetization, in T.</td>
</tr>
<tr>
<td>$M_0$</td>
<td>Net magnetization at equilibrium.</td>
</tr>
<tr>
<td>$M_i$</td>
<td>$i$th component of the magnetization. $i = x, y, z.$</td>
</tr>
<tr>
<td>$\omega_0$</td>
<td>Larmor angular frequency in rad $s^{-1}$.</td>
</tr>
<tr>
<td>$\nu_0$</td>
<td>Larmor frequency in Hz.</td>
</tr>
<tr>
<td>$T$</td>
<td>Tesla, the derived unit of the magnetic field flux density. In SI base units: $\text{kg} \cdot \text{s}^{-2} \cdot \text{A}^{-1}$</td>
</tr>
<tr>
<td>$\mathcal{H}$</td>
<td>Magnetic field homogeneity, in parts per million (ppm).</td>
</tr>
<tr>
<td>$I$</td>
<td>Nuclear spin.</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Gyromagnetic ratio, in rad $s^{-1} \cdot \text{T}^{-1}$.</td>
</tr>
<tr>
<td>$\hbar$</td>
<td>Reduced Planck constant</td>
</tr>
<tr>
<td>$\mu_0$</td>
<td>Magnetic permeability of free space.</td>
</tr>
<tr>
<td>$\phi_{\text{ext, int}}$</td>
<td>External/internal diameter.</td>
</tr>
<tr>
<td>$V_S$</td>
<td>Sample volume.</td>
</tr>
<tr>
<td>$R$</td>
<td>Resistance, in Ohm ($\Omega$).</td>
</tr>
<tr>
<td>$r$</td>
<td>Coil inner radius.</td>
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### APPENDIX B – DIMENSION MEASUREMENTS OF THE PERMANENT Magnets

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1 Introduction

Spectroscopic methods have been increasingly used to study electrochemical reactions *in situ*, known as spectroelectrochemical studies. The coupling of spectroscopy and electrochemistry has allowed scientists to gather information on electrochemical systems such as the real-time identification of the formed species and concentration of reagents and products. Two spectroscopic methods have been mostly used so far: ultraviolet-visible spectroscopy (UV-Vis) and Fourier transform infrared spectroscopy; this is because these methods are easily accessible to research and development laboratories and because coupling these techniques to electrochemistry does not bring significant technical difficulties, since little or no interference occurs during the coupling (1).

When working with electrochemical systems it would be most useful if the reaction pathway could be determined by coupling such systems to spectroscopic methods which provide data from which the molecular structures can be inferred. The methods most commonly used for this purpose are X-ray crystallography, nuclear magnetic resonance (NMR), mass spectrometry and gas/liquid chromatography. Of these methods, the most suited to determining molecular structures *in situ* during electrochemical reactions is NMR since it is the only method which allows the electrochemical cell to be inserted in the detection region. Furthermore, coupling NMR to electrochemistry (EC-NMR) can potentially allow scientists to determine the structure of reaction intermediates, which in turn could help understand reaction pathways.

Coupling electrochemistry to nuclear magnetic or even electron paramagnetic resonance (EPR) spectroscopies, however, poses some challenges. First of all, the electrodes which are used in the electrochemical cells are electrical conductors which, when inserted in the detection region of the NMR or EPR spectrometer interfere with the static magnetic field of the spectrometers ($B_0$) as well as with the ability of the probe to transmit and receive signals. For this reason, the spectral resolution and the signal-to-noise ratio (SNR) are greatly affected. In the case of EPR this is not such a limiting problem, since signals obtained from EPR measurements are inherently broad and its sensitivity is much higher than NMR. With NMR, however, these problems severely hinder the ability of the technique to deliver spectra from which important information can be extracted. This is why most of the studies which deal with EC-NMR focus on the development of electrochemical cells which reduce the interferences when high resolution NMR is coupled with the electrochemical studies (2–4).

In 2010 it was shown by our research group that coupling electrochemistry to low resolution NMR (also known as time-domain NMR) is a feasible way to monitor electrochemical reactions *in situ*, specially if the reaction involves the deposition of paramagnetic ions (5, 6). Aside from that, it has been shown that NMR can be used to monitor the
magnetoconvective effect (the effect of a magnetic field on a solution containing ions) which can be used to change the morphology of electrodeposits, reaction rate and other experimental parameters (7). Low resolution NMR spectrometers have a size and cost advantage over high resolution NMR spectrometers since they are much smaller (benchtop) and are based on permanent magnets rather than on superconducting magnets, which means that their maintenance costs are smaller, as no cryogenic liquids are required.

For their part, medium resolution NMR spectrometers combine the best of the high and low resolution spectrometers by operating with a permanent magnet as the magnetic field source capable of achieving a magnetic field homogeneity sufficient for obtaining chemical shift information from the sample with a resolution that comparable to that offered by high resolution spectrometers. Yet, their use hasn’t been explored for the analysis of electrochemical systems.

As mentioned previously, coupling electrochemistry and NMR is not a trivial task and therefore effort and time must be put into first optimizing the coupling between the techniques before the actual studies of the electrochemical system can begin. As such, it would be beneficial if a system existed where the coupling between electrochemistry and NMR was already optimized, allowing the user to dedicate his time to the study of his system of interest. Therefore, the aim of this Ph.D. thesis was to develop a medium resolution NMR sensor (both the magnet and the probe) which could be easily used to analyze electrochemical reactions. Furthermore, the probe was built using inductively coupled coils. This allows the system to be used to analyze high ionic strength samples, as well as allowing the probe to be used for low temperature experiments without fear of damaging the main probe circuitry.

1.1 EC-NMR coupling

This section is aimed at shedding some light into the state of the art regarding the coupling between electrochemistry and both high and low field NMR (EC-NMR) as well as a brief historical overview where the most important advancements in this area will be highlighted. Most of what will be shown here deals with the association of electrochemistry with liquid state NMR, as this Ph.D. thesis is focused in this field.

1.1.1 EC-high field NMR coupling

It was in 1975 that the in situ coupling between electrochemistry and nuclear magnetic resonance was first reported by Richards and Evans (8) when they observed the reduction of trans-1-phenyl-1-buten-3-one. To perform the EC-NMR experiments they built the electrochemical cell into a standard 5 mm NMR tube (Figure 1). Both the working (WE) and auxiliary (AE) electrodes were placed above the NMR detection region, the solution
was pumped into an inner tube containing the working electrode and later released into the NMR detection region through a capillary. The main advantage of this system was that it could be used directly with a conventional NMR probe (i.e. the probe requires no modifications). However, the working electrode (a platinum wire) was coated in mercury and the resolution of the NMR spectra was reduced due to the metallic components of the cell. Furthermore building this system was no easy task due to its complexity.

In 1987 Albert et al. studied the reduction of 2,4,6-tri-tert-butylphenol using $^{13}\text{C}$ NMR spectroscopy using a static procedure (as opposed to a flow setup) by inserting the electrodes directly into a rotating 10 mm NMR tube and a continuous flow procedure (i.e. pumping the solution from the electrochemical cell into the NMR detection region) (9). The working and auxiliary electrodes were mounted on a capillary where the former was melted into the capillary and the latter coiled around it. Due to technical difficulties, a reference electrode (RE) was not used and a special mounting unit was required to insert the electrode assembly into the NMR tube. The authors reported that in the static arrangement it was impossible to acquire $^{13}\text{C}$ NMR simultaneously with electrolysis but this was possible in the continuous flow arrangement. The main disadvantages of the methods described by the authors lie in the fact that the system is complex and, in the case of the continuous flow arrangement, a large amount of solution (and solvent) is required. Furthermore, the NMR probe required adaptations to fit the flow setup.

Figure 1 – First electrochemical cell used for electrochemistry and NMR coupling experiments.

Source: Reprinted with permission from Richards; Evans 1975 (8). Copyright 1975 American Chemical Society.
Mincey et al. used in 1990 an antimony-doped tin oxide (Sb-SnO$_2$) thin film which they deposited in the interior wall of a 5 mm NMR tube. This electrode was placed in the NMR detection region to successfully monitor the electrochemical reduction of $p$-benzoquinone (BQ) to hydroquinone (HQ). In this case, the metallic electrode in the NMR detection region had little effect on the resolution of the NMR spectra due to being a metallic thin film which makes the films transparent to radio-frequency waves (RF) as well as causing minimal distortions to the static magnetic field. The reaction was performed over a period of 12 minutes (the initial concentration of BQ was 0.1 mol L$^{-1}$ in D$_2$O) and the obtained $^1$H NMR are shown in Figure 2. However, the main drawbacks of this system are the use of a spinning NMR system and the complex apparatus required to perform the chemical vapor deposition of the Sb-SnO$_2$ within the NMR tube.

**Figure 2** – $^1$H NMR spectra obtained by Mincey et al. during the reduction of $p$-benzoquinone. 

a) Before the start of electrolysis (0.1 mol L$^{-1}$ in D$_2$O; supporting electrolyte was 0.1 mol L$^{-1}$ of KCl and 0.3 mol L$^{-1}$ of DCl as proton donor); b) after nearly 30 s, applied potential of -500 mV (vs. Ag/AgCl); c) after 80 s; d) after 140 s; e) after 200 s; f) after 250 s; g) after 308 s; h) after 360 s; i) after 410 s; j) after 480 s; k) after 550 s; l) after 680 s. The applied potential was 450 mV (vs. Ag/AgCl).

Following the work of Mincey, Prenzler et al. showed in 2000 that indeed metallic thin films can be used as electrodes inside the NMR detection region when they compared the NMR line broadening caused by a Pt wire, Pt mesh and Au thin film (11). The authors showed that a spiral-shaped Pt wire electrode increased the line width of the $^1$H NMR spectrum of semi-heavy water (HDO) by two orders of magnitude and the cylindrical Pt mesh electrode increased the line width by around one order of magnitude. Meanwhile the Au thin film barely affected the line width of the NMR signal (Figure 3). The thin film electrode was successfully used to monitor the electrochemical reduction of BQ.
1.1. EC-NMR coupling

**Figure 3** – Effect of introducing a WE in the NMR detection region. a) spiral Pt wire; b) cylindrical Pt mesh and; c) Au thin film.


For metallic films to be “transparent” to radio-frequency waves at least one of their dimensions must be smaller than its characteristic skin depth ($\delta$). The skin depth of a material is defined (12, 13) as the thickness of material required to reduce the intensity of the incident RF by 37%. Furthermore, $\delta$ is proportional to the frequency of the incident radiation, which means that as the magnetic field of the spectrometer decreases (and thus so too does the RF frequency decrease) the thickness of the films required for them to be effectively transparent to the RF frequency decreases as well.

**Figure 4** – Electrochemical cell developed by Klod et al. in 2009 with both working and auxiliary electrodes made from carbon microfibers.

Source: Reprinted with permission from Klod; Ziegs; Dunsch 2009 (14). Copyright 2009 American Chemical Society.

Since the previously mentioned thin film electrodes require specific technology that may not be readily accessible in all laboratories, Klod et al. developed carbon microfiber...
working and auxiliary electrodes in 2009 (14). These electrodes are both cheaper and much easier to assemble than their metallic thin film counterparts. The electrochemical cell was built into a standard 5 mm NMR tube (Figure 4) and noise suppression chokes were used to filter any noise that would enter the NMR spectra due to the presence of the electrodes in the NMR detection region. The researchers successfully used these electrodes to monitor the reduction of BQ to HQ which lasted for 6 h until the $^1$H NMR signal of BQ completely disappeared. However, carbon microfibers on their own are quite limited in the number of species which they can detect and, thus, require modifications to expand the range of detectable species (15).

1.1.2 EC-low field NMR coupling

The first paper reporting the use of low resolution NMR coupled to electrochemistry was published only as recently as 2010 (5) and focused on monitoring the concentration change of the copper-sorbitol complex during electrodeposition.

In 2012 Nunes et al. showed that low resolution NMR can be used to monitor the concentration change of paramagnetic species during electrodeposition (16). The researchers monitored the concentration of Cu$^{2+}$ using the idea developed by Bloembergen, Purcell and Pound in 1948 that $T_2$ is inversely proportional to the concentration of the paramagnetic species present in the solution (17). The WE and AE used for these experiments were made of Pt and an Ag wire was used as RE (Figure 5).

Figure 5 – a) The electrodes of the cell were as follows: WE and AE, platinum; RE, silver. b) Variation of the Cu$^{2+}$ concentration (□) and the potentiostat current (■) during the electrodeposition reaction.

(a) (b)

Source: Adapted with permission from Nunes et al. 2012 (16). Copyright 2012 American Chemical Society.
1.1. EC-NMR coupling

In 2014 Nunes et al. (18) monitored the reduction of 9-chloroanthracene using $^{13}$C NMR spectroscopy. They made use of the novel NMR pulse sequence SSFP (Steady State Free Precession) which greatly improved the SNR of the NMR experiment as well as the acquisition time. This study was performed using carbon microfiber working and auxiliary electrodes.

Also in 2014, Gomes et al. (7), using a system similar to that of Nunes et al. in 2012, observed that the electrodeposition rate of Cu$^{2+}$ increased when the reaction was monitored in situ. In this case, after one hour of reaction, 40% of the copper ions were deposited on the electrode. When the reaction was monitored ex situ only 27% of the copper ions were electrodeposited after the same reaction time (Figure 6a). This means that 48% more copper is deposited when the reaction is performed in situ$^1$ than when it is performed ex situ$^2$.

In 2015 Gomes et al. (19) again verified the same pattern of increased electrochemical reaction rates when in the presence of a magnetic field. This time, however, they used a unilateral NMR sensor (using a stray-field magnet which will be briefly discussed in Section 1.3.2.1). This study required building a Faraday cage around the system to isolate it from noisy RF signals present in the ambient and the results showed that, after 3 h of reaction, 40% of copper ions had been deposited when the reaction was performed in situ, compared to only 12% of ions that were deposited when the reaction was performed ex situ, after the same reaction time (Figure 6b).

Figure 6 – a) Results obtained by Gomes et al. in 2014 (7) using a center-field magnet: $B = 0$ (▲); $B \perp j$ (■) and $B \parallel j$ (●). b) Results obtained by Gomes et al. in 2015 (19) using a stray-field magnet: $B = 0$ (△); $B \perp j$ (□) and $B \parallel j$ (●)

Source: Reprinted from Gomes et al. 2014 (7) and Gomes et al. 2015 (19). With permission from American Chemical Society and Elsevier.

$^1$ in situ reactions are performed with the electrochemical cell in the NMR spectrometer detection region.

$^2$ ex situ reactions are performed outside the NMR spectrometer and samples are measured by NMR when the reaction is completed.
1.1.3 Magnetic field effect on electrochemical reactions

The results from Gomes et al. in 2014 and 2015 (7, 19) show that performing an electrochemical reaction in the presence of the magnetic field, \( B \), of the NMR spectrometer is not quite the same as performing it in the absence of \( B \). The reason for this is the magnetoelectrolysis effect which is known to stir the solution and increase the quantity of ions that reach the surface of the electrode, thus accelerating the reaction.

The magnetoelectrolysis effect is driven primarily by the magnetic field force, \( F_B \), which is equal to the cross product between the ion flow, \( j \), and the magnetic field, \( B \), and has units of N m\(^{-3}\), as shown in Equation 1.1.

\[
F_B = j \times B \tag{1.1}
\]

From the equation above we can immediately see that \( F_B \) should be zero when \( j \) and \( B \) are parallel and maximum when they are perpendicular. However, if we recall the results from Figure 6a we do not see a difference in the results obtained when the orientation between these quantities changes. This has been explained by Monzon and Coey in 2014 (20) who explain that local distortions of the electric field, caused by the edges of the electrodes as well as by imperfections on the electrode surface and gas bubbles that form on the electrode surface, create microscopic regions of space where \( j \) and \( B \) are no longer parallel, even if they are so at a macroscopic level.

The gradient of the magnetic field also generates a force that agitates the solution and can alter the morphology of the deposits on the electrode surface. This is known as Kelvin’s force and is given by Equation 1.2 (21).

\[
F_{\nabla B} = \frac{1}{\mu_0} c \chi_m (B \cdot \nabla) B \tag{1.2}
\]

where \( \mu_0 \) is the magnetic permeability of free space in units of T m A\(^{-1}\), \( c \), given in mol m\(^{-3}\), is the concentration of paramagnetic species in solution, \( \chi_m \) is the molar magnetic susceptibility, \( B \), in T, is the external magnetic field, \( \nabla \) is the Del operator and \( F_{\nabla B} \) has units of N m\(^{-3}\). Kelvin’s force effect may be seen in action in the results of Gomes et al. 2015 (19), where the magnet that was used for the experiment was a stray-field magnet which produces a high magnetic field gradient that also increases the electrodeposition rate of Cu\(^{2+}\) ions (Figure 6b).

As shown, both high and low resolution NMR have been successfully coupled with electrochemistry to study electrochemical reactions with the adaptations made to the electrochemical cell varying in complexity. A system where the problem of the coupling between the techniques has already been optimized would greatly benefit researchers in allowing them to focus more time on studying their electrochemical systems rather than on dealing with this time consuming process.
1.2 Brief NMR theory

To understand nuclear magnetic resonance, we must first understand what "resonance" is. Imagine that you are sitting at a swing and your friend gives you a push. The frequency at which you will oscillate (or swing) after he has applied the force is the natural frequency of the swing, or $\omega_0$. However, if your friend were to start pushing you periodically and the frequency of his pushes matched the natural frequency of the swing, then the amplitude of the swings will steadily increase to large values. In the same way, some atomic nuclei possess a natural frequency at which they resonate and is the fundamental property that NMR takes advantage of. This section covers the most basic concepts in NMR spectroscopy. Should you, the reader, be interested in a more detailed explanation of the concepts please refer to reference (22). From this point forward, the convention will be that \textbf{bold symbols refer to vector quantities}.

Ever since it was discovered that the resonance frequency of a nucleus depends on its environment, NMR has become one of the best methods for elucidating molecular structure, as well as being used in a variety of other applications, ranging from organic chemistry to medicine. Although the first reports of nuclear magnetic resonance were published in 1938 after observations of the phenomenon in molecular beams (23) it was only in 1945 that two independent research groups, at the Massachusetts Institute of Technology (MIT) and at Stanford University, observed the first NMR signals in bulk materials. The first group, led by Edward M. Purcell, observed the phenomenon on a sample of paraffin wax (24), while the second group, led by Felix Bloch, observed an NMR signal from the hydrogen nuclei of a water sample (25). These findings earned both scientists the Nobel prize in Physics in 1952.

The phenomenon of nuclear magnetic resonance occurs when the nuclei of certain atoms, possessing nuclear spin different from zero ($I \neq 0$) and magnetic moment ($\mu$), are placed under the influence of an external static magnetic field ($B_0$) (an interaction known as Zeeman interaction) and an oscillating magnetic field ($B_1$). When such a magnetic moment, $\mu$, interacts with $B_0$ the nuclei will try to align with the magnetic field and precess around it (26) - as a result of the torque exerted on the nucleus by the magnetic field - and the resulting energy levels of the system are (22):

$$E_m = -\frac{\gamma}{2\hbar} m B_0$$  (1.3)
Figure 7 – a) Energy levels with and without an applied $B_0$ for a system of nuclei with $I = \frac{1}{2}$; b) Representation of the precession of a magnetic moment $\mu$ around $B_0$.

(a) No magnetic field

(b) Applied magnetic field

where $m$ may assume the values $\{-I, -I + 1, \cdots, I - 1, I\}$ and $\hbar$ is Planck’s constant divided by $2\pi$. $\gamma$ is called the \textit{magnetogyric ratio}, a constant which is different for every nuclei. Nuclei with $I = \frac{1}{2}$ can either align themselves in favor or against $B_0$, however a small excess will align in the same direction as the magnetic field (if $\gamma > 0$), creating a net magnetization, $M_0$, that is aligned with $B_0$. A visual representation of the energy levels of a system constituted by nuclei with $I = \frac{1}{2}$ is shown in Figure 7a - where it can be seen that before a magnetic field is applied the magnetic moments are randomly aligned, as opposed to the case where $B_0 \neq 0$ - and a representation of the precession movement and the resulting magnetization is shown in Figure 7b.

The excess amount of atoms that align in favor of the magnetic field is governed by Boltzmann’s distribution which, for $I = \frac{1}{2}$, is given by:

$$
\frac{n_\beta}{n_\alpha} = \exp\left(\frac{-\Delta E}{k_B T}\right) = \exp\left(\frac{-\gamma \hbar B_0}{k_B T}\right) = \exp\left(\frac{-2\mu B_0}{k_B T}\right) \tag{1.4}
$$

where $n_\alpha$ is the number of particles in state $\alpha$ (the state with the lowest energy, $m = \frac{1}{2}$), $n_\beta$ is the number of particles in state $\beta$ (the state with the highest energy, $m = -\frac{1}{2}$), $\Delta E$ is the energy difference between both states, $k_B$ is Boltzmann’s constant, $T$ is the absolute temperature and we have used the equality stating that $2\mu = \gamma \hbar$ (for $I = \frac{1}{2}$). Since the argument of the exponential in Equation 1.4 is very small except at very low temperatures, and since the sensitivity of NMR is proportional to it, we can immediately see why NMR is not a very sensitive technique and why great efforts are directed at improving it.

The frequency with which the nuclear spins precess around the magnetic field, the
1.2. Brief NMR theory

resonance frequency or Larmor frequency, is given by Equation 1.5.

\[ \nu_0 = \frac{\gamma B_0}{2\pi} \]  

(1.5)

However, this resonance frequency, is also dependent on the local chemical environment of the nucleus, which allows NMR to provide information regarding the structure of the molecules (26).

1.2.1 Relaxation

To measure the resonance frequencies of the nuclei present in the molecules it is necessary to flip \( M_0 \) away from the direction of \( B_0 \). This can be accomplished in several ways, but it is most commonly done by pulsing an oscillating magnetic field, \( B_1 \). The length and power of the pulse will determine the flip angle, \( \theta \), which is given by the relationship (22):

\[ \theta = \gamma B_1 t_p \]  

(1.6)

where \( t_p \) is the duration of the pulse and:

\[ B_1 \approx 3 \left( \frac{PQ}{\nu_0 V_S} \right)^{1/2} \]  

(1.7)

where \( P \) is the transmitter power, \( Q \) is the quality factor of the probe circuit (which will be discussed in detail in Section 1.4.1.1), \( \nu_0 \) is the resonance frequency and \( V_S \) is the volume in the sample coil (27). Since the detection coil is placed on the \( x'y'z' \) plane (which is perpendicular to the direction of \( B_0 \)) the maximum signal induced on the detection coil will be when \( \theta = 90^\circ \).

After \( B_1 \) is turned off, \( M \), will gradually return to the equilibrium state, \( M_0 \), again aligning with \( B_0 \). This process is called relaxation and is achieved by two processes.

The first is spin-lattice relaxation, or longitudinal relaxation, which is governed by the rate constant \( T_1 \). \( T_1 \) measures the restoration of \( M \) to its equilibrium value of \( M_0 \) (Figure 8) (22).

\[^3 \] x' and y' refer to the axes in the rotating frame of reference. More and detailed information can be found in reference (28)
Chapter 1. Introduction

Figure 8 – Illustration of the spin-lattice relaxation process, governed by the rate constant $T_1$, which measures the rate at which $M$ returns to its equilibrium value of $M_0$. In this case $M_0$ has been rotated by an angle $\theta = 90^\circ$.

The second relaxation process is spin-spin relaxation, or transverse relaxation, which is governed by the rate constant $T_2$. $T_2$ measures the rate at which the component of $M$ on the $x'y'$ plane, $M_{x'y'}$, falls to zero through dephasing. This occurs because not all spins precess at the same frequency, therefore some of them spin slightly faster than the average while some precess at a slightly lower frequency than the average frequency, which, in time, reduces the intensity of $M_{x'y'}$ (Figure 9) (22).

Figure 9 – Illustration of the spin-spin relaxation process, governed by the rate constant $T_2$, which measures the rate at which the precessing spins dephase on the $x'y'$ plane.

However, $T_2$ is also affected by inhomogeneities in the magnetic field, which have the effect of reducing the value of $T_2$ to a value commonly known as $T_2^*$, which is related to $T_2$ through Equation 1.8.

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \gamma \Delta B_0$$

(1.8)

where $\Delta B_0$ is the inhomogeneity of the magnetic field.
1.2.2 Pulse sequences

As stated previously, to measure the $T_1$ and $T_2$ of the sample it is necessary to first rotate $M_0$ away from its equilibrium state by applying an oscillating magnetic field, $B_1$. $B_1$ is applied in short pulses, which means that a range of frequencies (rather than a single frequency) can be excited simultaneously and thus, all of the nuclei within the sample can be analyzed during the same measurement. The range of frequencies that is excited while $B_1$ is turned on is inversely proportional to the duration of the pulse.

$T_1$ and $T_2$ can be determined by using certain pulse sequences. The most common sequence used to determine $T_1$ is called inversion-recovery (29), while the sequence known as Carr-Purcell-Meiboom-Gill (CPMG - named after the scientists who developed it) is most commonly used to determine $T_2$ (28). Information about how the inversion-recovery pulse sequence works is not given here, but the reader is referred to reference (29) for the details, should curiosity arise.

1.2.2.1 CPMG pulse sequence

The CPMG sequence begins with a $90^\circ$ pulse\(^4\), which brings $M_0$ to the $x'y'$ plane. Due to imperfections of $B_0$, the FID\(^5\) decays with the constant $T_2^\star$ (Figure 10a).

To determine the value of $T_2$, a train of $180^\circ$ follows the initial $90^\circ$ pulse. The first $180^\circ$ pulse occurs after a time $\tau$ has passed and the remaining pulses occur after $2\tau$ (Figures 10a and 10b). The $180^\circ$ pulses rotate the spins around the $y'$ axis so that the spins that were previously dephasing due to their different frequencies, now start coming back together, or refocusing, on the $y'$ axis, creating a maximum in the net magnetization (an "echo" - Figure 10a), after which they dephase once again due to the inhomogeneity of $B_0$. The maximum amplitude of each successive echo will be exponentially lower than the previous one due to pure $T_2$ relaxation (the exponential decay rate is $T_2$ - Figure 10b).

\(^4\) The pulses are usually named after the flip angle that they induce in the sample spins.

\(^5\) The Free Induction Decay (FID) signal is the signal that is observed by the detector when the sample is allowed to relax to its equilibrium state.


**Figure 10** – a) Echo formed during the CPMG experiment b) CPMG pulse sequence used to determine $T_2$ and its resulting signal. The 90° pulse is represented by a black square, while the 180° pulses are represented by the white squares.

1.3 Magnets used in NMR spectrometers

A fundamental requirement for nuclear magnetic resonance experiments to be performed is the presence of a magnetic field, $B_0$, that will polarize the sample. This magnetic field should, ideally, be as intense as possible and completely homogeneous over the sample (with variations in the order of $10^{-8}$ T) while also being stable over time (30).

Nowadays, there are several magnetic configurations which can be used to generate the static magnetic field required by the NMR experiments. The different magnets that are
commonly used today can be classified in two distinct types: superconducting magnets and permanent magnets.

1.3.1 Superconducting magnets

**Figure 11** – Simplified diagram of the superconducting magnets routinely used in NMR investigations. The superconductor material must be kept cool by surrounding it with liquid helium and nitrogen.

Superconducting magnets are used in high resolution (or high-field) NMR spectrometers. These magnets consist of an electrical superconductor which generates the magnetic field as the current flows through the material. The main drawback of using superconducting magnets is their operation temperature, since electrical superconductivity can only be achieved at very low temperatures, usually below the boiling point of nitrogen (although some materials can become superconductors at temperatures as high as 134 K) (31). Therefore, cryogenic liquids, which must be periodically refilled (liquid helium and liquid nitrogen), must be used to keep the material in its superconducting state (Figure 11). While these magnets are capable of generating magnetic fields with an intensity in the range from 4.7 T to 23.5 T (31) the cost associated with the purchase and maintenance
of such spectrometers limits their use to laboratories and institutions with considerable financial resources. However, a new commercial magnet which does not require cryogenic liquids has been reported and could pave the way for new cryogen-free spectrometers with a much lower maintenance cost (32).

1.3.2 Permanent magnets

Permanent magnets, as the name suggests, are materials that generate their own magnetic field after they have been magnetized by an external magnetic field (33). Permanent magnets produce a magnetic field that is much less intense than their superconducting counterparts but require little maintenance, work well in ambient temperatures (and therefore require no cryogenic liquids to operate) and, depending on the geometry used, have the advantage of being portable, which enables their use in different locations such as within a fume hood, high pressure environments or even outside the laboratory. It is important to point out that permanent magnets still require a controlled temperature environment since their magnetization, which is responsible for the produced magnetic field, changes with the magnet’s temperature (33), although it is possible to use two different permanent magnetic materials to produce a thermally stable magnetic field at the expense of a lower magnetic field strength (34).

Several materials can be used to build the permanent magnet for NMR applications. Before the discovery of rare-earth magnetic materials, most magnets were made from the alloy consisting of iron, aluminum, nickel and cobalt (alnico) (35). Since 1970, when rare-earth magnets were discovered, magnets have increasingly been built with either samarium and cobalt (SmCo) or neodymium, iron and boron (NdFeB) alloys.

Permanent magnet structures can be classified in two types: stray-field magnets and center-field magnets (36). Next, a brief description of these types of magnets will be given, as well as some of their advantages and shortcomings.

1.3.2.1 Stray-field magnets

Stray-field magnets produce a magnetic field that is not confined in space but rather spreads out in space. This makes handling such magnets quite dangerous, as the stray magnetic field can attract magnetic objects in their vicinity. The bottom side of the magnet, however, is usually shielded with a ferromagnetic yoke. These magnets allow scientists to study large samples, since they can be simply placed on top of the magnet. The magnetic field, \( B_0 \), can be oriented either parallel to the magnet surface (Figures 12a and 12c) or perpendicular to it (Figures 12b and 12d). A simple way to adjust the magnetic field to increase its homogeneity in the region of interest is to add gaps between the magnets (this process is also known as passive *shimming* - Figures 12c and 12d).
Magnets similar to those in Figures 12a and 12c collect the signal from a thin slice parallel to the sensor surface, while magnets similar to those in Figures 12b and 12d collect the signal from a larger volume. Furthermore, by tuning the probe to different frequencies it is possible to collect the signal from different heights, typically ranging from a few millimeters to a few centimeters which translates to field strengths ranging approximately from 0.1-0.5 T (36).

Figure 12 – Stray-field magnets with soft ferromagnetic yokes (gray) used for NMR measurements. The sample (not shown) is placed on top or above the magnet. The field lines are either parallel (a,c) or perpendicular (b,d) to the magnet surface. Gaps between the magnets are a simple way to shim the magnetic field (e,d). The magnetization direction of the permanent magnets is represented by the white arrow.

1.3.2.2 Center-field magnets

There are three main magnetic structures used in NMR devices that generate a magnetic field that is confined to its bore (or confined to its center). The first two are the H-type and C-shaped magnets, where the magnetic materials are mounted on to a soft magnetic material of high permeability and saturation magnetization box (such as low-carbon steel), which closes the magnetic circuit (Figure 13a and 13b ). However, the weight and volume of these structures is much larger than the weight of the permanent magnet, which does not allow for much mobility of the devices.
Another structure is the Halbach array, developed in 1980 by Klaus Halbach (Figure 13c) (37), in which the mass and volume of the magnetic material is greatly reduced in comparison to the other previously discussed structures (38, 39). In theory, the Halbach array would be comprised of a single hollow magnetic cylinder whose magnetization angle is rotated continuously by 360° from one side to the other (the magnetization direction is perpendicular to the vertical axis of the cylinder). This would create a magnet whose magnetic field is completely confined within its bore (without a stray field) and which is perfectly homogeneous (37).

Figure 13 – Configurations of dipoles made with permanent magnets: a) H-type, b) C-shape and c) Halbach array. The magnetization orientations of the permanent magnets and the resulting magnetic field \( B_0 \) are indicated by black and red arrows, respectively. \( B_{0S} \) is the magnetic field generated in the Halbach array due to its segmentation.

In practice, however, it is impossible to build a Halbach array with a perfectly rotating magnetization in a single piece. Therefore, many segments of different magnetization directions must be used. This practical limitation has its effects both on the magnetic field strength, \( B_{0S} \), and homogeneity, \( H \), of the Halbach array, since both improve with an increase in the number of segments, \( k \), used, as shown by Equations 1.9 and 1.10, respectively (41).

\[
B_{0S} = K_0 B_r \ln \left( \frac{r_{outer}}{r_{inner}} \right) \quad (1.9)
\]

\[
H(\text{ppm}) = 2 \frac{|K_k|\gamma_k}{K_0 \ln \left( \frac{r_{outer}}{r_{inner}} \right)} \left( \frac{r}{r_{inner}} \right)^k \times 10^6 \quad (1.10)
\]
where:

\[
K_n = \frac{\sin \left( \frac{n+2}{K} \pi \right)}{\frac{n+2}{K} \pi} \tag{1.11}
\]

\[
\gamma_n = \frac{n+1}{n} \left[ 1 - \left( \frac{r_{\text{inner}}}{r_{\text{outer}}} \right)^n \right] \tag{1.12}
\]

\(B_r\) is the remanent magnetization which is the magnetization that remains in a material after an external magnetic field is removed and \(r\) is the radius within which the homogeneity is being calculated.

Aside from the magnetic field homogeneity that can theoretically be achieved, the Halbach array is extensively studied by scientists (many papers are found in the literature, but only a small selection of them is presented in the bibliography) (42–47) due to three main reasons (48):

- They possess the highest ratio of magnetic field intensity per magnet mass, which can be perfectly homogeneous in ideal conditions.
- They generate a magnetic field that is perpendicular to the longitudinal axis of the cylinder. This allows the use of solenoidal coils for NMR sample excitation (the advantage of using a solenoid coil will be evident in Section 1.4.1.2).
- They have no need for ferromagnetic yokes and therefore saturation effects do not need to be considered during the magnet design.

However, even with these favorable characteristics, the Halbach array still requires several magnetic pieces to produce a strong and homogeneous magnetic field (recall Equations 1.9 and 1.10). This poses some challenges due to the repulsion and attraction forces that such pieces generate during the construction of the array which must be countered by a strong mechanical structure, capable of keeping the magnets in place and always oriented in the right direction. Furthermore, not all permanent magnets may be equally magnetized (both in strength and orientation) even if they all undergo the same magnetization process, which affects the quality of the magnetic field intensity and homogeneity of the Halbach array (40).

1.4 NMR probes

The probe of the NMR spectrometer is a very important piece of hardware that allows the user to carry out the NMR experiments. It functions as an antenna where the sample is placed, irradiated with RF radiation and its RF response detected. The probe may also perform other functions, depending on the hardware that is installed, such rotating the sample (this is done to reduce the width of the NMR peaks), temperature stabilization
of the sample, cooling of the electronic circuitry of the probe (to around 20 Kelvin to improve the signal detection efficiency - these are called cryogenic probes) or even creating magnetic field gradients (which are required for imaging experiments and other methods) (49).

The probe alone, however, can’t do much, as it is incapable of generating the RF waves (pulses) with which the sample needs to be irradiated or of processing the acquired signal from the sample. Therefore, the probe is only one part in the larger electronic circuit required for the NMR experiment which can be schematically synthesized as shown in Figure 14.

**Figure 14** – Block diagram representation of the circuitry required in an NMR spectrometer.

The function of each of the blocks in Figure 14 is, broadly speaking, the following (30, 50):

- The *RF transmitter* is responsible for generating, amplifying, adjusting the phase, and modulating the RF frequency (into pulses).

- The *signal receiver* is responsible for amplifying the small NMR signal, digitizing and sending it to a computer for processing and visualization.

- The *probe* is where the sample is inserted and is responsible irradiating the sample with RF waves and for detecting the signal induced by the sample, as well as maintaining its temperature at a constant value.

- The *duplexer* is basically a switch that allows the probe to first transmit the RF radiation from the transmitter to the sample and then receive the response signal from the sample and send it to the receiver.

The most common electric circuit of the NMR probe is shown in Figure 15 and consists of one variable capacitor, $C_T$, in parallel with the transmission/detection coil, $L_P$, with both connected to capacitor $C_M$, with both capacitors being non-magnetic.
C\textsubscript{T} is the capacitor that will allow the circuit to resonate\textsuperscript{6} at the appropriate resonance frequency (which is the Larmor frequency of the observed nuclei) thereby increasing the detected signal. The resonance frequency of the circuit in Figure 15, in radians per second, is inversely proportional \( L\textsubscript{P}, C\textsubscript{T} \) and \( C\textsubscript{M} \) (Equation 1.13). The variable capacitor \( C\textsubscript{M} \) is called the matching capacitor and its function is to adjust the impedance\textsuperscript{7} of the circuit so as to match the purely resistive impedance of the rest of the circuit and transmission lines (which is usually 50 \( \Omega \)) and thus receive and transmit the signals with maximum power transfer and minimum signal reflection (49, 30, 51).

\[
\omega_0 = \sqrt{\frac{1}{L_p (C_T + C_M)}} \tag{1.13}
\]

**Figure 15** – Electric circuit of the most common NMR probe, consisting of two variable capacitors, \( C\textsubscript{M} \) and \( C\textsubscript{T} \), and one coil, \( L\textsubscript{P} \).

The coil, \( L\textsubscript{P} \), must be designed in such a way that it produces an oscillating magnetic field, \( B_1 \), that is perpendicular to the magnetic field produced by the magnet, \( B_0 \). It is also important that \( B_1 \) be as homogeneous as possible within the detection region.

### 1.4.1 The coil

As mentioned in Section 1.3, NMR spectrometers may operate using two different kinds of magnets: center-field or stray-field magnets. In the same way, two types of coils exist that can be used with each type of magnet.

Stray-field magnets require surface coils which, just as the magnets, generate a magnetic field that is not contained to a single region of space. Several geometries exist for

\textsuperscript{6} Electric circuits containing capacitors and inductors resonate because as the current flows from the capacitor to the inductor it builds up its magnetic field. As the capacitor is discharged and the current reaches zero, the magnetic field of the inductor will generate a current (since inductors are opposed to changes in the current) in the circuit, thus recharging the capacitor.

\textsuperscript{7} Impedance is the overall opposition that an electric circuit or component shows to the passage (resistance - Resistors) and/or change (reactance - Capacitors and Inductors) of current.
surface coils, such as a single-loop, spiral and multi-loop coils (Figure 16). Probes using these coils are useful as they can detect signals at different altitudes above the surface of the magnet, depending on the frequency to which the probe has been tuned. However, as the height of the detection slice increases, the acquired signal becomes much lower and the maximum altitude is limited to the few millimeters range. However, these coils are not the focus of this work and the reader is referred to reference (52) to find more information on them.

Figure 16 – Some of the surface coils developed for use with stray-field magnets. a) single loop coil; b) spiral coil and; c) double loop coil.

Source: Personal collection.

Center-field magnets require the use of volume coils. These coils also generate a magnetic field that is (ideally) homogeneous within the detection volume. As is the case with surface coils, several configurations exist of volume coils such as the solenoid, saddle-coil and birdcage coil (Figure 17).

Figure 17 – Some of the volume coils developed to be used with center-field magnets. a) Solenoid coil; b) Saddle-coil and; c) Birdcage coil. The red arrows represent the direction of the resulting magnetic field, $B_1$, and the black arrows represent the direction of the current, $i$, flowing through the coil. The yellow circle represents the sample position within the coil.

Source: Personal collection.

The solenoid is the simplest type of coil consisting of a single wire wound into a tightly packed helix. This type of coil produces a magnetic field that is parallel to its vertical axis. The saddle coil is, perhaps, not as simple as the solenoid, but still quite simple to
build. It consists of two square loops that have been pressed on to a cylindrical shell. Both loops carry the same current and generate a magnetic field that is perpendicular to its longitudinal axis. The birdcage coil consists of two circular loops connected to each other by several strips (or wires) of an electrical conductor.

Regardless of the coil that is ultimately used, all coils share some parameters that can be used to help compare them and their performance to each other. The most important parameters are the Q factor, the signal-to-noise ratio (or SNR) and the produced $B_1$ (both its intensity and homogeneity).

### 1.4.1.1 Quality factor

If an electric circuit containing an inductor (coil) and a capacitor (this is also known as a tank circuit) were to oscillate at its resonance frequency without any power losses (due to the resistance of the wires, for example) it would oscillate perpetually. However, since some power is lost due to the resistance of the wires (Ohmic heating), at some point in time, the oscillations will die out. These circuits are said to be damped. The quality factor (also known as Q factor) is a measure of how long these oscillations last in the circuit, or how damped it is, with higher Q’s corresponding to less damped circuits (i.e. the circuit resonates for much longer) and lower Q’s corresponding to very damped circuits (i.e. the oscillations die out very quickly). Another way to think of the Q factor is that it is a measure of how much energy is lost per oscillation. High Q factors describe circuits where energy is lost at a very small rate and therefore will oscillate a lot longer. Conversely, low Q factor circuits lose energy at a higher rate and therefore oscillate for a smaller period of time (Figure 18) (53).

**Figure 18** – Current oscillating within a circuit without any losses (undamped - black line), a damped circuit with high Q factor (red line) and a damped circuit with a low Q factor (blue line).

The Q factor can be determined using Equation 1.14, which is the ratio between the
central frequency, $f_c$, at which the circuit is tuned and its bandwidth, $\Delta f_{-3dB}$. The limits of the bandwidth, $f_1$ and $f_2$, are the frequencies around the central peak where the energy stored in the circuit has fallen by 3 dB (or around 50%) and the current intensity has fallen to nearly 70.8% of the maximum amplitude, as shown in Figure 19.

$$Q = \frac{f_c}{\Delta f_{-3dB}} = \frac{f_c}{f_2 - f_1} \quad (1.14)$$

**Figure 19** – The bandwidth of an oscillator circuit, $\Delta f_{-3dB} = f_2 - f_1$, is shown on a graph of current intensity as a function of frequency.

Equation 1.14 gives us the Q factor of the whole tank circuit and Equation 1.15 gives us the Q factor of the coil itself:

$$Q = \frac{\omega_0 L}{R_L} \quad (1.15)$$

where $\omega_0$ is the angular frequency at which the coil is operating (the Larmor frequency of the analyzed nuclei), $L$ is its inductance and $R_L$ is the resistance of the coil.

The next section will show that the Q factor of the coil is closely related to the signal-to-noise ratio (SNR) that can be obtained from the NMR experiment and is, therefore, an important parameter which needs to be controlled when building the coil for the NMR probe as it controls the bandwidth and consequently the range of frequencies that can be detected by the probe.
1.4. NMR probes

1.4.1.2 Signal-to-noise ratio

The signal-to-noise ratio, or SNR for short, is, as the name implies, a measure of how much larger the signal obtained with the probe is than the noise that is also detected. The signal is the desired information that we desire to obtain which, in the case of NMR, is the small magnetization produced by the sample that induces a voltage in the detection coil. This signal is induced in the coil by each of the magnetic moments, \( \mathbf{m} \), present in the sample (which collectively generate \( \mathbf{M}_0 \)). It is shown in Annex A that the SNR of the NMR experiment is given by (54):

\[
\psi_{\text{RMS}} = \frac{KB_1^\top V_S N \gamma^2 \hbar (I + 1)}{7.13 k_B T_S} \left( \frac{p}{l T_c \Delta f k_B F \zeta} \right)^{1/2} \frac{\omega_0^{7/4}}{(\mu \mu_0 \rho(T_c))^{1/4}} \tag{1.16}
\]

where \( K \) is a factor that accounts for the inhomogeneity of \( \mathbf{B}_1 \), \( B_1^\top \) is the component of \( \mathbf{B}_1 \) (\( \mathbf{B}_1 \) is the magnetic field produced by the coil by unit current) perpendicular to \( \mathbf{B}_0 \), \( V_S \) is the volume of the sample, \( N \) is the number of nuclear spins at resonance per unit volume, \( k_B \) is Boltzmann’s constant and \( T_S \) is the temperature of the sample, \( l \) is the conductor’s length, \( p \) is its circumference, \( \mu \) is the relative magnetic permeability of the wire and \( \rho(T_c) \) is the resistivity of the conductor, which is a function of its temperature, \( F \) is the noise figure of the preamplifier (which is a measure of the quality of the preamplifier) and \( \zeta \) is the term that accounts for the contributions of the Q factor and fill factor\(^8\) of the coil which may be reasonably well known from experience. Of these factors, three are solely dependent on the geometry of the coil: \( K B_1^\top \), which is the effective magnetic field produced by a unit current flowing in coil over the sample volume and \( p \) and \( l \) which are the perimeter and length of the conductor, respectively. Thus it may also be shown (also in Annex A) that the SNR of different coil geometries is different. For the case of the solenoid and saddle-coil their respective SNR is given by (54):

\[
\psi_{\text{Solenoid}} \propto 0.29 \mu V_S / r \quad \psi_{\text{Saddle}} \propto 0.094 \mu V_S / r \tag{1.17}
\]

where \( r \) is the radius of the coils. From the above equations we can see that the SNR of the solenoid coil is around 3 times larger than the SNR of the saddle coil. Furthermore, it may also be shown that to achieve the same SNR with the solenoid and saddle-shaped coils, the 90° pulse when using the saddle coil is three times longer than the 90° pulse when using the solenoid (54).

The main takeaway from the section above is that it is more advantageous to use solenoid coils than saddle coils, since they are much easier to build and produce a higher SNR (provided all geometric parameters of the coils are equal) as well as having a shorter 90° pulse length.

---

\(^8\) The fill (or filling) factor is a measure of the fraction of the volume of the coil that is occupied by the sample.
1.4.2 Probes with inductively coupled coils

Now that we have looked at the properties of single-coil probes, we look at the use of a secondary coil and its advantages to the NMR experiment. To clarify, the secondary coil is not physically connected (through a wire) to the rest of the probe. Instead, it is magnetically linked to the primary coil of the system, which allows it to be placed much closer to the sample. At this point it is worth explaining some terminology here: the primary coil, $L_P$, is the coil that is connected to the variable capacitors, $C_M$ and $C_T$, and the RF transmission/detection system, while the secondary coil, $L_S$, is only connected to a non-magnetic fixed capacitance capacitor, $C_S$. The circuit in Figure 20a shows simplest electric circuit of a probe with a secondary coil. From now on, this type of probe will be called an inductively coupled probe.

Figure 20 – a) Electric circuit of an NMR probe using a secondary coil (inductively coupled probe). The secondary coil is connected to a single fixed capacitance non-magnetic capacitor, $C_S$, and M represents the mutual inductance between the two coils. b) Equivalent circuit of the NMR inductively coupled probe. The mutual inductance between the coils has been replaced by a coil of inductance $M=k\sqrt{L_P L_S}$, where $k$ is the coupling coefficient which ranges from 0 (inductors are not coupled) to 1 (highly coupled inductors), and two coils of inductances $L_P-M$ and $L_S-M$, respectively.

To understand how the introduction of the secondary coil improves the overall performance of the NMR coil, we must understand what a balanced circuit is. A circuit is said to be balanced with respect to ground if its two sides are symmetrical. When circuits are imbalanced, currents in the ground start to flow because part of the current that should be carried by conductor having the largest capacity to earth is diverted to the ground. Therefore, the current in the two sides of the circuit becomes unequal and results in a component of current that flows, in parallel to the circuit, and returns through the ground. These ground currents give rise to more energy loss (electric or ohmic losses) and cause the radiation from the system to be greatly increased (55). These radiative energy
losses occur in antennas due to the emission of electromagnetic waves as the electrons move through the wires, which dissipates energy.

It may not immediately be clear that a circuit such as that represented in Figure 20a is balanced. However, if we look at the equivalent circuit, shown in Figure 20b it becomes clear that this circuit is indeed balanced. In this equivalent circuit the mutual inductance between the coils has been replaced by a coil of inductance \( M = k \sqrt{L_P L_S} \), where \( k \) is the coupling coefficient, a parameter that measures the degree of coupling between the coils (it is a measure of the fraction of the magnetic flux lines from the primary coil that enter the secondary coil) which ranges from 0 (inductors are not coupled) to 1 (highly coupled inductors), and two coils of inductances \( L_P - M \) and \( L_S - M \), respectively. Therefore, such a probe, because it is balanced, will have lower electric and radiative losses and will also prevent any currents from flowing in the ground. Furthermore, the use of a secondary coil allows the volume in the sample to be reduced which brings its own advantages like a lower total energy required to drive the reactions as well as a lower power requirement for the \( B_1 \) pulses used to flip the magnetization in the sample, which reduces the chances of heating it.

It is possible to show that circuits such as that of Figure 20a have two angular resonance frequencies given by the two positive solutions of Equation 1.18 (the full calculation is given in Appendix A).

\[
\omega_0 = \pm \frac{1}{\sqrt{2}} \sqrt{\omega_P^2 + \omega_S^2 \pm \sqrt{\left(\omega_P^2 + \omega_S^2\right)^2 - 4\omega_P^2\omega_S^2(1-k^2)}} \quad (1.18)
\]

From Equation 1.18 we can find that the angular resonance frequencies of the probe lie outside the interval \( [\omega_P, \omega_S] \). The intensity of the current at each of the coils can be calculated and is given by (56):

\[
i_P(\omega) = \left[ k^2 + \left\{ \frac{1}{Q_P} + j \left( 1 - \frac{\omega_P^2}{\omega^2} \right) \right\} \left\{ \frac{1}{Q_S} + j \left( 1 - \frac{\omega_S^2}{\omega^2} \right) \right\} \right]^{-1} \left\{ \frac{1}{Q_S} + j \left( 1 - \frac{\omega_S^2}{\omega^2} \right) \right\} \frac{v}{\omega L_P} \quad (1.19)
\]

\[
i_S(\omega) = \left[ k^2 + \left\{ \frac{1}{Q_P} + j \left( 1 - \frac{\omega_P^2}{\omega^2} \right) \right\} \left\{ \frac{1}{Q_S} + j \left( 1 - \frac{\omega_S^2}{\omega^2} \right) \right\} \right]^{-1} \frac{jkv}{\omega \sqrt{L_P L_S}} \quad (1.20)
\]

where \( j \) is the imaginary unit.

From Equations 1.19 and 1.20 we can see that the current intensity in the coils is dependent on the Q factor, inductances and resonance frequencies of the coils, the coupling coefficient, \( k \), and the voltage, \( v \), delivered by the voltage source. Two distinct peaks will only be observed if the two coils are overcoupled, which is when the coupling coefficient, \( 0 < k < 1 \), is close to 1\(^9\). This coefficient quantifies the fraction of magnetic flux lines of the

\(^9\) as \( k \) becomes smaller, the resonance peaks come closer together, eventually merging into a single broad peak.
primary coil that enters the secondary coil. If $k = 1$ all magnetic flux lines of the primary coil enter the secondary coil.

**Figure 21** – Current modulus (a) and phase (b) as a function of frequency for a probe with the following characteristics: $\omega_0, P = 16$ MHz, $\omega_0, S = 29.6$ MHz, $L_P = 2.03 \mu$H, $L_S = 0.93 \mu$H, $Q_P = 106$, $Q_S = 120$ and $k = 0.46$.

![Current Modulus and Phase](image)

Figure 21 shows the current modulus and phase in the primary and secondary coils plotted using Equations 1.19 and 1.20. We see that the phase of the currents in both coils is opposite at the lower frequency peak and equal at the higher frequency peak (Figure 21b). This means that the magnetic fields produced by the coils interfere destructively at the lower frequency resonance peak and constructively at the higher frequency resonance peak. Thus, when using such probes for NMR applications, it is desirable to use the higher frequency resonance peak to avoid deteriorating $B_1$. Furthermore, given that the magnetic fields of both coils interfere constructively at this peak, the total $B_1$ at the sample will be the sum of these fields, which allows the $B_1$ of the primary coil to be
less intense (which reduces the power needed to generate it) than in the case where no secondary coil is used to achieve the desired magnetization rotation.

1.5 Brief electrochemistry theory

The last topic that needs to be discussed before the results of this project is the theory of electrochemistry. Electrochemistry is a vast field of chemistry that deals with the interrelation between electricity and chemical effects. This field deals with both the creation of electricity due to chemical reactions as well as the chemical transformations that occur due to the passage of electricity. Electrochemical reactions are present in our day-to-day lives in devices such as batteries (which are going to be more and more relied on in the future) and fuel cells, products such as aluminum and chlorine which are obtained through electrochemical processes or even corrosion phenomena. The basic principles that govern all of these processes will be discussed next.

Electrochemistry is, essentially, concerned with the processes and factors that govern the passage of charge from an ionic conductor (the electrolyte) to an electronic conductor (the electrode). The events that occur at the electrode/electrolyte interface when an electric potential is applied and current passes is of utmost importance to electrochemistry. In the electrode, charge is transported by the movement of electrons (and holes\textsuperscript{10}), while charge moves in the electrolyte through the movement of ions. An important feature of the electrolyte is that it must have a low resistance (i.e. it must be sufficiently conductive) to allow the movement of the charges to occur (1).

Since electrochemistry is concerned with the events that occur at the electrode/electrolyte interface, it would be ideal if one such isolated boundary could be studied. However, it is experimentally impossible to study one isolated boundary and instead we must be content with studying the systems commonly known as electrochemical cells which generally consist of two electrodes separated by one or more electrolyte phases (Figure 22).

Within the cell, the overall reaction taking place is composed of two independent reactions, or half-reactions, which occur at each of the two electrodes. Furthermore, each half-reaction is dependent on the interfacial potential difference at the respective electrode. However, we are generally interested in only one of this reactions and the electrode at which this reaction of interest occurs is called the working electrode. To be able to focus on the reactions that occur at this electrode, the other half of the cell is standardized by using a reference electrode whose composition remains essentially unaltered during the reaction. The hydrogen electrode is the internationally recognized standard reference electrode (it is also known as the standard hydrogen electrode or SHE), which has all components at unit activity (\(a=1\)). From an experimental point of view, this electrode

\textsuperscript{10} An electron hole is the lack of an electron at a position within an atom or atomic lattice where an electron could exist.
is not very convenient and therefore other reference electrodes are generally used such as those presented in Table 1.

**Figure 22** — Example of an electrochemical cell consisting of two electrolytic phases separated by a porous disk.

**Table 1** — Common aqueous reference electrodes used for electrochemical experiments.

<table>
<thead>
<tr>
<th>Reference electrode</th>
<th>Potential vs. SHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard hydrogen electrode (SHE)</td>
<td>0.000 V</td>
</tr>
<tr>
<td>Saturated calomel electrode</td>
<td>+0.242 V</td>
</tr>
<tr>
<td>Silver-silver chloride electrode</td>
<td>+0.222 V</td>
</tr>
<tr>
<td>Copper-copper(II) sulfate electrode</td>
<td>+0.340 V</td>
</tr>
</tbody>
</table>


Because the composition of the reference electrode is constant so too is its potential. Therefore, any changes within the electrochemical cell can be credited to the working electrode. For this reason, when performing an electrochemical reaction we are controlling/observing the potential of the working electrode with respect to the reference electrode. Another way to view this is that we are controlling/observing the energy of the electrons within the working electrode (58, 59). During electrolysis, when the potential of the working electrode is driven to more negative values (e.g. by connecting it to the negative side of a battery or power supply), the energy of the electrons within it is raised. If this raise is high enough, the electrons may transfer to the lowest unoccupied molecular orbital of species in the electrolyte (thus creating a reduction or cathodic current - Figure 23 a). On the other hand, if the potential of the electrode is shifted towards more positive values then the energy of the electrons will be decreased. If this energy decrease
is large enough, electrons from the highest occupied molecular orbital from species in the electrolyte may transfer to the electrode (creating an oxidation or anodic current - Figure 23 b). The standard reduction potentials$^{11}$, $\varepsilon^0$, of the specific chemical substances in the system dictate the critical potentials at which these processes occur (1).

**Figure 23** – Representation of the energy levels of the electrons in the working electrode. a) Reduction of species A occurs when the energy levels of the electrons shift to more negative values. b) Oxidation of species A occurs when the energy levels of the electrons shift to more positive values. The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of species A are shown.

1.5.1 Three-electrode electrochemical cells

As previously mentioned, it would be ideal if one could measure the potential drop across a single electrode/electrolyte boundary to study the events that occur there. Since this is not possible, one always measures the potential between across two electrode/electrolyte boundaries as well as the potential drop through the solution itself. In a two-electrode cell where the potential drop across the solution, $E_s = iR_s$ (where $i$ is the current and $R_s$ is the resistance of the solution), is small and doesn’t affect the potential of the reference electrode we can approximate the potential drop at the working electrode to be equal to the applied potential $E_{WE} \approx E_{app}$, which allows us to effectively study the interface of the working electrode independently of the other (1).

$^{11}$ Standard reduction potentials (SRP) are a measure of how likely a substance is to be reduced at standard conditions. The more positive this potential, the more likely the species is to be reduced. Conversely, the more negative this potential, the more likely the species is to be oxidized. If the applied potential is more positive than the SRP, then a reduction current will flow through the electrode/electrolyte boundary. If the applied potential is more negative than the negative SRP, then an oxidation current will flow at the boundary. No current flows if the applied potential lies in the range between SRP and -SRP.
Chapter 1. Introduction

In many systems, however, \( E_s \) is high and may change the potential of the reference electrode as the reaction progresses. In these cases, a three-electrode electrochemical cell is preferred. In this arrangement the current flows between the working electrode and the newly inserted electrode known as the auxiliary (or counter) electrode. Since the electrochemical properties of the auxiliary electrode do not affect the behavior of the working electrode, WE, it may be chosen to be any convenient electrode and it is commonly chosen such that any species produced at its surface will not reach the surface of the WE and cause interferences there. The potential of the WE is measured, as before, relative to the reference electrode whose tip is placed as close as possible to the surface of the WE (1).

1.5.2 The supporting electrolyte

When working with an electrochemical cell, molecules move through the solution (mass transport) by three different modes:

- **Migration**: charged particles move due to the influence of an electric field (electric potential gradient).
- **Diffusion**: species move due to the influence of a chemical (concentration) gradient.
- **Convection**: species in the solution move due to stirring or hydrodynamic transport. Convection can be natural (due to density gradients) or forced.

Mass transfer to the electrode is governed by the Nernst-Planck equation which, for one dimension, is written as:

\[
J_i(x) = \text{Diffusion} + \text{Migration} + \text{Convection} \tag{1.21}
\]

\[
J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x) \tag{1.22}
\]

where \( J_i(x) \) is the flux of species \( i \) (given in units of mol s\(^{-1}\) cm\(^{-2}\)) at distance \( x \) from the electrode surface, \( D_i \) is the diffusion coefficient (with units of cm\(^2\) s\(^{-1}\)), \( \frac{\partial C_i(x)}{\partial x} \) and \( \frac{\partial \phi(x)}{\partial x} \) are the concentration and electric potential gradients at distance \( x \), \( z_i \) and \( C_i \) are, respectively, the charge (dimensionless) and concentration (mol cm\(^{-3}\)) of species \( i \) and \( v(x) \) is the velocity of a volume element that moves along the axis (1).

When all three forms of mass transport are present, it is generally not easy to solve Equation 1.22. However, it can be shown that adding an excess of nonelectroactive ions (a supporting electrolyte) nearly eliminates the contribution of migration to the mass transfer of the electroactive species, which simplifies Equation 1.22. Furthermore, adding the supporting electrolyte reduces the power dissipated in the solution by reducing the resistance of the solution between the WE and the reference electrode, thus also increasing the
accuracy with which the potential of the working electrode is measured/controlled. The supporting electrolyte also brings with it some chemical contributions, as it is responsible for establishing the solution composition in terms of pH, ionic strength, etc. which are important parameters on which electrochemical reactions depend.

Now that the basic terminology and theory of the relevant topics to this thesis have been presented, we move to the focus of this work and will now detail the objectives, materials and methods used as well as the results obtained during these four years of work.
2 General objectives

The general objective of this Ph.D. thesis was to build a medium resolution NMR sensor using an inductively coupled coil in its probe for use in spectroelectrochemical applications.

2.1 Specific objectives

To achieve the general goal of building the NMR sensor the following specific objectives were established:

- To study (through computational simulations) three different permanent magnet arrangements in terms of the magnetic field strength and homogeneity. The three configurations that were studied were the H-type magnet, the Halbach array (Figures 13 a) and c), respectively) and a configuration that has not yet been used for NMR applications which we call the HCM magnet (for reasons that will become clear in the next chapter).

- After the simulations, the optimal magnet design was built and tested to find whether it produced a magnetic field with the desired specifications by analyzing an oil sample and checking its $T_2^*$.

- To design probes using inductively coupled coils to improve the sensitivity of the NMR probe by determining what parameters most improved the signal of the coil.

- The system was tested by following the electrochemical deposition of copper ions.
3 Magnets for medium resolution NMR

The first half of this Ph.D. thesis was dedicated to optimizing the magnetic field intensity and homogeneity of a new magnet design which we called the HCM magnet\(^1\) (which stands for Hollow Cylindrical unioriented Magnet). The magnetic field of the HCM magnet (its strength and homogeneity) was compared to the magnetic field of the most usual magnet configurations used in NMR spectrometers: the H-type and Halbach array. The HCM magnet consists of a single permanent magnet tube, magnetized perpendicular to its vertical axis, surrounded by a high permeability ferromagnetic material (see Figure 39 on page 80). This results in a magnetic field within the bore of the magnet, parallel to the magnetization direction of the permanent magnet and which can, in theory, produce a perfectly homogeneous magnetic field \((\mathcal{B})\), making it ideal for application in a medium resolution NMR sensor.

3.1 Materials and methods

3.1.1 Simulations

Simulations of the magnetic fields were performed both in 2D and 3D. 2D simulations were performed using the free software Finite Element Method Magnetics (FEMM) \((61)\). 3D simulations were performed using Cedrat’s software Flux with a trial license. The simulations were performed to theoretically evaluate the magnetic field intensity and homogeneity from the various magnet designs. The homogeneity (in ppm) of the simulated magnets was defined as the average absolute deviation between the magnetic field at \(n\) points \((B_i)\) within the central air gap and the magnetic field at the center of the air gap \((B_0)\), as shown in Equation 3.1. The precision of the simulators was set to \(10^{-10}\).

\[
\mathcal{H}(\text{ppm}) = \frac{1}{n} \sum_{i=1}^{n} \left| B_i - B_0 \right| \divides{B_0 \times 10^{-6}}
\]  

3.1.2 Magnet construction

All magnets were constructed using the permanent magnetic material NdFeB. The required magnetic pieces were acquired from the Chinese manufacturer Dailymag \((62)\). Measurements of the dimensions of the permanent magnets were performed at the metrology laboratory of the engineering school of the University of São Paulo (LAMAFE).

Low carbon steel (A36 standard) was used for the construction of the magnets.

\(^1\) The design itself is actually not new, but has so far not been explored for medium resolution NMR applications.
Probes for the developed magnets were constructed using an aluminum box as it is not magnetic in nature. Ceramic variable capacitors were used and the coil was built from AWG 21 enameled copper wire.

The electronics of the NMR spectrometer were composed of an Apollo Tecmag console, RF preamplifier from Miteq model 1114 and power amplifier AMT-2065.

To measure the homogeneity of the magnets an oil sample was analyzed and the FID, after applying a 90° pulse, was recorded. The width of the Fourier transform of the FID was then used as a measure of the homogeneity of the magnet, given that the more homogeneous the magnet, the thinner the Fourier transform will be.

### 3.2 Results and discussion

The first step that was taken to build the magnet assemblies was to simulate them and optimize the geometrical parameters. Since the Halbach array is the one that produces the highest magnetic field intensity (with a magnetic field that is, under ideal conditions, homogeneous with no stray fields) per unit mass of permanent magnet (63), it was decided that they would be the standard against which all magnet assemblies would be compared.

#### 3.2.1 H-type magnet

**3.2.1.1 Simulations**

H-type magnets (seen in Figure 24) were chosen as a starting point for the design of the magnets so that experience could be gained in the characterization of the permanent magnets and in the assembly of the magnets. They were simulated first and were designed to output a magnetic field intensity of at least 0.5 T with three homogeneity cylinders in the center of the magnet gap within which the homogeneity would be better than 1, 10 and 100 ppm, as shown in Table 2. The reason why these homogeneity values were chosen is that we desired to be able to perform relaxometric, imaging and spectroscopic experiments using the same magnet. Thus, the highest homogeneity volume (1 ppm) would be a spacial region where spectroscopic measurements would be possible. The next volume (10 ppm) would be the region where imaging experiments should be possible while the 100 ppm region would be the largest volume where relaxometry measurements could be performed.
3.2. Results and discussion

Figure 24 – Technical drawing of the simulated H-type magnet with a mid-plane cut allowing the interior to be seen. The permanent magnets are the black pieces while the gray areas represent the steel.

![Figure 24 - Simulation of H-type magnet](image)

Source: Personal collection.

Figure 25 – Simulated H-type magnet. The permanent magnets (PM) are NdFeB and are magnetized in the direction of the black arrow. The polar pieces are also made from steel. The permanent magnets have a radius of 65 mm and 25 mm in height. The magnet structure has 135 mm of external radius (which includes the steel structure), 194 mm in height and the air gap is 30 mm wide.

![Figure 25 - Simulation of H-type magnet](image)

Source: Personal collection.
Chapter 3. Magnets for medium resolution NMR

Table 2 – Diameter and height of the desired magnetic field homogeneity regions.

<table>
<thead>
<tr>
<th>$B_0$ (T)</th>
<th>$H$ (ppm)</th>
<th>Diameter (mm)</th>
<th>Height (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>10</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>100</td>
<td>40</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>

Source: Personal collection.

Figure 26 – Volumes in the H-type magnet where the homogeneity is better than 1 ppm (black squares), 10 ppm (red circles) and 100 ppm (blue triangles). The desired dimensions of the homogeneity volumes are shown by the colored lines. Only one quarter of the magnet was simulated due to its symmetry. a) magnet simulated with a straight boundary between air and the polar piece (no shim); b) magnet with shim. The shape of the polar piece is shown below the graphs.

Source: Personal collection.

The magnet that was designed is schematically shown in Figure 25. This figure shows that the permanent magnets are sandwiched between two pieces of steel, one of which acts as a passive polar piece since its shape can mold the magnetic field in the air gap. To show that this is indeed the case, the magnet was simulated with the polar pieces having a straight surface at their boundary with the air and with modifications to this surface (Figure 26). Figure 26a shows the simulation of the H-type magnet with a flat polar piece (i.e. there is no shimming of the magnetic field). It is clear to see that in this scenario it is not possible to achieve the desired homogeneity volumes (shown by the dashed lines). In contrast, Figure 26b shows a magnet whose polar piece has been modified. In this figure we can see that the volumes of homogeneity that we set out to find have been achieved with the most notable increase in volume being found in the first volume (homogeneity better than 1 ppm). To achieve this homogeneity profiles it was necessary to slightly
reduce the thickness of the polar pieces in the center (by only 0.01 mm - shown below the graph in Figure 26b).

The magnet that had been simulated to this point was circular in shape and the outer steel structure completely enclosed the inside of the magnet. To reduce the amount of material needed to build the magnet and to facilitate its construction and use (since a completely closed structure requires entry points for the sample and probe) the shape of the magnet was changed to a rectangular cuboid (as shown in Figure 27 below) while still maintaining the expected homogeneity volumes. This was possible given that the outer walls of the magnet do not have an effect on both the intensity and homogeneity of the magnetic field (which was confirmed by simulations).

![Figure 27](source: Personal collection.)

3.2.1.2 Magnetic field profile of the PM’s

The magnets ordered for the H-type magnet were nearly 130 mm in diameter with a height of 25 mm. After confirming their dimensions (details of how this process was conducted are shown in Appendix B), it was necessary to check the magnetic field that they produced. This was done by using a Hall sensor mounted on a base that allowed the probe to move in a controlled fashion and at a fixed height. However, the amplitude of the movement provided by the moving base was not enough to cover the entirety of the magnet. Therefore the magnet was divided into four semi-axes where the magnetic field was measured (as shown in Figure 28).
Figure 28 – Semi-axes at which the magnetic field of the PM’s was measured.

Source: Personal collection.

Figure 29 – Magnetic field of two permanent magnets. Each color represents the magnetic field of one magnet, measured at its four semi-axes. The blue line represents the simulated magnetic field that the magnets should output.

Source: Personal collection.

Figure 29 shows the results of the measurements of the magnetic field of only two permanent magnets, since all magnets had a magnetic field profile similar to one of the two that are shown. In this figure we see that the magnetic field of some of the magnets was quite different in each of the axes (red lines) while other magnets had a much more uniform magnetic field (black lines). Magnets with a profile similar to the black lines were used to assemble the H-type magnet. The difference in the magnetic field along the semi-axes of the permanent magnets may be due to a magnetization process that is not very efficient, leading to PM’s that are not equally magnetized, even if the process that they all undergo is equal.
3.2. Results and discussion

3.2.1.3 Assembly of the H-type magnet

Prior to beginning the assembly of the H-type magnet, the intensity of the forces involved in the assembly of the magnet were calculated so that an assembly device could be designed and built to withstand such forces, allowing the PM’s to be safely mounted on the steel structure and the two halves to be joined without any risk of catastrophic failures of the assembly device. Figure 30 shows the four forces that were calculated through simulation and the resulting intensity of the forces is presented in Table 3. These forces were calculated when the involved pieces were close to each other (i.e. less than 1 mm apart) as this is the moment when the magnetic force is largest since it is inversely proportional to the distance between the pieces.

Figure 30 – Illustration of the main forces involved during the assembly of the H-type magnet.

![Illustration of main forces](image)

Source: Personal collection.

<table>
<thead>
<tr>
<th>Force</th>
<th>Distance between pieces</th>
<th>Intensity (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_1$</td>
<td>0.5 mm</td>
<td>1463</td>
</tr>
<tr>
<td>$F_2$</td>
<td>0.1 mm</td>
<td>1998</td>
</tr>
<tr>
<td>$F_3$</td>
<td>0.5 mm</td>
<td>4258</td>
</tr>
</tbody>
</table>

As shown in Table 3, the forces when assembling the magnet can reach intensities above 4000 N. With this information, our colleagues at FIT Instruments designed and built an assembly device that would approximate the permanent magnet to the outer steel structure as well as the polar piece to the permanent magnet after it had been mounted. This process is illustrated in Figure 31.
Figure 31 – Photographs of the assembly process of the H-type magnet. a) The assembly device used to bring the PM/polar piece safely close to the outer steel shell/PM; b) The PM being mounted on the steel shell; c) The two “halves” of the H-type magnet ready to be brought together. The silver ring around the PM’s is a piece needed to hold the PM on the assembly device.

To bring the two “halves” of the H-type magnet together a hydraulic crane was used while holding the larger half in place with sturdy materials found in the laboratory. This process is illustrated in Figure 32.

Figure 32 – Photographs of the assembly process of the H-type magnet. a) The lower (and largest) half firmly held in place; b) The whole setup with the lower half in the center of the crane; c) The upper (and smallest) half being lowered onto the lower half; d) the assembled H-type magnet with the probe and a sample in it.

3.2.1.4 Testing the H-type magnet

After assembling the magnet, it was necessary to confirm whether it did meet the desired specifications of magnetic field strength and homogeneity. To do this, an oil
sample was used which had 37.5 mm of diameter and 45 mm in height. The homogeneity of the magnet was determined using the definition given by Equation 3.2.

\[
\mathcal{H}(\text{ppm}) = \frac{\text{FWHM}(\text{Hz})}{\nu_{\text{acquisition}}(\text{MHz})}
\]  

(3.2)

where FWHM is the full width half maximum of the Fourier transform (in Hertz) of the echo and \(\nu_{\text{acquisition}}\) is the acquisition frequency in MHz (which was very close to 22.5 MHz, indicating that the magnetic field is very nearly equal to 0.5 T). The FWHM of the Fourier transform of the echo was used as an indication of the homogeneity as the more homogeneous the magnet is, the narrower the Fourier transform. The Fourier transform of the signal acquired is shown in Figure 33 and using this data the homogeneity of the magnetic field was calculated to be nearly 110 ppm which is not far from what was expected, considering that the analysis region had been doubled in height while the homogeneity was maintained at nearly 100 ppm. Smaller samples, and thus the higher magnetic field homogeneity regions, were not tested since the probe was designed and built by FIT Instruments only for the sample size that was used.

Figure 33 – Fourier transform of the FID signal obtained using an oil sample with the H-type magnet. The FID was acquired at 22.52 MHz using a single 90° pulse with a width of 5 µs. A dead time of 70 µs was used before the signal acquisition, which was recorded for a total of 4.096 ms. The last delay was set to 1 s and 150 scans were acquired.

Source: Personal collection.

\(^2\) oil was used instead of water due to its higher density which limits diffusion effects during measurements as well as due to its lower \(T_1\).
3.2.1.5 Variable gap H-type magnet

An H-type magnet with the capability of adjusting the gap size and the magnetic field homogeneity was developed by LMA and tested at our laboratory. This magnet could, in theory, be capable of achieving homogeneities below 100 ppm for any of the gap sizes which ranged from 28 to 60 mm. The advantage of such a magnet is that one device would be able to be used for a range of different samples as long as the gap could contain them. The drawback is that with an increased gap the intensity of the magnetic field is decreased. This magnet (shown in Figure 35) has two cranks which control the gap width and the homogeneity of the magnetic field. To adjust the homogeneity of the magnetic field, it was necessary to first adjust the parallelism between both PM’s and then to use the crank that controlled the shim mechanism, which caused a steel ring placed around the PM’s to slide up or down relative to the PM (Figure 34).

Figure 34 – The shim mechanism used in the variable gap H-type magnet. The magnetic field is shimmed by moving the steel rings placed around the PM’s.

Source: Personal collection.

Four probes were built for the magnet which had diameters of 11, 26, 46 and 56 mm, corresponding to the following operational frequencies: 22.1, 17.2, 14.4 and 12.0 MHz (for $^1$H), respectively (see Table 4). Figure 36 shows the Fourier transform of the signals obtained at the different gaps. From this figure we can see that all transforms have a shoulder and therefore using the definition of homogeneity that is shown in Equation 3.2 is not very adequate. Therefore, the homogeneity was calculated as the average homogeneity, as shown in Equation 3.3, where $f_i$ is the frequency at point $i$, $\bar{f}$ is the average frequency of all points and $S_i$ is the signal intensity at point $i$. A result of this definition is that we now take into consideration all of the spins within the sample, as opposed to the definition given by Equation 3.2, in which only the spins that precess near the central frequency are taken into account.

The shoulder in the peaks may be the result of a lack of homogeneity within the magnet in the Z direction, since this peak shape is usually seen in high-field NMR systems when the Z direction is not homogeneous (64). Furthermore, the signal at the operating frequency of 17.2 MHz is the one that shows the most noise (Figure 36c) in it due to the sample holder not being very well isolated from external RF signals which allowed such signals to enter the sample as noise. Table 4 also shows that the homogeneity at any gap is never below 160 ppm. This lack of homogeneity may result from the faces of the
3.2. Results and discussion

PM’s which might not have been completely parallel, which was difficult to ascertain. In addition, each of the gaps required a different configuration for adjusting the parallelism between the PM’s which could not be replicated once the gap was changed, making the application of this magnet very difficult in practice, resulting in the project being abandoned.

Figure 35 – Variable gap H-type magnet with the largest sample holder in place (56 mm diameter). The cranks on the left and right sides of the magnet are used to adjust the homogeneity of the magnetic field and the gap size, respectively.

Figure 36 – Fourier transform of the signals obtained with the variable gap H-type magnet: a) with a gap of 60 mm; b) with a gap of 54 mm; c) with a gap of 40 mm and; c) with a gap of 28 mm. The FID signals were acquired at 12.0 (a), 14.4 (b), 17.2 (c) and 22.1 MHz (d) using a single 90° pulse with a width of 12 (c), 20 (a, d) or 34 µs (b). A dead time of 200 (b) or 400 µs (a, c, d) was used before the signal was recorded for a total of 4.096 ms. The last delay was set to 1 s and 50 scans were acquired.
### 3.2.2 HCM magnet

#### 3.2.2.1 Simulations

The HCM magnets were simulated in hopes that they would be able to generate magnetic field intensities and homogeneities comparable to that of the Halbach array, a magnet configuration that is already in use in medium resolution NMR spectrometers. Before settling on the final design of the HCM magnet, both Halbach and HCM magnets were simulated with an internal radius of 15 mm and having the same external diameter of the PM (i.e. both had a PM thickness of 20 mm) so that they could be directly compared to each other. The simulated HCM magnet is shown in Figure 37.

\[
H(\text{ppm}) = \frac{1}{\sum S_i} \times \sum_i \left| \frac{f_i - \overline{f}}{\overline{f}} \right| S_i \times 10^6 \tag{3.3}
\]
3.2. Results and discussion

**Figure 37** – Simulation of an HCM magnet with \( r_{int} = 15 \) mm, PM thickness of 20 mm and a 55 mm thick steel layer.

![Simulation of an HCM magnet with \( r_{int} = 15 \) mm, PM thickness of 20 mm and a 55 mm thick steel layer.](image)

Source: Personal collection.

**Figure 38** – Simulation of an HCM magnet without the external ferromagnetic shell.

![Simulation of an HCM magnet without the external ferromagnetic shell.](image)

Source: Personal collection.

The outer ferromagnetic shell of the HCM magnet is required as without it, most of the magnetic field will stray outside its external radius, with its intensity within the bore falling by more than 95%. The steel shell acts by focusing the magnetic field lines on the inside of the magnet bore. A permanent magnet without an external ferromagnetic shell is shown in Figure 38.
The thickness of the outer steel shell is also an important parameter as it affects the homogeneity of the magnetic field. The thicker the shell the better the homogeneity of the magnet, as is shown in Table 5, which shows the results of the simulation of the HCM magnet with varying thicknesses of the steel layer, starting from 20 to 50 mm and it is clear that the homogeneity drastically improves. This occurs because as the thickness of the steel layer decreases it slowly becomes magnetically saturated, which means that it can no longer hold all of the magnetic field lines coming from the PM, which are then forced out of the magnet.

Table 5 – Effect of the steel shell thickness on the magnetic field strength and homogeneity of the HCM magnet. The homogeneity was calculated at an internal radius equal to 10 mm using Equation 3.1. The magnet had \( r_{int} = 15 \) mm and PM thickness of 20 mm.

<table>
<thead>
<tr>
<th>Steel thickness (mm)</th>
<th>( B_0 ) (T)</th>
<th>( \mathcal{H} ) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.504</td>
<td>157</td>
</tr>
<tr>
<td>30</td>
<td>0.511</td>
<td>3.13</td>
</tr>
<tr>
<td>40</td>
<td>0.511</td>
<td>0.45</td>
</tr>
<tr>
<td>50</td>
<td>0.511</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Source: Personal collection.

At this point, the Halbach arrays were also simulated to compare their performance to that of the HCM magnet. Since the magnetic field intensity and homogeneity of the Halbach array increases with an increasing number of PM’s used in its assembly, the 32 piece Halbach was compared to the HCM magnet. Two HCM and two Halbach magnets, with different inner radii were simulated, one with \( r_{int} = 5 \) mm and another with \( r_{int} = 15 \) mm. These values were chosen as they would be the magnets that would ultimately be built. Table 6 shows that the Halbach magnet with 32 pieces produces a much higher magnetic field intensity, especially with a smaller internal radius, where the ratio of its outer to inner radius is greater\(^3\) and its intensity can reach 2 T. The HCM magnet, however, can only reach a magnetic field intensity equal to half of the PM’s remanent magnetization, \( B_r \) (60).

Table 7 shows the homogeneity of the HCM and Halbach magnets and it can be seen that the HCM magnets produce a magnetic field that is as homogeneous or even better than that of the Halbach magnet. This is the greatest advantage of the HCM magnet in comparison to the Halbach array. While it may not output large intensities of \( B_0 \), it can achieve sub-ppm homogeneities nearly within its whole bore. Whereas the Halbach array requires 32 PM’s to achieve these homogeneities, the HCM magnet requires only one PM and an external steel layer. This makes constructing the HCM magnet much more simple than the Halbach array, which has to contend with the forces of multiple PM’s during

---
\(^3\) Recall Equation 1.9, which states that the magnetic field intensity of the Halbach array is directly proportional to the ratio between its outer and inner radius.
its assembly thus requiring a more robust structure to hold the PM’s (a more detailed comparison between the Halbach array and HCM magnets is shown in Section 3.2.2.3).

### Table 6 – Comparison of the magnetic field intensity of the simulated HCM magnets and a Halbach magnet made with 32 pieces.

<table>
<thead>
<tr>
<th>$r_{int}$ (mm)</th>
<th>PM thickness (mm)</th>
<th>32 piece Halbach $B_0$ (T)</th>
<th>Steel thickness (mm)</th>
<th>HCM $B_0$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>20</td>
<td>2.014</td>
<td>35</td>
<td>0.604</td>
</tr>
<tr>
<td>15</td>
<td>20</td>
<td>1.061</td>
<td>55</td>
<td>0.511</td>
</tr>
</tbody>
</table>

Source: Personal collection.

### Table 7 – Comparison of the magnetic field homogeneity of the simulated HCM magnets and a Halbach magnet with the same dimensions made with 32 pieces.

<table>
<thead>
<tr>
<th>$r_{int}$ (mm)</th>
<th>$r_H$ (mm)</th>
<th>32 piece Halbach $H$ (ppm)</th>
<th>HCM $H$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1</td>
<td>0.087</td>
<td>0.040</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.436</td>
<td>0.198</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.294</td>
<td>0.549</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>6.733</td>
<td>1.816</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>$5.2 \times 10^{-4}$</td>
<td>$5.2 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.018</td>
<td>0.136</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.123</td>
<td>0.656</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>395</td>
<td>1.682</td>
</tr>
</tbody>
</table>

Source: Personal collection.

Finally, the reason for building two distinct HCM magnets lies in the fact that the larger magnet could potentially be used to image some larger samples such as seeds, since its bore is large enough to fit the required gradient coils. The smaller magnet would be used for spectroscopic measurements of liquid samples within a standard 5 mm NMR tube as well as for coupling experiments between electrochemistry and NMR.

#### 3.2.2.2 Magnetic anisotropy

At this point it is worth discussing magnetic anisotropy, since it is an important characteristic of the PM’s that affects the output magnetic field (intensity and homogeneity) of the HCM magnets. Permanent magnets are said to be anisotropic if there exists at least one direction over which magnetizing the material is easier than over others (i.e. a direction that requires a less intense external field to magnetize the material), this direction is called the 

\textit{easy axis}.

Conversely, magnetically isotropic materials have no such direction and all directions require an equally strong external magnetic field to magnetize them. Magnetic anisotropy occurs due to the shape of the material, its crystalline structure and can even be induced by submitting the material to stress (65).
The effect of magnetic anisotropy on the HCM was studied because previous scientific papers did not reference this important property when dealing with HCM magnets. The paper by Peng et al. (60), for example, studied this type of magnet but did so only for the case of isotropic magnets, with magnetic permeability equal to one, which permanent magnets may not always be. As a matter of fact, most commercially available magnets (including most NdFeB or Alnico magnets) are anisotropic.

Some parameters were kept constant in all scenarios. These were the inner radius, $r_1$ (see Figure 39) of the PM which was kept equal to 10 mm, the thickness of the external ferromagnetic layer was kept equal to 50 mm and its relative magnetic permeability, $\mu_r$, was set to $10^{10}$. The high value of $\mu_r$ allowed us to consider this outer layer as a perfect magnetic conductor (which have $\mu_r = \infty$) and thus use the equation derived by Peng et al. (60) to calculate the intensity of the magnetic field generated by the HCM magnet.

**Figure 39** – Illustration of the HCM magnet. The bore of the magnet has a radius equal to $r_1$, the thickness of the permanent magnet (PM) is given by $r_2-r_1$ and the thickness of the high permeability ferromagnetic material is given by $r_3-r_2$. The permanent magnet cylinder is magnetized in the $y$ direction (black arrows) and the resulting magnetic field is in the same direction (red arrow).

The outer radius of the PM, $r_2$ was varied from 15 to 100 mm in steps of 5 mm (thus the ratio $r_2/r_1$ varied from 1.5 to 10). The results obtained are scalable to any value of $r_1$ since the magnetic fields of permanent magnets are scale invariant. To simulate the anisotropy in the PM’s the magnetic permeability in the $x$ and $y$, $\mu_{r,x}$ and $\mu_{r,y}$, axes was varied from 0.9 to 5. First in steps of 0.1 up to 1.5 and later from 1.5 to 5 in steps of 0.5. The remanent magnetization, $B_r$, was changed from 0.5 to 2 T. The values of $\mu_r$ and $B_r$ were chosen as they cover most of the commercially available magnetic materials (see...
3.2. Results and discussion

Table 8 – Data of commercially available materials as retrieved from Eclipse Magnetics data-sheets (Chinese standards).

<table>
<thead>
<tr>
<th>Material</th>
<th>( B_r (T) )</th>
<th>( \mu_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NdFeB</td>
<td>1.03-1.43</td>
<td>1.01-1.43</td>
</tr>
<tr>
<td>Ferrite</td>
<td>0.20-0.46</td>
<td>0.97-2.36</td>
</tr>
<tr>
<td>SmCo</td>
<td>0.30-1.15</td>
<td>0.78-1.77</td>
</tr>
<tr>
<td>AlNiCo</td>
<td>0.31-1.35</td>
<td>3.12-19.89</td>
</tr>
</tbody>
</table>


3.2.2.2.1 Magnetic field intensity vs. PM magnetic permeability

The first analysis was performed by varying \( \mu_{r,x} \) and \( \mu_{r,y} \) from 0.9 to 1.5 to determine \( B_0 \) of the HCM magnet. These values of magnetic permeability were chosen because NdFeB magnets mostly have permeabilities in this range.

The starting point for this analysis was Equation 3.4 which was derived by Peng et al. in 2003 (60). This equation was derived using ideal conditions in which the PM is isotropic with \( \mu_r = 1 \) and tells us that \( B_0 \) depends only on the thickness of the PM and its \( B_r \).

\[
B_0 = \frac{B_r}{2} \times \left[ 1 - \left( \frac{r_1}{r_2} \right)^2 \right] \quad (3.4)
\]

By first evaluating how the upper limit of \( B_0 \) changes with the anisotropy while maintaining either \( \mu_{r,x} \) or \( \mu_{r,y} \) equal to one, later incorporating the effect of the thickness of the PM and finally varying both permeabilities simultaneously, it was determined that \( B_0 \) is given by Equation 3.5 (the full description of the process to find this equation is described in reference (40)).

\[
B_0 \left( \mu_{r,x}, \mu_{r,y}, \frac{r_2}{r_1} \right) = B_r \left[ \frac{1}{2} - 0.125 \ln \mu_{r,x} - 0.122 \ln \mu_{r,y} \right] \times \left[ 1 - \left( \frac{r_1}{r_2} \right)^2 \right] \\
- \left\{ [0.012 - 0.008 \ln (\mu_{r,x} - 1)] \times (\mu_{r,x} - 1) + [0.09 - 0.02 \ln (\mu_{r,y} - 0.88)] \times (\mu_{r,y} - 1) \right\} \times \\
\exp \left( -0.283 \frac{r_2}{r_1} \right) + \left[ -7.83 \exp (-1.32 \mu_{r,x} \mu_{r,y}) - \frac{0.65}{\mu_{r,y}} \ln (\mu_{r,x} - 1) - \frac{0.49}{\mu_{r,x}} \ln (\mu_{r,y} - 1) \right] \times \\
(\mu_{r,x} - 1) (\mu_{r,y} - 1) \exp \left( -0.21 \frac{r_2}{r_1} \right) \quad (3.5)
\]

The equation above shows that when anisotropic PM’s are used in the HCM magnet, the limit of \( B_0 \) is reduced. It must be mentioned that Equation 3.5 can predict \( B_0 \) of the
HCM magnet with an error that does not exceed 3.5%, however, if using a PM thickness of \( r_2/r_1 = 6 \) or higher then the error of the equation is limited to 1.4%.

When extending the analysis of higher magnetic permeabilities (from 1.5 to 5) the resulting equation became far too complicated to be of any use to magnet designers. The limit of \( B_0 \), however, can be determined by using the first line of Equation 3.5:

\[
B_0 \left( \mu_{r,x}, \mu_{r,y}, \frac{r_2}{r_1} \right) = B_r \left[ \frac{1}{2} - 0.125 \ln \mu_{r,x} - 0.122 \ln \mu_{r,y} \right] \times \left[ 1 - \left( \frac{r_1}{r_2} \right)^2 \right] \tag{3.6}
\]

### 3.2.2.2.2 Magnetic field homogeneity vs. PM magnetic permeability

**Figure 40** – Magnetic field distribution in different simulated scenarios.

(a) \( \frac{r_2}{r_1} = 1.5; \mu_{r,x} = 1.5 \) and \( \mu_{r,y} = 1.5 \)

(b) \( \frac{r_2}{r_1} = 1.5; \mu_{r,x} = 1.5\) and \( \mu_{r,y} = 1 \)

(c) \( \frac{r_2}{r_1} = 5; \mu_{r,x} = 1.5 \) and \( \mu_{r,y} = 1 \)

(d) \( \frac{r_2}{r_1} = 5; \mu_{r,x} = 1.2 \) and \( \mu_{r,y} = 1 \)
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(e) \( \frac{r_2}{r_1} = 5; \mu_{r,x} = 1.5 \) and \( \mu_{r,y} = 1.5 \)

(f) \( \frac{r_2}{r_1} = 10; \mu_{r,x} = 1.5 \) and \( \mu_{r,y} = 1 \)

The homogeneity of the HCM magnet is also greatly affected by anisotropic properties of the PM. Simulations showed that the homogeneity of the HCM magnets is nearly perfect (below 0.075 ppm) if \( \mu_{r,x} = \mu_{r,y} \) and gets progressively worse as \( |\mu_{r,x} - \mu_{r,y}| \) increases and as \( r_2/r_1 \) decreases, as exemplified in Figure 40. However, a single equation to link the homogeneity of the HCM magnets and the magnetic permeability of the PM was not found.

If PM’s are found to be anisotropic it is possible to insert an air gap between the PM and the soft ferromagnetic layer, such as the one shown in Figure 41, which can help to increase the homogeneity of the magnetic field in the magnet.

**Figure 41** – Illustration of the air gap that may be inserted between the steel shell and the PM to compensate for anisotropy of the PM. The white areas represent air, light gray, the PM and dark gray the outer steel shell. The black arrow represents the magnetization direction of the PM.

Source: Personal collection.

3.2.2.3 Halbach array vs. HCM magnets

The advantages and disadvantages of the HCM magnets and of the Halbach array have been pointed out throughout the text so far but they will now be briefly summarized.
Halbach arrays, as previously stated, are limited in the intensity and homogeneity of the magnetic field that they produce by the number of pieces that are used in their assemblies (Equations 1.9 and 1.10). In practice, this means that to achieve an acceptable homogeneity for NMR experiments it is necessary to have at least 32 PM’s to achieve the homogeneity required for spectroscopic NMR measurements. Figures 42a and 42b show how the magnetic field strength and homogeneity change with an increase in the cross-section area of the PM’s (i.e. with an increasing outer radius of the PM’s) in the Halbach array and HCM magnets (the Halbach array pieces are annular sectors). We can see that the Halbach array has (in theory) no upper limit to its magnetic intensity, while the magnetic field intensity of the HCM magnets is limited to half of B_r. Regarding the homogeneity, this was calculated in the Halbach arrays within a radius equal to 0.8 r_int. It is clear from Figure 42b that increasing both the number of pieces that compose the array as well as increasing their thickness has the effect of increasing the magnetic homogeneity. In this figure, the homogeneity of the HCM magnet has not been plotted since it is (in theory) perfectly homogeneous.

The Halbach array’s biggest drawback is the number of PM’s that are required. This is problematic because many attractive and repulsive forces between the PM’s must be dealt with during the assembly. This means that the structure that holds the PM’s must be strong enough to contain them, which in practice means that this must be a bulky structure. Furthermore, not all PM’s are magnetized equally, even if they undergo the same magnetization process, the final magnetization intensity, homogeneity and direction
of each piece may differ from the others which affects the quality of the Halbach array. This increases the cost of the Halbach array, since more PM’s must be ordered to ensure that enough equal pieces exist to assemble the magnet and sorting procedures are required prior to assembly. Some solutions that have been proposed to improve the magnetic field of the Halbach array include placing movable PM’s to shim the magnetic field (42), changing the shape of the PM pieces so the inner radius changes linearly from both ends of the PM to its center, or placing either small PM’s or soft iron in the bore or on the surface of the array (66). Table 9 summarizes the advantages and disadvantages of the HCM magnet and Halbach array.

Table 9 – Comparison of the advantages and disadvantages of the HCM and Halbach array magnets.

<table>
<thead>
<tr>
<th>HCM magnet</th>
<th>Halbach array</th>
</tr>
</thead>
<tbody>
<tr>
<td>✓ $B_0$ is (theoretically) perfectly homogeneous.</td>
<td>✗ $B_0$ is limited to $B_r/2$.</td>
</tr>
<tr>
<td>✓ $B_0$ is perpendicular to the longitudinal axis of the magnet.</td>
<td>✓ $B_0$ increases as the amount of PM increases.</td>
</tr>
<tr>
<td>✓ Only one PM is needed; and one soft ferromagnetic layer around it.</td>
<td>✗ Not all PM’s are created equally; this affects the quality of the magnet.</td>
</tr>
<tr>
<td>✓ Easy assembly process.</td>
<td>X Strong (and bulky) structure required to hold the PM’s in place.</td>
</tr>
</tbody>
</table>

3.2.2.4 Magnetic field profile of the PM’s

Two types of PM’s were ordered. The first with a height, $H$, of 100 mm, $\phi_{int} = 10$ mm and $\phi_{ext} = 50$ mm. The second type had a height, $H$, of 50 mm, $\phi_{int} = 30$ mm and $\phi_{ext} = 50$ mm. After confirming the dimensions of the PM’s (details of how this process was conducted are shown in Appendix B), the magnetic field of the PM’s for the HCM magnets was measured and its profile was compared to the simulated magnetic field profile to see whether the magnet produced the magnetic field that was expected. The magnetic field was measured on the vertical axis of the PM’s.

The largest PM’s ($r_{int} = 15$ mm) were evaluated first and the magnetic field of the six PM’s that were chosen to be used in the final assembled magnet (due to their similar magnetic field profile) is shown in Figure 43. It is clear from this figure that the PM’s are not all equal which is not what was expected given that all PM’s should have undergone the same magnetization process. The magnetic field profile was used to determine the remanent magnetization, $B_r$, of each of the magnets (which should have been equal) and it was found that it ranged from 1.128 to 1.18 T. PM’s 1 and 2 were chosen, due to having the most similar magnetic field profile (and remanent magnetization), to be in the middle of the assembled magnet with the remaining magnets occupying the peripheral positions.
Figure 43 – Magnetic field profile of the PM’s of \( r_{int} = 15 \text{ mm} \) that were used to assemble the larger HCM magnet.

![Magnetic field profile of the PM’s of \( r_{int} = 15 \text{ mm} \)](image1)

Source: Personal collection.

Figure 44 – Magnetic field profile of the larger HCM magnet (black squares) compared to the simulated magnetic field profile (red circles).

![Magnetic field profile of the larger HCM magnet](image2)

Source: Personal collection.

The magnetic field output after all the PM’s with their respective steel shells were stacked was also measured and is shown in Figure 44. Clearly the magnetic field is not close to what was expected, due to the large difference between the magnetic field profile of the individual PM’s. This probably occurred due to the magnetization process not being very efficient and not being able to equally magnetize all PM’s.

Figure 45 shows the magnetic field of two PM’s ordered for assembling the smaller HCM magnet (with \( r_{int} = 5 \text{ mm} \)) as well as the simulated magnetic field of the magnets.
3.2. Results and discussion

(green line). Just as happened with the PM’s for the H-type magnet, the device used to move the Hall sensor through the inside of the PM did not have enough range to map the entirety of the PM. Therefore, the magnet was measured once from every side. In Figure 45 we can see that the PM’s are not well magnetized, since the profile of the magnetic field does not match that obtained through simulations. One possible explanation for the difference in the magnetic field profile of the PM’s is related to the magnetic field strength within the PM itself. PM’s are characterized by a parameter called the coercive field, \( H_C \) (in units of A m\(^{-1}\)), which is the strength of an external magnetic field required to demagnetize the PM. Simulations showed that the magnetic field within the these PM’s was close to the coercive field (for these PM’s, \( H_C \approx 1050 \text{ kA m}^{-1} \)) with values as high as 900 kA m\(^{-1}\). These values are not high enough to completely demagnetize the PM but are strong enough to partially demagnetize it. A partial and localized demagnetization of the PM can cause the lump seen in the magnetic field profile of PM 2 which further aggravates the resulting magnetic field of the HCM magnet. Therefore, PM 1, which showed no lumps in its magnetic field profile, was used to build the HCM magnet.

**Figure 45** – Magnetic field profile of two PM’s of \( r_{int} = 5 \) mm that were used to assemble the smaller HCM magnet as well as the simulated magnetic field of the magnets (green line).

3.2.2.5 Construction of the magnet assemblies

To mount the steel shell on the PM, it was necessary to divide it into two pieces that would then be slowly brought together around the PM (Figure 46). Both halves were fitted with holes for screws that would allow the steel to be firmly attached to the magnet while removing as much as possible any air gaps between the PM and the steel.
**Figure 46** — Illustration of how the steel layer (white pieces) was mounted on the PM (gray piece).

![Illustration of how the steel layer was mounted on the PM.](image)

Source: Personal collection.

**Figure 47** — a) Photograph of the device used to approximate the steel shell pieces to the PM. The red areas indicate the holders of the PM and the black areas indicate the fixation points of the steel pieces. b) Photograph of the assembled HCM magnets. The taller magnet (with a silver PM) has $r_{int} = 15$ mm and the smaller one (with a black PM) has $r_{int} = 5$ mm.

![Device for approximating steel pieces to the PM.](image)

![Assembled HCM magnets.](image)

Source: Personal collection

A special device was also required for the assembly of the steel on the PM’s due to the forces that act on the steel pieces during the assembly and so that this process could be done as safely as possible. This device was capable of slowly approximating the steel halves to the PM that was placed in its center (a photograph of the device is shown in Figure 47a). Furthermore, the larger HCM magnet was composed of six modules (smaller HCM magnets), as previously stated, so another device was built to keep the pieces from rotating when another segment was added on top. The resulting magnets are shown in
3.2. Results and discussion

Figure 47b, where copper sheets can be seen between some of the modules. These copper sheets were used as an attempt to add an air gap between the steel layers which has previously been shown to be an effective shimming procedure (60).

3.2.2.6 Testing the HCM magnets

The HCM magnets were tested again using an oil sample which measured 15.7 mm in diameter and 50 mm in height, for the larger HCM magnet, and 4.7 mm in diameter and 5 mm in height, for the smaller HCM magnet. The Fourier transform of the NMR signal of the larger HCM magnet is shown in Figure 48 from which it was possible to determine, using Equation 3.2, that the homogeneity of the magnetic field was around 3400 ppm, much worse than what the magnet was expected to output, but not entirely unexpected, given the difference in magnetization of the PM’s used.

Figure 48 – Fourier transform of the FID obtained using the large HCM magnet (r_int = 15 mm). The sample had 15.7 mm of diameter and 50 mm of height. The FID was acquired at 22.25 MHz using a 90° pulse with a width of 5 µs. A dead time of 50 µs was used before the signal acquisition, which was recorded for a total of 1.024 ms. The last delay was set to 1 s and 100 scans were acquired.

Attempts were made to homogenize the magnetic field of the magnet, by switching the positions of the PM’s within the structure, using PM’s that had not been previously used and even by attempting to reduce the height of the magnet (i.e. by assembling the magnet with 5 instead of 6 PM’s). Unfortunately, all attempts failed at significantly improving the magnetic field and nothing else could be done to further improve it aside from ordering new PM’s and hoping that they would all be equally and homogeneously magnetized.
Figure 49 shows the Fourier transform of the signal obtained using the smaller HCM magnet. From this figure and, again, using Equation 3.2 it was found that the homogeneity of this magnet was around 700 ppm, which is once again much higher than was expected for this magnet (which was expected to have a sub ppm homogeneity). An attempt was made to try to have a functioning HCM magnet by ordering two new PM’s with $r_{int} = 5$ mm but of a higher grade that could resist higher demagnetizing fields. The same process was repeated, with the PM’s being characterized in terms of their physical dimensions and the output of the magnetic field. However, once again the magnets output a profile similar to those shown in Figure 45. Given that the new magnets were supposed to withstand the demagnetizing fields within them, the reason why they produced a magnetic field profile that was not more similar to the simulated profile is likely to be a magnetization process that is not very efficient for this magnet configuration. Therefore the resulting assembled HCM magnet did not improve on the previous iteration and the development of the HCM magnets was abandoned.

**Figure 49** – Fourier transform of the FID obtained using the smaller HCM magnet ($r_{int} = 5$ mm). The sample had 4.7 mm of diameter and 5 mm of height. The FID was acquired at 25.07 MHz using a 90° pulse with a width of 5 µs. A dead time of 50 µs was used before the signal acquisition, which was recorded for a total of 512 µs. The last delay was set to 1 s and 200 scans were acquired.

---

### 3.3 Conclusion

The development of the H-type magnets was considered to have been successful, having achieved a magnetic field intensity of nearly 0.5 T and a magnetic homogeneity around
110 ppm, which is what was predicted by the computational studies previously performed in this work. The construction of these magnets required the development of additional equipment to safely mount the PM on the external steel shell as well as to mount the polar piece on the PM. Furthermore, to assemble the two "halves" of the magnet a crane and sturdy materials to keep the lower "half" firmly in place was required to ensure that this process was done as safely as possible. The magnetic field intensity and homogeneity were determined by analyzing an oil sample measuring 37.5 mm of diameter and 45 mm in height, which is slightly larger than our desired 100 ppm homogeneity volume (which was sought to be 40 mm in diameter and 20 mm in height). As mentioned earlier, these magnets were designed in collaboration with FIT instruments and the fixed gap magnet has gone on to be integrated in their commercially available low-field NMR spectrometer (67).

The HCM magnet was the real novelty of this project, as there haven’t been reports of the application of this sort of magnet in an NMR spectrometer. Unfortunately, the magnets that we received from our supplier were not homogeneously magnetized, leading to the final products not producing the magnetic field homogeneity that was expected for this model. One hypothesis is that the supplier had not previously been asked to produce such magnets and as such, its magnetization process for this type of PM was not adequate. Furthermore, the cost of importing PM’s from other more reliable sources was limited by the cost of such PM’s which were more than twice as expensive. Recently, a paper detailing the construction of the HCM magnet was found. This paper, by Nath et al. (68) showed the construction of a miniature version of the HCM magnet where they achieved a very homogeneous magnetic field (the magnet was 80 mm in diameter - including the soft ferromagnetic layer - and 50 mm tall). However, as this is a magnet configuration that is not in popular use, it has no fixed name and therefore this reference was not found until very recently. It is my belief that if a reliable PM source is found and sufficient funding is provided, then the HCM magnet can be successfully used in a medium resolution NMR spectrometer.
4 Inductively coupled probes

This part of the Ph.D. thesis was dedicated to designing and testing NMR probes using inductively coupled probes for the analysis of electrochemical reactions performed inside the NMR spectrometer (in situ). The performance of the probe using an inductively coupled coil (which we call the secondary coil) was compared to the performance of a probe not using the secondary coil so as to ascertain that it indeed improves the performance of the probe.

The reason why inductively coupled probes were chosen as a way to improve the performance of electrochemical reaction analysis by NMR is: first, because it is an approach that had not previously been tried for this application and; secondly, because most approaches to improve the quality of the coupling between electrochemistry and NMR focus on alterations to the electrochemical itself (3, 8–11, 14, 18, 69–84) and don’t tend to focus on improvements to the NMR probe. Some solutions involve placing the electrodes outside the detection region (81–84), using RF chokes (filters) (14, 18, 81, 82), using non-metallic electrodes such as carbon microfibers (81–83) or even metallic thin-films (11, 70, 71).

The use of inductively coupled probes in NMR is not in itself new as they have been used to investigate biological systems with surface coils (56, 85–87), as well as to study liquid and solid samples using unilateral (88) and high-field NMR measurements (89, 90). However, the analysis of electrochemical systems using NMR has not benefited from the use of such coils. Such a design is useful in systems where the use of a small sample volume is desirable, but access to the NMR probe is restricted.

The reason why the developed H-type magnet was not used here is because this part of the work was not developed at our home institution and was instead performed at the working group of Prof. Dr. Bernhard Blümmich of RWTH Aachen University (Germany).

4.1 Materials and methods

4.1.1 Solutions

Copper(II) sulfate pentahydrate (98% purity) was acquired from J&K Scientific. The sodium sulfate (1 mol L\(^{-1}\)), acquired from Merck KGaA, was used as the supporting electrolyte. The volume of the solution was 450 µL with an initial concentration of Cu\(^{2+}\) equal to 0.1 mol L\(^{-1}\). The deposition of copper was chosen as the reaction to follow due to its simplicity.
4.1.2 NMR probe

Copper wire was used to build the coils. 0.71 mm diameter wire was used to wind the primary coil, and the secondary coils were wound using wires with diameters of 0.1 mm, 0.375 mm and 0.71 mm. The height of the primary coil was nearly 18.3 mm with an inner diameter of 10 mm. The secondary coils were nearly as tall as the primary coil with an inner diameter of 5 mm. The resonance circuits were built using non-magnetic capacitors and cyanoacrylate adhesive was used to glue the primary and secondary coils to standard 10 mm and 5 mm NMR tubes, respectively.

4.1.3 Electrochemical cell

The electrochemical cell was built in a standard 5 mm NMR tube that had its bottom removed and replaced with a Teflon cap. The cap was covered with a platinum plate of approximately 3.5 mm diameter to serve as the working electrode. Platinum wire was used as the auxiliary electrode and a silver wire covered with a AgCl film was the reference electrode (91).

Copper was deposited by chronoamperometry with applied potentials, $E_{app}$, of -1 V and -4 V (vs. Ag/AgCl). All experiments were performed in triplicate and the average from those experiments is shown.

4.1.4 Other hardware and NMR sequence used

A home-built Halbach magnet operating at 34.34 MHz for $^1$H was used. A spectrum analyzer model GSP-810 from Instek was used to check the resonance frequency of the NMR probe. A Keysight Technologies network analyzer model E5061A ENA was used to check the $Q$ factor of the coils and the potentiostat from BioLogic Science Instruments model SP-150 was used to drive the electrochemical reaction.

$T_2$ of $^1$H in the solution was measured with the CPMG sequence during the electrode-position experiments. The 90° pulse was calibrated by changing the amplitude of the pulse rather than its length, which was fixed at 5 µs. A calibration curve was built to relate the $T_2$ values to the concentration of Cu$^{2+}$ in the solution.

4.2 Results and discussion

4.2.1 Optimization of secondary coil parameters

The secondary coils were designed such that the secondary resonant circuit would have a natural resonance frequency ($\frac{\omega_0}{2\pi}$) lower than 34.34 MHz with the variable capacitors of the primary resonant circuit being used to tune circuit the higher frequency peak of
4.2. Results and discussion

the coupled circuit to 34.34 MHz (for the reasons explained on page 56). Adding the secondary coil to the NMR probe also had a stabilizing effect on the probe which made it possible to tune and match much easier than when only the primary coil was used. This stabilizing effect is likely due to the high ionic strength of the solution which has been reported to lengthen the duration of the 90° pulse or even prevent the probe from being tuned and matched correctly (92, 93).

As shown in Equations 1.19 and 1.20 (on page 55) the parameters that control the current in the primary and secondary coils are the resonant frequencies of the coils \( \frac{\omega_0}{2\pi} \) (\( P \) and \( S \)), the self inductances of the coils \( L_P \) and \( L_S \), the Q factor of the coils \( Q_P \) and \( Q_S \) and the coupling coefficient \( k \). Of these parameters, \( k \) and \( \frac{\omega_0}{2\pi} \) control the spacing between the peaks while \( L_{(P,S)} \) and \( Q_{(P,S)} \) affect the intensity of the current flowing through each of the coils.

4.2.1.1 Coil height

Figure 50 – NMR signals obtained with a rubber sample using a CPMG sequence. Black line: signal obtained using only the primary coil. The secondary coils were built with a 0.375 mm thick wire. The height of the primary coil was 21 mm and heights of the secondary coils were 16.75 mm and 20.3 mm. NMR parameters for all experiments: echo time was 300 µs, 1024 echoes were acquired and acquisition time was 10 µs.

The optimal parameters of the secondary coil were found by first evaluating the relationship between the height of both coils using a rubber sample. The secondary coils were built using a 0.375 mm thick wire and with heights of 16.75 and 20.3 mm, while the
primary coil was 21 mm tall. Figure 50 shows that the NMR signal increases the most when the height of the secondary coil, \( H_S \), is similar to the height of the primary coil, \( H_P \). More specifically, at time \( t = 0.8 \) ms the signal intensity is 2.2 times higher when \( H_S \approx H_P \) than when no secondary coil is used. The configuration where \( H_S > H_P \) was not tested because the volume of the coil would be greater than the sensitive volume of the magnet and therefore inhomogeneities of \( B_0 \) would have a greater effect on \( T_2 \).

4.2.1.2 Wire thickness and turn spacing

Once the height of the secondary coil was determined, the thickness of the wire itself and the spacing between the turns of the coil were evaluated. This time, a \( \text{Cu}^{2+} \) solution was used. The thinnest wire tested was 0.1 mm thick but required too many turns to achieve a homogeneous magnetic field. This fact coupled with the wire’s thickness meant that the coil had a very large resistance which reduced the maximum signal intensity to nearly zero. For this reason, only the 0.375 and 0.71 mm thick wires were tested (wires thicker than 0.71 mm were not tested due to space constraints). The height of the coils was slightly reduced to 18.3 mm to allow the probe to be tuned and matched when using all secondary coils.

The spacing between the turns was specified in terms of the wire radius and three spacing configurations were tested: 0, 2 and 6 radii. To control the spacing between the turns, the number of turns needed to achieve the desired spacing within the coil height was first calculated (Table 10). From now on, \( \text{w375} \) refers to the wire that is 0.375 mm thick and \( \text{w710} \) refers to the wire that is 0.71 mm thick.

<table>
<thead>
<tr>
<th>Wire spacing (wire radius)</th>
<th>( \text{w375} )</th>
<th>( \text{w710} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 0 ) r</td>
<td>52</td>
<td>22</td>
</tr>
<tr>
<td>2 r</td>
<td>26</td>
<td>12</td>
</tr>
<tr>
<td>6 r</td>
<td>13</td>
<td>7</td>
</tr>
</tbody>
</table>


Figure 51 summarizes the results obtained using the different wires and spacings between coil turns. We can see that the coils that produced the highest signal intensity were the \( \text{w375-2r} \) (the coil made with the 0.375 mm thick wire and 2 r spacing between turns) and the \( \text{w710-0r} \) (the coil made with the 0.71 mm thick wire and 0 r spacing between turns) coils, with the \( \text{w375-2r} \) coil outputting the highest signal intensity.

It is not surprising that the \( \text{w375-2r} \) coil produces the highest signal intensity, since this coil is very close to being optimized in relation to the proximity effect \(^1\), which requires

\(^1\) The proximity effect can be thought of in the following way: when two wires carrying a current are...
4.2. Results and discussion

The turns to be separated by 1\(r\) (54). However, it is harder to maintain such a small spacing throughout the coil and thus, coils with a 2\(r\) spacing between turns were built, which is still very close to optimum, regarding this effect. Unsurprisingly, the coils with 6\(r\) spacing are those that perform the worst since such a big spacing between the turns prevents the coil from producing a homogeneous $B_1$.

**Figure 51** – NMR signal intensity of a Cu$^{2+}$ test solution. Solid lines represent the signal obtained when using a secondary coil made with the 0.375 mm diameter wire. Dashed lines represent the signal obtained when using a secondary coil made with the 0.710 mm diameter wire. All coils had a height of approximately 18.3 mm. All signals were obtained under the same experimental conditions.

![Graph showing NMR signal intensity](source: Lobo et al. 2019 (57). Copyright 2019 Electrochimica Acta.)

The SNR of the coils was also determined and it is shown in Figure 52. The SNR was calculated by dividing the signal intensity at $t = 1.8$ ms by the root mean square (RMS) of the signal acquired without a sample (the noise). As expected, the coils that produced the highest signal intensity also showed the largest SNR (these are the points surrounded by a red square in Figure 52). The fact that the w710-0r coil produces a larger SNR than the w375-2r coil can be explained by analyzing Equation 4.1, which is a simplification of Equation 1.16.

$$\text{SNR} \propto \frac{V_S B_1}{i \sqrt{R}} \approx \frac{V_S i \frac{\mu_0 n}{2 (r^2 + (H/2)^2)^{1/2}}} {\sqrt{R}} = \frac{V_S i \frac{\mu_0 n}{2 (r^2 + (H/2)^2) \sqrt{1/2}}}{\sqrt{\rho L}} \left(4.1\right)$$

near each other, the current in the first wire induces a current in the second wire, and vice-versa, which increases the resistance of the wire (94).
Figure 52 – SNR of the coils used in the experiments. The points surrounded by a red square represent the coils that showed the largest signal intensity.

\[ \text{SNR} = \frac{V_s}{\sqrt{R}} \]

where \( V_s \) is the sample volume, \( B_1 \) and \( R \) are the magnetic field produced by the coil and its resistance, respectively, \( i \) is the current flowing through the coil, \( \mu_0 \) is the magnetic permeability of vacuum, \( N, H \) and \( r \) are the number of turns, the height and the radius of the coil (measured from the center of the wire), \( A \) and \( L \) are the wire cross section area and its total length, and \( \rho \) is the resistivity of the wire.

As Equation 4.1 shows, the SNR is proportional to \( N \) and inversely proportional to the square root of \( R \). In terms of the number of turns, the w375-2r coil has slightly more turns than the w710-0r coil (26 versus 22 turns - Table 10), which means that the \( B_1 \) of the w375-2r is the larger of the two, by a small margin. However, as shown in Table 10, the resistance of the w375-2r coil is at least four times larger than the resistance of the w710-0r (DC resistance of 63.6 mΩ versus 15.0 mΩ) because of its smaller cross section area and greater length. Thus, even if \( B_1 \) of the w375-2r coil is higher, the difference in the resistance of the coils is very large and is the reason why the SNR of the w710-0r coil is larger than that of the w375-2r coil.

The quality factor, \( Q \) factor, of both primary and secondary coils was measured and the results obtained are shown in Table 11. As can be seen, the w375-2r and w710-0r are the coils that have the largest \( Q \) factors. By recognizing that the term \( B_1/\sqrt{R} \) in Equation 4.1 is approximately equal to \( 3(Q/\nu_0 V_{\text{coil}})^{1/2} \), where \( \nu_0 \) and \( V_{\text{coil}} \) are the resonant frequency of the coil and its volume, respectively (95), we can see why this result is not unexpected. The w375-2r coil was chosen to be used during the electrochemistry experiments, due to...
4.2. Results and discussion

its higher signal intensity.

**Table 11** – Q factor of the secondary and primary coils when the system was tuned to 34.34 MHz. The cells colored in blue represent the coil pairs that yielded the highest signal intensity.

<table>
<thead>
<tr>
<th>Wire spacing (wire radius)</th>
<th>Q factor</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>w375</td>
<td>w710</td>
<td></td>
</tr>
<tr>
<td>Secondary</td>
<td>Primary</td>
<td>Secondary</td>
<td>Primary</td>
</tr>
<tr>
<td>0 r</td>
<td>106</td>
<td>100</td>
<td>130</td>
</tr>
<tr>
<td>2 r</td>
<td>120</td>
<td>106</td>
<td>92</td>
</tr>
<tr>
<td>6 r</td>
<td>77</td>
<td>90</td>
<td>75</td>
</tr>
</tbody>
</table>


The product $Q_{Primary} \times Q_{Secondary}$ may play a role in the low signal intensity obtained using the w710-2r and 6r and the w375-6r coils (which have the lowest products) since, as explained in Section 1.4.1.1, the lower the Q factor, the more power is dissipated in the coil and the smaller the signal becomes. By having a smaller Q factor on both coils, the signal becomes lower due to the power that is dissipated in both coils.

4.2.2 Electrochemical experiments

To avoid interferences between the electrochemistry setup and NMR measurements, the working electrode, WE, was placed at the bottom of a standard 5 mm NMR tube, outside the NMR detection region. The auxiliary and reference electrodes, AE and RE, were placed above the detection region. Radio-frequency filters (chokes) were placed between each electrode and the potentiostat to further reduce the interference between both techniques. Furthermore, the Halbach magnet was placed in a Faraday cage to filter ambient RF noise. The electrochemical cell and the experimental setup are shown in Figure 53. If the WE were to be placed above the detection region of the coil, there would be the risk that during the reaction some of the accumulated copper could fall off and go through the detection region as the reaction progressed. This would hamper the NMR measurements and it is for this reason that the WE was placed below the detection region. On the AE, the oxidation reaction that occurs is the formation of oxygen and since the AE is placed above the detection region, the electroformed oxygen will not pass through the detection region as it is released from the surface of the electrode, thus also not affecting the NMR measurements. Regarding the hydrogen gas that may form at the WE, tests were performed by stopping the copper reduction reaction after a certain amount of time and then agitating the solution to homogenize it and measuring its $T_2$, which was then compared to the $T_2$ value obtained after the same amount of time during the *in situ* reaction. A statistically significant difference was not observed which indicates that such bubbles do not interfere with the NMR measurements. Furthermore, when increasing the
applied potential from -1 to -4 V (vs. Ag/AgCl) the noise in the NMR signal did not increase significantly and no bubbles were observed on the walls of the NMR tube after the reaction was stopped, which further confirms that hydrogen bubbles do not affect the NMR signal.

To quantify the copper ions in the solution, a calibration curve was constructed which relates the inverse of $T_2$ as a function of the concentration of copper ions in solution. The resulting calibration curve is given by Equation 4.2.

$$\frac{1}{T_2} (\text{ms}^{-1}) = 1.009 \left( \text{mol}^{-1} \cdot \text{L} \cdot \text{ms}^{-1} \right) \times \left[ \text{Cu}^{2+} \right] (\text{mol} \cdot \text{L}^{-1})$$  \hspace{1cm} (4.2)

**Figure 53** – Electrochemical cell and experimental setup for the EC-NMR experiments. a) Schematic of the electrochemical cell. b) Schematic of the experimental setup for the electrochemical experiments. c) Pictures of both the primary coil and secondary coil. d) Electrochemical cell in the Halbach magnet. e) Magnet inside the Faraday cage with the chokes inside a green protective rubber casing.
4.2. Results and discussion

Using the calibration curve it was possible to quantify the concentration of Cu\textsuperscript{2+} during the electrodeposition reactions, using the secondary coil. The reaction was performed at two different applied potentials, $E_{\text{app}}$, -1 V and -4 V vs. Ag/AgCl. The results obtained from the NMR T\textsubscript{2} measurements were compared to the chronoamperometric data to ensure that they were consistent. The raw NMR signals obtained from the electrodeposition reactions are shown in Figure 54.

**Figure 54** – a) NMR signals of the Cu\textsuperscript{2+} solution during the electrodeposition performed at $E_{\text{app}}$=-1 V (vs. Ag/AgCl). b) NMR signals of the Cu\textsuperscript{2+} solution during the electrodeposition performed at $E_{\text{app}}$=-4 V (vs. Ag/AgCl).
When $E_{app} = -1$ V (vs. Ag/AgCl) the reaction was stopped after sixty minutes while for the larger potential, $E_{app} = -4$ V (vs. Ag/AgCl), the reaction was stopped after thirty minutes since, as expected from such a high potential, the copper ions are consumed much faster. This is confirmed by the large $T_2$ of the $^1$H in solution after thirty minutes (Figure 54b), by the color of the solution which changed from blue to transparent to the naked eye and by the amount of copper that was found on the WE after the reaction was stopped. The calibration curve (Equation 4.2) was used to quantify the amount of copper in the solution during the reaction and the results are plotted in Figure 55. These results confirm that copper is consumed much faster when $E_{app} = -4$ V (vs. Ag/AgCl).

The concentration of Cu$^{2+}$ after the end of the reaction was also calculated from chronoamperometric charge data and was compared to the results obtained from the NMR measurement. The results are shown in Table 12 and we can see that both NMR and the electrochemical data agree well when $E_{app} = -1$ V. However, when the potential was increased to -4 V, electrochemical data would suggest that a negative amount of copper ions remains in the solution (i.e. more copper was consumed than was initially in the solution). This occurs because not all charge that flows during the electrodeposition reaction goes into reducing copper ions to their solid state, but also to the formation of hydrogen gas, which at higher potentials is formed at a much faster rate. Therefore, the NMR data is much more reliable, since the $T_2$ values can be directly correlated with the concentration of Cu$^{2+}$. 

4.2. Results and discussion

Table 12 – Comparison of the final Cu\(^{2+}\) concentrations determined by NMR measurements and electrochemical data.

<table>
<thead>
<tr>
<th>(E_{\text{app}}) vs. Ag/AgCl (V)</th>
<th>Final ([\text{Cu}^{2+}]) (mol L(^{-1})) NMR</th>
<th>Chronoamperometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1 (after 60 min)</td>
<td>((5.3 \pm 0.2) \times 10^{-2})</td>
<td>((5.4 \pm 0.1) \times 10^{-2})</td>
</tr>
<tr>
<td>-4 (after 30 min)</td>
<td>((1.5 \pm 0.2) \times 10^{-3})</td>
<td>((-6.1 \pm 0.7) \times 10^{-2})</td>
</tr>
</tbody>
</table>


Figure 55 – Cu\(^{2+}\) concentration over deposition time. Black squares and red circles represent the depositions performed at \(E_{\text{app}}=-1\) V and \(E_{\text{app}}=-4\) V (vs. Ag/AgCl), respectively.


4.2.3 Effect of the electrodes on the NMR probe

As mentioned in the introduction of this thesis, the electrodes of the electrochemical cell interfere with the ability of the probe to transmit and receive signals, when they are placed in the vicinity of the detection region. To show how this happens, the electrochemical cell (with the secondary coil attached to it but without the RE) was placed in the probe, with the electrodes disconnected from the potentiostat, which was then tuned to 34.34 MHz (Figure 56a). In this setup we are sending a RF signal to the probe and observing the reflected signal. When the RF frequency equals the frequency at which the probe is tuned, the signal is absorbed by the probe which is observed as a dip in the network analyzer\(^2\). When connecting the AE to the potentiostat (Figure 56b), the

\(^2\) The probe was considered to be well matched if the dip was at least -80 dB
impedance match of the circuit is severely deteriorated as observed by the smaller dip, and slightly shifts the tuning frequency to higher values. Connecting only the WE to the potentiostat severely detunes the probe, by shifting its tuning frequency to lower values) as well as its impedance matching ((Figure 56c). Connecting both the WE and the AE to the potentiostat does shift the probes frequency to lower values (but not quite as much as connecting only the WE) and also deteriorates the impedance matching of the circuit (Figure 56d). Furthermore, connecting both WE and AE to the potentiostat increases the bandwidth of the probe. For this reason, it is important to check the tuning and matching of the NMR probe when the electrochemical cell is connected to the potentiostat and placed in the NMR detection region.

Figure 56 – Effect of the electrodes on the tuning and matching of the NMR probe. a) Probe tuned to 34.34 MHz with electrodes not connected to the potentiostat. b) Auxiliary electrode connected to potentiostat. c) Working electrode connected to potentiostat. d) Both WE and AE connected to potentiostat.

4.2.4 Advantages of using secondary coils

As previously mentioned, the main advantage of using inductively coupled coils is the increase in the SNR due to the closer proximity between the coil and the sample, since
4.2. Results and discussion

the secondary coil can be wound directly around the sample or placed near it (in the case of surface coils). It is, however, important that the spectrometer which is used allows the probe to be tuned as needed, since the addition of the secondary coil to the probe splits the resonance peak into two.

Of course, it is also be possible to increase the fill factor of the coil by using a larger electrochemical cell with a larger sample volume. However, there are advantages in using smaller sample volumes together with the secondary coil instead of a larger sample volume (Figure 57). First, if a smaller sample is used, then the reactions can be performed faster and requiring less current. This means that less energy will be spent to drive the reactions. A smaller sample volume also has an effect on the RF pulses, as they will require less power to flip the magnetization in the sample, thus reducing the risk of heating the sample. The most important advantage of using secondary coils to investigate electrochemical systems is that they stabilize the probe in relation to the ionic strength of the sample. The instability of regular probes when analyzing high ionic strength samples is translated into longer 90° pulses or even the inability to correctly tune and match the probe (93) which is more evident when working at higher frequencies (92).

Figure 57 – a) Setup using a secondary coil and a smaller sample volume. b) Setup using only the regular NMR probe and a larger sample volume, where $\varnothing_2 > \varnothing_1$.

Experiments were performed to check how the use of the secondary coil affects the length of the 90° pulse by evaluating liquid mixtures of copper sulfate and sodium sulfate with ionic strengths ranging from 0.04 mol·L$^{-1}$ to 7 mol·L$^{-1}$. The length of the 90° pulse when using the secondary coil changed from 3.3 $\mu$s to 3.5 $\mu$s. A larger 8 mm diameter NMR tube was then used to analyze the same solutions without using the secondary coil. The pulse width remained nearly constant throughout the various ionic strength samples,
but were longer than in the previous case, this time ranging from 4.0 to 4.2 µs. Since long 90° pulse widths have been reported when evaluating high ionic strength samples at high field (92), it is expected that the stabilizing effect be more notable in these cases. Indeed, Tang and Jerschow (96) performed an experiment on the same spectrometer that Voehler et al. used (92), this time using a secondary coil, and reported the length of the 90° pulse for 1H to be less than a quarter of the length reported by Voehler et al.

4.3 Conclusions

The development and use of NMR probes using inductively coupled coils for the analysis of electrochemical systems was successful. The optimal parameters of the secondary coil were determined and the setup was used to follow the electrodeposition reaction of copper (II) due to its simplicity. This arrangement may be useful in situations where changing the NMR probe is not feasible or when the electrochemical cell is smaller than the detection volume of the probe. In the latter case, the use of a secondary coil in the probe increases the SNR of the NMR experiment and stabilizes the probe with respect to the ionic strength of the sample (which is more apparent at higher frequencies), allowing the quantification of Cu²⁺ to be possible. Furthermore, data obtained from NMR experiments may be more reliable than the electrochemical data, especially when several reactions occur simultaneously, such as the formation of gas bubbles. The main disadvantage of the secondary coils is their effect on the resonance peak of the probe (which gets split into two when the secondary coil is inserted) which requires it to be re-tuned.

A system such as the one shown in this thesis may be used to follow the electroplating reactions of other paramagnetic ions such as Ni²⁺ or Cr³⁺. However, this setup may be even more advantageous if used in conjunction with high or medium resolution spectrometers where more complex mixtures may be analyzed and followed during electrochemical reactions. In such cases it should, in theory, be possible to follow the formation of reaction intermediaries (if they exist) to determine the reaction pathways. This, however, may require not just the use of inductively coupled coils but also the use of ultrafast NMR pulse sequences to allow possible reaction intermediates to be detected. Unfortunately, since the HCM magnet did not function as expected, it was not used in conjunction with the probe setup on a spectroelectrochemical application.
5 Resulting published scientific articles

From the work done for the duration of this Ph.D. project, two scientific articles were published in peer-reviewed journals. They are listed below:


In addition, several collaboration papers were published, most of them dealing with the effect of the magnetic field of the NMR spectrometer during the *in situ* analysis of electrochemical systems. These are listed below.


- Strong magnetoelectrolysis effect during electrochemical reaction monitored *in situ* by high-resolution NMR spectroscopy, Analytica Chimica Acta, v. 983, p. 91-95, 2017.


References


APPENDIX A – Resonance frequency of an inductively coupled probe

To calculate the resonance frequencies of the NMR probe using a secondary inductively coupled probe we start with the circuit shown in Figure 58 where we are disregarding the resistance of the circuits to facilitate the math.

![Figure 58](Source: Personal collection.)

We begin by writing Kirchoff’s voltage laws for the primary and secondary circuits as follows:

\[ v_0 = Z_P i_P + Z_M i_S = \left[ \frac{1}{j\omega C_P} + j\omega L_P \right] i_P + j\omega M i_S \]  \hspace{1cm} (A.1)

\[ 0 = Z_M i_P + Z_S i_S = j\omega M i_P + \left[ \frac{1}{j\omega C_S} + j\omega L_S \right] i_S \]  \hspace{1cm} (A.2)

where \( Z_{P,S} \) is the complex impedance of the primary/secondary circuit equal to the sum of the impedances of the capacitor \( Z_C = \frac{1}{j\omega C} \) and inductor \( Z_L = j\omega L \) (and \( j \) is the imaginary unit), \( Z_M \) is the complex impedance that results from the mutual inductance between the coils, given by \( Z_M = j\omega M \) and \( i_{P,S} \) is the current flowing through the primary/secondary circuit.

The condition for resonance is that the reactive part (or imaginary part) of the impedance of the circuit is equal to zero. Thus, we must first determine the equivalent impedance of the circuit which is given by \( Z_{eq} = \frac{Z_M}{1} \). Rearranging the equations above
we find

$$Z_{eq} = \frac{\left[\frac{1}{j\omega C_P} + j\omega L_P\right]\left[\frac{1}{j\omega C_S} + j\omega L_S\right] + \omega^2 M^2}{\frac{1}{j\omega C_S} + j\omega L_S} = -\frac{\left[\omega L_P - \frac{1}{\omega C_P}\right]\left[\omega L_S - \frac{1}{\omega C_S}\right] + \omega^2 M^2}{j \left(\omega L_S - \frac{1}{\omega C_S}\right)} \quad (A.3)$$

Since the impedance of the circuit is purely reactive (imaginary) we need only set the numerator to zero to find the resonance frequencies of the circuit. Using the equalities $\omega_i^2 L_i = \frac{1}{C_i}$ and $M = k\sqrt{L_P L_S}$ we can rewrite the numerator in terms of the resonance frequencies of the primary and secondary circuits:

$$-L_P L_S \left(\omega_0 - \frac{\omega_P^2}{\omega_0}\right)\left(\omega_0 - \frac{\omega_S^2}{\omega_0}\right) + \omega_0^2 k^2 L_P L_S = 0 \quad (A.4)$$

Rearranging this equation we get the fourth degree polynomial below:

$$\omega_4^4 \left(k^2 - 1\right) + \omega_0^2 \left(-\omega_P^2 - \omega_S^2\right) + \omega_0^2 k^2 \omega_S^2 = 0 \quad (A.5)$$

the solutions to this polynomial are

$$\omega_0 = \frac{1}{\sqrt{2}} \sqrt{\frac{\omega_P^2 + \omega_S^2 \pm \sqrt{(\omega_P^2 + \omega_S^2)^2 - 4\omega_P^2 \omega_S^2 (1 - k^2)}}{1 - k^2}} \quad (A.6)$$

Q.E.D.
APPENDIX B – Dimension measurements of the permanent magnets

B.1 H-type magnet PM’s

For the H-type magnet, six permanent magnets with a diameter of 130 mm and a height of 25 mm were ordered and their dimensions were measured upon arrival. This was done using a height gauge available at LAMAFE. However, since this equipment is digital and we were dealing with magnetic pieces, a longer rod was designed and built so the magnets could be measured at a greater distance from the height gauge, so no damage would come to its electronics. All measurements were performed five times and Table 13 shows the results. In it, we can see that the diameter of all magnets was very close to 130 mm.

Table 13 – Measurements of the permanent magnets for the H-type magnet.

<table>
<thead>
<tr>
<th>PM</th>
<th>Diameter (mm)</th>
<th>Height (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>129.939 ± 0.012</td>
<td>24.557 ± 0.004</td>
</tr>
<tr>
<td>2</td>
<td>129.934 ± 0.002</td>
<td>24.554 ± 0.010</td>
</tr>
<tr>
<td>3</td>
<td>129.925 ± 0.004</td>
<td>24.548 ± 0.005</td>
</tr>
<tr>
<td>4</td>
<td>129.973 ± 0.006</td>
<td>24.555 ± 0.009</td>
</tr>
<tr>
<td>5</td>
<td>129.949 ± 0.010</td>
<td>24.551 ± 0.004</td>
</tr>
<tr>
<td>6</td>
<td>129.929 ± 0.002</td>
<td>24.533 ± 0.006</td>
</tr>
</tbody>
</table>

Source: Personal collection.

B.2 HCM magnet PM’s

The PM’s that were ordered for the assembly of the HCM magnets had the following dimensions: the PM’s for the smaller magnet were ordered with a height, H, of 100 mm, \( \phi_{int} = 10 \) mm and \( \phi_{ext} = 50 \) mm and; PM’s for the larger magnet were ordered with a height, H, of 50 mm, \( \phi_{int} = 30 \) mm and \( \phi_{ext} = 50 \) mm. The dimensions were confirmed through measurements, as done with the PM’s for the H-type magnet. The results are presented in Tables 14 and 15. The inner diameter of the smaller magnet was not measured because the rod used for the measurements did not fit in the PM’s bore. All measurements were performed four times.

The HCM magnet with the larger bore would be built by stacking six smaller HCM magnets (with a height of 50 mm each) because magnetizing such a large piece (with a height of 300 mm) in a very homogeneous way would not be feasible due to its size.
Table 14 – Measurements of the permanent magnets for the larger HCM magnet. The magnets were ordered with the following dimensions: \( H = 100 \text{ mm} \), \( \phi_{ext} = 50 \text{ mm} \) and \( \phi_{int} = 10 \text{ mm} \).

<table>
<thead>
<tr>
<th>Magnet</th>
<th>( H ) (mm)</th>
<th>( \phi_{ext} ) (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100.046 ± 0.007</td>
<td>49.970 ± 0.007</td>
</tr>
<tr>
<td>2</td>
<td>99.981 ± 0.010</td>
<td>49.915 ± 0.122</td>
</tr>
<tr>
<td>3</td>
<td>99.911 ± 0.169</td>
<td>49.941 ± 0.008</td>
</tr>
</tbody>
</table>

Source: Personal collection.

Table 15 – Measurements of the permanent magnets for the larger HCM magnet. The magnets were ordered with the following dimensions: \( H = 50 \text{ mm} \), \( \phi_{ext} = 90 \text{ mm} \) and \( \phi_{int} = 30 \text{ mm} \).

<table>
<thead>
<tr>
<th>Magnet</th>
<th>( H ) (mm)</th>
<th>( \phi_{int} ) (mm)</th>
<th>( \phi_{ext} ) (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50.001 ± 0.005</td>
<td>29.963 ± 0.027</td>
<td>89.960 ± 0.005</td>
</tr>
<tr>
<td>2</td>
<td>49.983 ± 0.003</td>
<td>29.993 ± 0.003</td>
<td>89.956 ± 0.002</td>
</tr>
<tr>
<td>3</td>
<td>49.973 ± 0.007</td>
<td>29.985 ± 0.001</td>
<td>89.918 ± 0.003</td>
</tr>
<tr>
<td>4</td>
<td>49.986 ± 0.004</td>
<td>29.875 ± 0.005</td>
<td>89.938 ± 0.002</td>
</tr>
<tr>
<td>5</td>
<td>49.999 ± 0.004</td>
<td>29.980 ± 0.005</td>
<td>89.972 ± 0.008</td>
</tr>
<tr>
<td>6</td>
<td>50.021 ± 0.007</td>
<td>29.958 ± 0.003</td>
<td>89.913 ± 0.001</td>
</tr>
<tr>
<td>7</td>
<td>50.009 ± 0.011</td>
<td>29.980 ± 0.005</td>
<td>89.938 ± 0.003</td>
</tr>
<tr>
<td>8</td>
<td>50.000 ± 0.004</td>
<td>30.000 ± 0.025</td>
<td>89.927 ± 0.002</td>
</tr>
<tr>
<td>9</td>
<td>50.003 ± 0.003</td>
<td>29.978 ± 0.002</td>
<td>89.922 ± 0.001</td>
</tr>
<tr>
<td>10</td>
<td>49.981 ± 0.022</td>
<td>30.000 ± 0.005</td>
<td>89.929 ± 0.006</td>
</tr>
</tbody>
</table>

Source: Personal collection.

The height of the magnets was measured at four different points of the cylinder, as shown in Figure 59, since this is a critical parameter. It was important for the height not to change much from point to point, since this would indicate that both faces are parallel. If this was not the case, then the magnetic field of the magnet would not achieve the desired homogeneity within the specified regions. Table 13 shows that the height of the permanent magnets does not change significantly, as the standard deviation of all measurements is quite small.
Figure 59 – Points at which the height of the cylinders was measured.

Source: Personal collection.
APPENDIX C – Magnetic field at the center of a saddle coil

To calculate the magnetic field at the center of the saddle coil geometry we will split the contribution from all four straight wires from the contribution of all four arcs. Thus, the total magnetic field at the center of the saddle coil will be given by:

$$B_T = B_{Arcs} + B_{Verticals}$$  \hspace{1cm} (C.1)

First, we will calculate the magnetic field due to the verticals. To do this, we will use Biot-Savart’s law for the magnetic field generated by an electric current flowing through one turn of the coil, which we consider to be constant (Equation C.2).

$$\frac{dB}{dl} = \frac{\mu}{4\pi} \frac{I dl \times \hat{R}}{R^2}$$  \hspace{1cm} (C.2)

where $\mu$ is the magnetic permeability of the medium (equal to the product of its relative permeability, $\mu_r$, and the permeability of vacuum, $\mu_0$), $I$ is the current flowing in the wire, $dl$ is the infinitesimal length element where the current is flowing, $R$ is the displacement vector that points from $dl$ to the point at which the field is being calculated and $\hat{R}$ is the unit vector of $R$. The problem is drawn in Figure 60.

Figure 60 – Determining the magnetic field created by the verticals of the saddle coil.

Source: Personal collection.
From Figure 60, and since we consider $I$ to be constant, we can immediately see that

$$I\,dl \times \hat{R} = I\,dl \sin \theta = I\,dz \sin \theta$$

$$R = \left( z^2 + r^2 \right)^{1/2}$$

$$\sin \theta = \frac{r}{R} = \frac{r}{\left( z^2 + r^2 \right)^{1/2}}$$

The total magnetic field, $B_{\text{Verticals}}$ due to the vertical wires of the coil will be the sum of all four contributions which, as a result of the symmetry of the problem, will be oriented in the $x$ direction. The magnetic field generated by the infinitesimal length, $dl = dz$, is oriented at an angle $\varphi$ from $x$ (as shown in blue in Figure 60). $B_{\text{Verticals}}$ is thus given by

$$\vec{B}_{\text{Verticals}} = \frac{4\mu I}{4\pi} \int_{-h}^{h} \frac{rdz}{\left( z^2 + r^2 \right)^{3/2}} \cos \varphi \hat{x}$$  \hspace{1cm} (C.3)

The cosine term in the above Equation gives us the projection of the magnetic field onto the $x$ direction, $\hat{x}$ is the unit vector in the $x$ direction and, since the angle $\angle OPQ = 2\pi/3$, then $\angle OPS = \pi/3$ and $\varphi = \pi/6$, which means that $\cos \varphi = \sqrt{3}/2$. We now get

$$\vec{B}_{\text{Verticals}} = \frac{\sqrt{3} \mu I r}{2\pi} \int_{-h}^{h} \frac{dz}{\left( z^2 + r^2 \right)^{3/2}} \hat{x}$$  \hspace{1cm} (C.4)

The integral of Equation C.4 can be solved by performing the following change of variable: $z = r \tan \eta$ which leads to $dz = rd\eta / \cos^2 \eta = r \sec^2 \eta d\eta$. The integral can now be solved as follows:

$$\int \frac{dz}{\left( z^2 + r^2 \right)^{3/2}} = \int \frac{r \sec^2 \eta d\eta}{\left( r^2 \tan^2 \eta + r^2 \right)^{3/2}} = \int \frac{r \sec^2 \eta d\eta}{\left( \frac{r^2 \sin^2 \eta + r^2 \cos^2 \eta}{\cos^2 \eta} \right)^{3/2}} = \int \frac{r \sec^2 \eta d\eta}{\left( \frac{r^2}{\cos^2 \eta} \right)^{3/2}} = \int \frac{r \sec^2 \eta d\eta}{r^3 \sec^3 \eta} = \int \frac{d\eta}{r \sec \eta} = \int \frac{\cos \eta d\eta}{r^2} = \sin \eta = \frac{z}{r^2} \left( z^2 + r^2 \right)^{1/2}$$

In the last step we have used the equality $\sin \eta = z/R$. We can now solve Equation C.4 to find the total magnetic field produced by the verticals of one turn of the saddle coil.

$$\vec{B}_{\text{Verticals}} = \frac{\sqrt{3} \mu I r}{2\pi} \left[ \frac{h}{r^2 \left( h^2 + r^2 \right)^{1/2}} - \frac{-h}{r^2 \left( (-h)^2 + r^2 \right)^{1/2}} \right] \hat{x} = \frac{\sqrt{3} \mu I}{\pi} \frac{h}{r \left( h^2 + r^2 \right)^{1/2}} \hat{x}$$ \hspace{1cm} (C.5)

We now move on to determine the magnetic field generated by the arcs of the saddle coil. The problem is depicted in Figure 61.
We again start with Biot-Savart’s law (Equation C.2) to calculate the contribution from one arc. We now have the following equalities

\[
\vec{dl} = r d\theta \hat{\theta}
\]

\[
R = \left( h^2 + r^2 \right)^{1/2}
\]

\[
\hat{R} = -\sin \varphi \hat{x} + \cos \varphi \hat{z}
\]

where \( \hat{\theta}, \hat{x} \) and \( \hat{z} \) are the unit vectors in the angular (from the cylindrical coordinate system), \( x \) and \( z \) directions, respectively, \( \cos \varphi = h/R \) and \( \sin \varphi = r/R \). We must now bring all parameters to the same coordinate system. This is easiest to do if we bring \( \vec{dl} \) to the Cartesian coordinate system and we do this using the following relationship:

\[
\hat{\theta} = -\sin \theta \hat{x} + \cos \theta \hat{y}
\]

Using the above equality we can now calculate the cross product \( \vec{dl} \times \hat{R} \) as follows:

\[
\vec{dl} \times \hat{R} = rd\theta \hat{\theta} \times (-\sin \varphi \hat{x} + \cos \varphi \hat{z}) =
\]

\[
rd\theta (-\sin \theta \hat{x} + \cos \theta \hat{y}) \times \left(-\frac{r}{R} \hat{x} + \frac{h}{R} \hat{z}\right) = \frac{r}{R} (h \cos \theta \hat{x} - h \sin \theta \hat{y} + r \cos \theta \hat{z}) d\theta
\]

Equation C.2 thus becomes:

\[
\vec{d}B = \frac{\mu I}{4\pi R^3} \left(h \cos \theta \hat{x} - h \sin \theta \hat{y} + r \cos \theta \hat{z}\right) d\theta \quad \text{(C.6)}
\]
Integrating Equation C.6 over $\theta$ ranging from $[-\pi/3, \pi/3]$ we finally get

$$\overrightarrow{B} = \frac{\mu I}{4\pi R^3} \int_{-\pi/3}^{\pi/3} (h \cos \theta \hat{x} - h \sin \theta \hat{y} + r \cos \theta \hat{z}) \, d\theta = \frac{\mu I r}{4\pi R^3} \left[ (h \sin \theta \hat{x} + h \cos \theta \hat{y} + r \sin \theta \hat{z}) \bigg|_{-\pi/3}^{\pi/3} \right] = \frac{\mu I r}{4\pi R^3} \left[ \sqrt{3}h \hat{x} + \sqrt{3}r \hat{z} \right]$$

(C.7)

The total magnetic field contribution from all four arcs is now given by multiplying Equation C.7 by four and the $z$ component vanishes due to the symmetry of the problem, leading to

$$\overrightarrow{B}_{Arcs} = \frac{\mu I r}{\pi R^3} \sqrt{3}h \hat{x}$$

(C.8)

We now combine Equations C.5 and C.8 and multiply them by the number of turns of the coil, $N$, to find the total magnetic field at the center of a saddle coil:

$$\overrightarrow{B}_T = \frac{\sqrt{3} \mu NI}{\pi} \left[ \frac{h}{r (h^2 + r^2)^{3/2}} + \frac{rh}{(h^2 + r^2)^{3/2}} \right] \hat{x}$$

(C.9)
ANNEX A – SNR of the NMR experiment

The voltage (formally named electromotive force or emf) induced in the detection coil by a single magnetic moment, \( \mathbf{m} \), is proportional to both \( \mathbf{m} \) and the magnetic field, \( \mathbf{B}_1 \), produced by unit current. It can be determined using Faraday’s law of induction which results in Equation A.1 (54) (The full derivation of this equation is shown in Annex B).

\[
\varepsilon = -\frac{d}{dt} (\mathbf{B}_1 \cdot \mathbf{m}) \tag{A.1}
\]

To find the total voltage induced in the coil after the sample has been subjected to a 90° pulse we need to know the value of \( \mathbf{B}_1 \) at all points in the sample and integrate Equation A.1 along the volume of the sample, \( V_S \), which, if the total magnetization, \( \mathbf{M}_0 \), lies in the \( xy \) plane, gives (54):

\[
\varepsilon = -\int_{\text{Sample}} \frac{d}{dt} (\mathbf{B}_1 \cdot \mathbf{M}_0) \, dV_S \tag{A.2}
\]

For most coil geometries \( \mathbf{B}_1 \) can be calculated and if we consider it to be reasonably homogeneous then Equation A.2 may be simplified to give the total voltage induced in the coil (54):

\[
\varepsilon = K\omega_0 B_1^\perp M_0 V_S \cos \omega_0 t \tag{A.3}
\]

where \( K \) is inhomogeneity factor, \( B_1^\perp \) is the component of \( \mathbf{B}_1 \) perpendicular to \( \mathbf{B}_0 \) and \( M_0 \) is given by (54):

\[
M_0 = N\gamma^2 h^2 (I+1)B_0/3k_B T_S \tag{A.4}
\]

where \( N \) is the number of nuclear spins at resonance per unit volume, \( \gamma \) is the gyromagnetic ratio, \( I \) is the nuclear spin, \( k_B \) is Boltzmann’s constant and \( T_S \) is the temperature of the sample. Now that we know how to calculate the voltage that will be induced in the coil, we need to know how to define and calculate the noise, which will then allow us to finally calculate the SNR during an NMR experiment.

The thermal noise is composed from all other signals which contain no useful information and that we do not want to detect but show up in our measurements. If the probe is correctly designed, then the noise should originate solely from the resistance of the coil and the induced voltage in the coil is given by Equation A.5 (54).

\[
V_{\text{Noise}} = (4k_BT_c \Delta f R)^{1/2} \tag{A.5}
\]
where $T_c$ is the temperature of the coil, $R$ is its resistance and $\Delta f$ is the bandwidth of the probe. For a long straight conductor operating at frequencies of interest to NMR (above 5 MHz, for example), $R$ is given by (54):

$$R = \left(\frac{l}{p}\right) \left(\mu \mu_0 \omega_0 \rho(T_c) / 2\right)^{1/2} \quad (A.6)$$

where $l$ is the conductor’s length, $p$ is its circumference, $\mu$ is the magnetic permeability of the wire and $\rho(T_c)$ is the resistivity of the conductor, which is a function of the temperature.

We are now ready to write down the equation that describes the SNR in the NMR experiment. The resulting equation, giving the root mean square of the SNR $\psi_{\text{RMS}}$, is (54):

$$\psi_{\text{RMS}} = \frac{K B_1^1 V_S N \gamma h^2 I (I + 1)}{7.13 k_B T_S} \left(\frac{p}{l T_c \Delta f k_B F \zeta}\right)^{1/2} \frac{\omega_0^{7/4}}{(\mu \mu_0 \rho(T_c))^{1/4}} \quad (A.7)$$

where we have used the equality $\omega_0 = -\gamma B_0$ and introduced the terms $F$ and $\zeta$. $F$ is the noise figure of the preamplifier (which is a measure of the quality of the preamplifier) and $\zeta$ is the term that accounts for the contributions of the Q factor and fill factor of the coil which may be reasonably well known from experience. Three factors are solely dependent on the geometry of the coil: $KB_1^1$, which is the effective magnetic field produced by a unit current flowing in coil over the sample volume, $p$ and $l$ which are the perimeter and length of the conductor, respectively.

### A.1 Solenoid vs. Saddle coil

Now that we have established that the SNR of a coil depends on certain geometric parameters of the coil, we can compare the performance of a solenoid and saddle coil. The factors of interest for this comparison are the geometrical factors: $V_S$, $B_1^1$, $p$ and $l$. Thus, the important part of Equation A.7 is

$$\psi \propto V_S B_1^1 \left(\frac{p}{l}\right)^{1/2} \quad (A.8)$$

First we must calculate $B_1^1$ for both geometries. While this is an easy task for the solenoid, it is not so for the saddle coil and while Hoult and Richards (54) have shown how this is done, a different and more complete derivation is shown in Appendix C. The coils both have a length $2g$, diameter $2a$ and $N$ turns, as shown in Figure 62.

1 The root mean square of a sine or cosine wave of the form $y = A \cos \omega t$ is $A/\sqrt{2}$.
2 The fill (or filling) factor is a measure of the fraction of the volume of the coil that is occupied by the sample.
3 The birdcage coil is mostly used in clinical magnetic resonance imaging analyses and thus will not be discussed here.
Figure 62 – The solenoid and saddle coil geometries. The angular width of the saddle coil is $2\pi/3$ radians as it is the angle that gives the best homogeneity (54) and the width of the windings is approximately $h/5$.

Source: Reprinted from Hoult and Richards 1976 (54) with permission from Elsevier.

The magnetic field at the center of both geometries produced by a unit current is given by

\[
\begin{align*}
B_{1}^{solenoid} & = \frac{\mu N}{2} \frac{1}{(r^2 + h^2)^{1/2}} \\
B_{1}^{saddle} & = \frac{\sqrt{3} \mu N}{\pi} \left[ \frac{r h}{(r^2 + h^2)^{3/2}} + \frac{h}{r (r^2 + h^2)^{1/2}} \right]
\end{align*}
\]

Because in most cases, $r \approx h$ we can simplify the above equations to

\[
B_{1}^{solenoid} \approx 0.354 \frac{\mu N}{r} \quad \quad B_{1}^{saddle} \approx 0.585 \frac{\mu N}{r}
\]

Now we calculate $l$ and $p$ and assuming that wire is used for the construction of the coils we have

\[
\begin{align*}
l & \approx 2\pi N r \\
\end{align*}
\]

and again, since $r \approx h$ in most cases:

\[
\begin{align*}
l & \approx 6.3 N r \\
l & \approx 16.4 N r
\end{align*}
\]

We can see now that the length of wire per unit turn is greater in the saddle-shaped coil by a factor of approximately 2.6. The manner in which the wire is wound influences
the radius of the wire, \(r_w\). In the case of the solenoid the \(N\) turns must fit into a length of \(2h\), while in the case of the saddle coil the turns must fit into a width of around \(h/5\) (54). Furthermore, to optimize the coils in relationship to the proximity effect (see footnote 1 on page 96), the centers of each turn must be separated by approximately \(3r_w\). Thus, for \(r \approx h\), we have:

\[
3r_w(N - 1/3) = 2r \quad \quad \quad 3r_w(N - 1/3) \approx r/5
\]

\[
\therefore p = 4\pi r/3(N - 1/3) \quad \quad \quad \therefore p = 2\pi r/15(N - 1/3)
\]

and, for \(N \gg 1\)

\[
p \approx 4.2r/N \quad \quad \quad p \approx 0.42r/N
\]

\[
\therefore \psi_{\text{Solenoid}} \propto 0.29\mu V_S/r \quad \quad \quad \therefore \psi_{\text{Saddle}} \propto 0.094\mu V_S/r \quad (A.9)
\]

From Equation A.9 we can see that the SNR of the solenoid coil is around 3 times larger than the SNR of the saddle coil.

Finally, it may also be shown that the length of a 90° pulse is a direct measure of the SNR that can be obtained with a single coil system (54). When the impedance of the probe is matched to the impedance of the transmitter the power supplied, \(W\), is dissipated in its entirety in the resistance of the coil, \(R\), and the current flowing through it will be given by:

\[
I = (W/R)^{1/2}
\]

When the transmitter is on, the current \(I\) will flow through the coil and the resulting magnetic field, \(B_1^*\) will be:

\[
B_1^* = IB_1^1 = B_1^1 (W/R)^{1/2}
\]

and from Equation A.8:

\[
B_1^* \propto W^{1/2}\psi/V_S \quad (A.10)
\]

Since \(\psi\) is the SNR after a 90° pulse, Equation A.10 shows that the length of the pulse is a direct measure of SNR and therefore it would be expected that its length be three times longer when using a saddle coil than when using a solenoid.
ANNEX B – Voltage induced in the NMR detection coil

Let's consider a loop C where a unit current flows in a clockwise direction. A sample is placed within the loop containing a magnetic moment, \( m \), at point P (Figure 63). Consider also that the static magnetic field is oriented in the \( z \) direction.

**Figure 63** – Illustration of the problem.

After a \( 90^\circ \) pulse, \( m \) will oscillate in the \( xy \) plane and the voltage that it induces in the coil is given by Faraday's law of electromagnetic induction which may be written in the following way:

\[
\nabla \times E = -\frac{\partial B}{\partial t} = -\frac{\partial}{\partial t} (\nabla \times A) = -\nabla \times \frac{\partial A}{\partial t} \\
\text{(B.1)}
\]

resulting in

\[
E = -\frac{\partial A}{\partial t} + \nabla \varepsilon \\
\text{(B.2)}
\]

where \( E \) is the electric field at point Q in the loop, \( A \) is the magnetic vector potential also at point Q and the scalar potential, \( \varepsilon \) is a constant of integration. The magnetic moment, \( m \), produces a magnetic vector potential at point Q that is given by (97):

\[
A = \left( \frac{\mu_0}{4\pi r^3} \right) m \times r
\]
where \( \mathbf{r} \) is the displacement vector that points from \( P \) to \( Q \). Substituting this in Equation B.2 gives us:

\[
E = -\frac{\partial}{\partial t} \left[ \left( \frac{\mu_0}{4\pi r^3} \right) \mathbf{m} \times \mathbf{r} \right] + \nabla \varepsilon \quad (B.3)
\]

To find the scalar potential, \( \varepsilon \), we now integrate Equation B.3 around the loop to obtain the potential difference, which must be zero:

\[
0 = -\frac{\partial}{\partial t} \left\{ \oint \left( \frac{\mu_0}{4\pi r^3} \right) (\mathbf{m} \times \mathbf{r}) \cdot d\mathbf{s} \right\} + \varepsilon \quad (B.4)
\]

where \( d\mathbf{s} \) is the unit distance element along the loop. The magnetic field that is produced by the unit current flowing in the coil is given by Biot-Savart’s law:

\[
\mathbf{B}_1 = \oint \left( \frac{\mu_0}{4\pi r^3} \right) (\mathbf{ds} \times \mathbf{r}) = -\oint \left( \frac{\mu_0}{4\pi r^3} \right) (\mathbf{r} \times d\mathbf{s})
\]

Hence, we may reorder Equation B.4 by noting that \( (\mathbf{m} \times \mathbf{r}) \cdot d\mathbf{s} = \mathbf{m} \cdot (\mathbf{r} \times d\mathbf{s}) \) to finally obtain:

\[
\varepsilon = -\frac{\partial}{\partial t}(\mathbf{B}_1 \cdot \mathbf{m}) 
\quad (B.5)
\]

Q.E.D.