New Developments in NMR

Mobile NMR and MRI

Developments and Applications

Edited by Mike Johns, Einar O Fridjonsson, Sarah Vogt and Agnes Haber

ROYAL SOCIETY OF CHEMISTRY

Mobile NMR and MRI

Developments and Applications

New Developments in NMR

Editor-in-Chief:
Professor William S. Price, *University of Western Sydney, Australia*

Series Editors:
Professor Bruce Balcom, *University of New Brunswick, Canada*
Professor István Furó, *Industrial NMR Centre at KTH, Sweden*
Professor Masatsune Kainosho, *Tokyo Metropolitan University, Japan*
Professor Maili Liu, *Chinese Academy of Sciences, Wuhan, China*

Titles in the Series:
1: Contemporary Computer-Assisted Approaches to Molecular Structure Elucidation
2: New Applications of NMR in Drug Discovery and Development
3: Advances in Biological Solid-State NMR
4: Hyperpolarized Xenon-129 Magnetic Resonance: Concepts, Production, Techniques and Applications
5: Mobile NMR and MRI: Developments and Applications

How to obtain future titles on publication:
A standing order plan is available for this series. A standing order will bring delivery of each new volume immediately on publication.

For further information please contact:
Book Sales Department, Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, CB4 0WF, UK
Telephone: +44 (0)1223 420066, Fax: +44 (0)1223 420247
Email: booksales@rsc.org
Visit our website at www.rsc.org/books

Mobile NMR and MRI
Developments and Applications

Edited by

Michael L. Johns
University of Western Australia, Crawley, Australia
Email: michael.johns@uwa.edu.au

Einar O. Fridjonsson
University of Western Australia
Email: einar.fridjonsson@uwa.edu.au

Sarah J. Vogt
University of Western Australia
Email: sarah.vogt@uwa.edu.au

and

Agnes Haber
University of Western Australia
Email: agnes.haber@uwa.edu.au

ROYAL SOCIETY OF CHEMISTRY

THE QUEEN'S AWARDS FOR ENTERPRISE: INTERNATIONAL TRADE 2013

New Developments in NMR No. 5

Print ISBN: 978-1-84973-915-3
PDF eISBN: 978-1-78262-809-5
ISSN: 2044-253X

A catalogue record for this book is available from the British Library

Published by The Royal Society of Chemistry,
Thomas Graham House, Science Park, Milton Road,
Cambridge CB4 0WF, UK

Registered Charity Number 207890

For further information see our web site at www.rsc.org

Printed in the United Kingdom by CPI Group (UK) Ltd, Croydon, CR0 4YY, UK

Preface

When asked by Prof. Bill Price and Prof. Bruce Balcom to put this book together I was somewhat surprised given my research to that point at the University of Cambridge as part of Prof. Lynn Gladden's MRRC had largely been using superconducting magnets. However, following a relocation to the University of Western Australia, I had started to work on applications using low field, portable NMR/MRI instruments; initially out of financial necessity! However it soon became apparent that a lot of my fears, and indeed prejudices, regarding low field were (in context) unfounded and in fact there was a suite of potential applications for which such NMR instrumentation was eminently suitable, although not necessarily optimal in terms of robustness and cost. I also got to interact with a suite of low field NMR companies, and associated applied academics in this space, who were collectively hugely impressive in terms of both their commitment and the developments that they had achieved. Who would have thought we could routinely acquire chemically resolved spectra on small portable benchtop systems a decade ago!

NMR and MRI obviously are extremely useful in medicine and in chemical characterisation. They are also extremely powerful in terms of their use as a laboratory research tool in a very broad range of disciplines. Penetration into other commercial/industrial applications has however been, I think we need to be honest, rather modest. There are a whole suite of reasons for this, dost and sensitivity being arguably the two main ones. Sensitivity is an interesting issue. NMR by comparison with other spectroscopic techniques is inherently insensitive. It really is not ideal for measuring at ppm levels; however, that is where the industry demand often is. NMR/MRI is however incredibly sensitive to a range of sample physical/chemical characteristics, usually in terms of how these impact on relaxation and diffusion measurements. This opens up enormous opportunities. However, this sensitivity to multiple characteristics and parameters also makes interpreting acquired signals quantitatively

New Developments in NMR No. 5
Mobile NMR and MRI: Developments and Applications
Edited by Michael L. Johns, Einar O. Fridjonsson, Sarah J. Vogt, and Agnes Haber

Published by the Royal Society of Chemistry, www.rsc.org

often inherently difficult. Being quantitative is an absolute necessity—this was really hammered home for me in my formative years by Prof. Lynn Gladden and later by Prof. Bruce Balcom. Yes, 'pretty MRI pictures' are often good at convincing 'management' to fund further research work; however, to be really useful for industry at large, techniques really need to be quantitative. What quantitative actually means in this context, is a conversation best left for another forum!

With the above in mind, the field of low field mobile NMR and MRI is clearly currently offering some significant developments that show promise to enable its true potential to be fully exploited. The confluence of developments in hardware, signal enhancement, pulse sequence design and data processing are all encouraging, and collectively will be greater than the sum of their parts. We have done our best to capture some of these in the current textbook. We hope it will enable or even inspire some new practical applications of mobile NMR/MRI and open up new product opportunities. I suspect that a few new applications might 'break the dam wall'. Let's see.

Finally, I would like to thank the chapter authors for their efforts in helping put this book together. I am in awe of their intellect, dedication and achievements in their respective fields. I would also like to thank my fellow editors—Einar Fridjonsson, Sarah Vogt and Agnes Haber. I recruited all of them to Perth, the most isolated city in the world, credit to them that they were still willing to contribute. I would particularly like to single out Sarah Vogt who essentially performed all the tedious editing required and a lot of the required author correspondence. Her efforts were immense and are greatly appreciated.

Mike Johns
University of Western Australia

Contents

New Developments in NMR No. 5
Mobile NMR and MRI: Developments and Applications
Edited by Michael L. Johns, Einar O. Fridjonsson, Sarah J. Vogt, and Agnes Haber

Published by the Royal Society of Chemistry, www.rsc.org

CHAPTER 1

Introduction

EIICHI FUKUSHIMA*[a]

[a]ABQMR, 2301 Yale Blvd., SE (Suite C2), Albuquerque, NM 87106, USA
*E-mail: eiichi@abqmr.com

Until recently, the thought of an NMR or MRI instrument that is compact and mobile was not congruent with laboratory or clinical NMR and MRI. The reason for this discrepancy is easy to discern: laboratory/clinical NMR/MRI instruments use well-characterized and reasonably strong magnetic fields that are difficult to achieve with portable (mostly permanent) magnets. In addition, the complexity of typical NMR experiments in terms of electronic requirements meant that the electronics modules occupied significant real estate, albeit often hidden in electronic racks and enclosures, and required nontrivial power consumption. This monograph describes many new developments that overcome these traditional barriers to mobile NMR.

Because of the lack of small and lightweight magnets with field strengths and homogeneity comparable to those used in laboratories, most applications of compact and mobile NMR were for specific and limited parameters, using magnets with lesser performance than that of laboratory NMR magnets, or no magnets at all. Such applications include simply measuring the magnetic field strength and progressing to detecting the presence or mobility of certain materials in samples of interest to oil, agricultural, and other industries. Many of the advances were realized in situations where the limitations of the magnet are accepted and the measurements tailored to a limited number of parameters that are important to that application but otherwise unobtainable.

New Developments in NMR No. 5
Mobile NMR and MRI: Developments and Applications
Edited by Michael L. Johns, Einar O. Fridjonsson, Sarah J. Vogt, and Agnes Haber

Published by the Royal Society of Chemistry, www.rsc.org

However, there have been recent advances in magnet technology that have significantly helped push the field of mobile NMR forward. Chapters 4 and 5 cover single sided and Halbach magnet developments, respectively, while there is also a recent review on low field magnets for industrial use.[1] A key development is the successful adaptation of mechanical shimming to small single sided magnets, described in Section 4.2.2, opening the possibility of resolving moderate resolution chemical shifts. Another exciting recent advance, that of using bulk high T_c superconductors, is introduced near the end of this chapter and is more fully described in Chapter 11.

Another factor that is contributing to the advance of compact mobile NMR and MRI is the amazing evolution that is still taking place in electronics that was unimaginable a few decades ago. Not only can the electronics be made much smaller than they were in the past, a given size of circuitry can perform at a much higher level, enabling not only miniaturization but also enhanced performance. Consequently, both complex experimental protocols as well as rapid and high-capacity data acquisition contribute to the progress of this field. NMR-on-a-board devices have now been on the market for a number of years and have contributed to the development of many mobile NMR systems. Chapter 6 contains a detailed description of these developments.

Throughout the history of NMR, there have been some examples of mobile or compact NMR that were outside the mainstream of the discipline. Probably the earliest example of mobile NMR was proton magnetometry, which simply measured the Earth's magnetic field strength. A 1955 article on the subject[2] even uses the word portable in the quotation "The apparatus consists of a rugged and portable nuclear magnetometer head, requiring no careful orientation in setting up…" It appears that the author was far ahead of his time. It is known that such proton magnetometers were used to successfully survey archeological sites as early as 1962.[3,4]

Strong[5] described an unusual proton magnetometer developed by Wadsworth[6] in his Scientific American Amateur Scientist column in 1968. This hand-carried device found buried marker magnets that defined areas in a field to study the encroachment of certain grasses into those areas over a period of a few years. The ingenious battery-powered device was operated *via* a spring-loaded manual plunger that created the "pulse sequence" and the free induction decay (FID) was detected in a set of earphones worn by the operator as he/she walked the field. The presence of a marker magnet was detected by a beat signal between two identical water samples spaced 2.6 m apart on a pole carried by the operator. Wadsworth stated that the device cost approximately £10 in parts, although the recently inflated price of copper has increased the present day cost many-fold!

Unbeknownst to most of us NMR practitioners, mobile proton magnetometry has continued to evolve, especially in the miniaturization of electronics as well as the development and application of modern software. There is at least one book that describes the construction and use of proton magnetometers[7] and articles on the modern uses of such devices also exist online[8,9] with major emphasis on studying the temporal variation of Earth's magnetic field. These inexpensive devices enable extremely accurate measurements of the temporal variation of Earth's magnetic field intensity by practitioners all over the world, and their results can be correlated with sunspot activity and rapidly communicated *via* the internet.

Until the mid-1990s, all Earth's field NMR operated in a manner similar to the proton magnetometer, *i.e.*, the spins were initially polarized along the axis of a coil that was energized for that purpose and then allowed to precess around the Earth's magnetic field, generating a FID that was analyzed, mostly for its Larmor frequency. Then, Stepišnik's group succeeded in obtaining magnetic resonance images in Earth's magnetic field. These workers realized that when the pre-polarization field decreases adiabatically, the magnetization follows the effective applied oscillating magnetic field to align with Earth's magnetic field. At that point, the standard spin-warp pulse sequence could be performed using spin echoes to yield images. This was a significant insight that made Earth's field NMR useful for diffusion measurements with pulsed-gradient spin-echo (PGSE) sequences. In contrast, it is still difficult to make magnetic resonance images in the Earth's magnetic field. This field is reviewed in detail by Mohorič and Stepišnik.[10]

One of the best-known research projects carried out with this technique is an experiment to measure the characteristics of brine in the pore structure of Antarctic sea ice by Callaghan's group, as described in another review.[11] The ability of these instruments to carry out standard pulse NMR experiments allowed the measurement of diffusion in the pores of ice cores with PGSE sequences, resulting in information about pore geometries. The harsh experimental conditions were compensated for by the near absence of electromagnetic noise and the presence of feathered observers.

While we are on the subject of Earth's field NMR, it is worth noting that, quite unexpectedly to most of us, ultra high-resolution heteronuclear *J*-coupling data have been obtained at Earth's field.[12] In subsequent experiments, it has been shown that even chemical shift information can be obtained under some circumstances in Earth's magnetic field.[13] This method is not required to be mobile but the hardware used for such experiments is quite minimal and any NMR experiment that does not use an artificial magnet is likely to be mobile. Above all, such an apparatus that does not use high quality artificial magnets is likely to be inexpensive, opening up the possibility of sophisticated experiments that are also affordable. In this experiment, a permanent magnet is used to pre-polarize the spins before the sample is physically transported to the NMR detector for the experiment. However, because the only function of pre-polarization is to enhance the signal, the magnetic field for this purpose need not be homogeneous.

The aforementioned sophisticated data processing, of course, affects all areas of NMR. Chapter 8 discusses two particular aspects of data processing, specifically, compressed sensing and Bayesian techniques. Such advances in data processing are relevant to mobile and compact NMR and MRI, even if for no other reason than usual mobile and compact NMR and MRI can always use more S/N. Of course, the additional information content arising from these new techniques represents an extra benefit to the field.

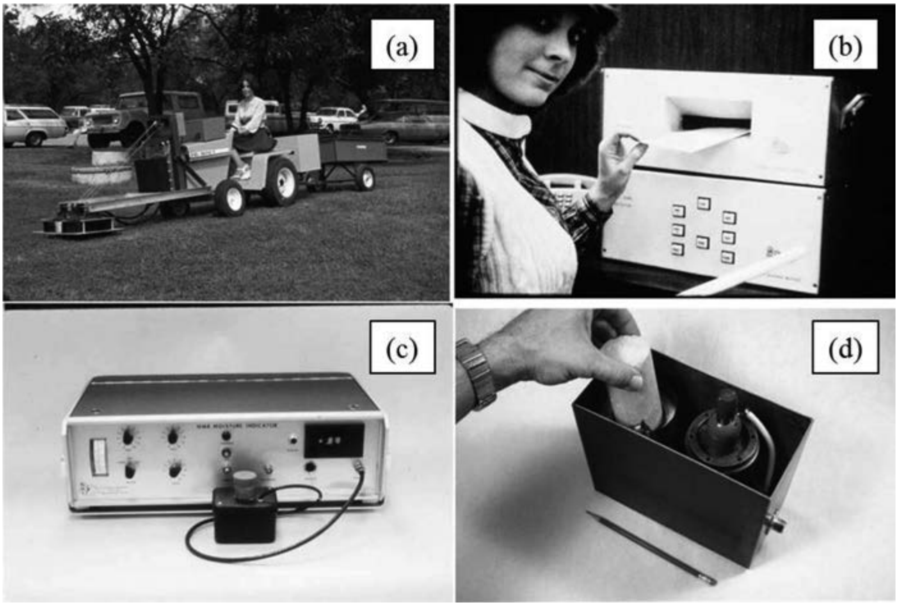

Figure 1.1 (a) Photo of a mine detector that is mounted in front of a tractor. The trailer carried the batteries. (b) Photo of a mail bomb detector based on ^{14}N nuclear quadrupole resonance (NQR). NQR is well-suited for mobile instrumentation because it requires no magnetic fields. (c) Photo of a soil moisture detector and (d) photo of a cement core moisture detector probe, presaging the modern rock core analyzers, such as those described in Chapter 10.

Another isolated effort to take NMR technology out of the laboratory and into the industrial atmosphere was initiated by Bill Rollwitz at Southwest Research Institute (SwRI) in 1953(!) and flourished in the 1970s through to the 1990s. Their numerous projects included landmine detection, moisture measurement in concrete and soil, studies of asphalt aging, inspection of solid rocket motors, tissue measurements, and dynamite detection in checked airline baggage. Because the NMR community-at-large was unaware of SwRI's efforts in NMR, it might be of some interest here to view a few of their mobile devices (Figure 1.1).

A major enabling technology utilized by SwRI, for example, in its landmine detector, is unilateral NMR whereby samples are positioned outside the magnet rather than between poles of electric or permanent dipole magnets or in axial holes of superconducting solenoids. Blümich and his colleagues at RWTH-Aachen led the movement to develop portable and industrial NMR with an emphasis on unilateral NMR. Nowadays, unilateral NMR is available commercially and this technology has been used for such tasks as analyzing frescos, determining the condition of restored paintings, and even an examination of a mummy![14]

Figure 1.2 Unilateral NMR device with which a signal is obtained from a sample of crude oil in a 500 mL plastic bottle on top of the device.

A compact unilateral NMR device at ABQMR that looks at fairly large samples, for example, coconuts, watermelon, and large bottles, is shown in Figure 1.2. It has a favorable spot, *i.e.*, a sweet spot, at a distance of 12–15% of the magnet's diameter (10 cm), in contrast to the more common devices without a sweet spot that look at shallower depths, albeit with much better S/N. The magnet for this scheme is discussed more fully in Chapter 4.

These developments are expected to advance applications in many other areas, such as agricultural products,[15] trees and plants,[16–18] and foods (Chapter 3), not to mention medical applications with possibly large societal consequences (Chapter 11). The unusual magnet designs involved in this technology will be covered in Chapters 4 and 5.

There is also a push towards smaller permanent dipole magnets that are lighter, cheaper, and more portable, largely facilitated by discoveries of rare-earth magnetic materials, such as SmCo and NdFeB. Figure 1.3 shows three 1 T permanent NdFeB-based magnets with 40, 25, and 5 mm gaps, the first two made by Neomax and the smallest made by Aster. The 5 mm gap magnet, also shown in Figure 11.2d, is suitable for performing NMR in capillaries, utilizing microcoils, as discussed in Chapter 6.

Prior to the discovery of these modern magnetic materials, the most common permanent magnets were made of alnico, an alloy of iron, aluminum, nickel, and cobalt. Possibly the earliest commercial "desk-top" NMR

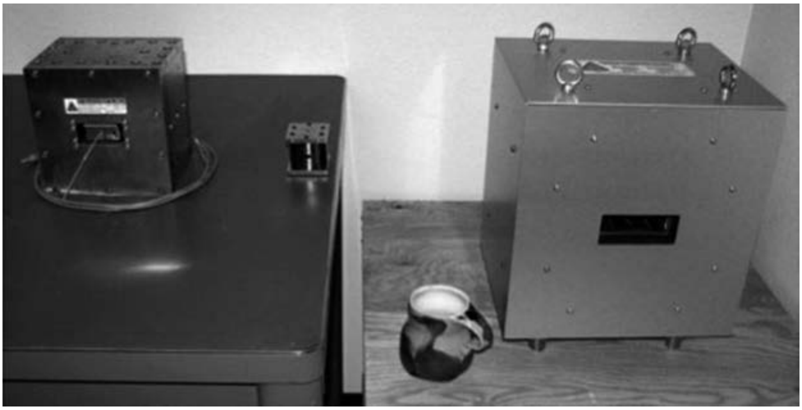

Figure 1.3 Three 1 T permanent NdFeB-based magnets with 40, 25, and 5 mm gaps. The first two were made by Neomax (Japan) and the third by Aster Enterprises in the US.

apparatus was the Spinloc pulse-NMR that used an alnico magnet covered by a stainless steel tea cozy. The operator would drop a seed into the sample chamber through a hole at the top of the tea cozy for the relaxation measurements to determine oil content and then blow it back out by squeezing a rubber bulb that injected air at the bottom of the sample tube.

Another technology that relies on seeing signals from outside the magnet is downhole well-logging, used by the oil industry to characterize the strata and determine the presence, distribution, and fluid permeability of oil. Initially, attempts were made to do these NMR experiments in Earth's magnetic field but the scheme became more practical with the idea of lowering magnets into the borehole in order to enhance the magnetic field strength outside the borehole.[19] It has quietly, at least to the laboratory NMR world, become a field unto itself over the past 25–30 years.[20] The presence of oil is distinguished from that of water by a distinct range of values of T_2 compared with water. In addition, the diffusion coefficient could be measured in order to distinguish liquid oil from gas, and a relatively new development of significance is to combine the diffusion information with T_2. This field will be described in Chapter 2.

An activity that started in the 1980s, termed NMR sounding, uses an ~100 m diameter loop coils for Earth's field NMR detection of water and other proton-containing fluids 50–100 m underground. Such technology is mobile but hardly qualifies as "compact" NMR because it requires a large truckload of wire to form the NMR coil. The large scale is needed because the technique depends on seeing an enormous volume of sample to overcome the very poor specific sensitivity of NMR in the very weak Earth's magnetic field. This is especially true here because there is no pre-polarization to enhance S/N as in the previously mentioned Earth's field NMR experiments. One of the major challenges in using such large coils is the sensitivity to long- and

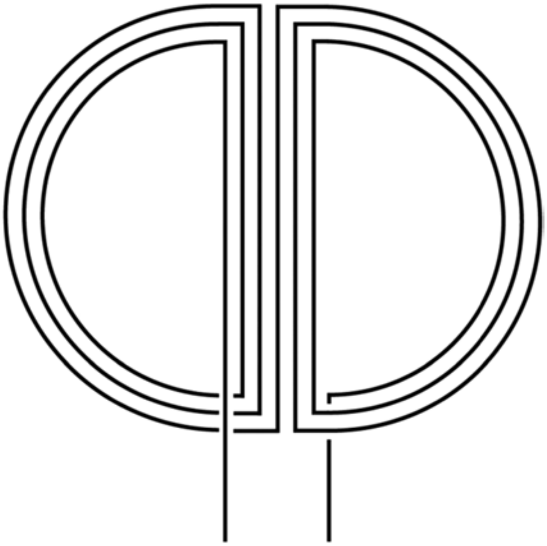

Figure 1.4 Schematic of a flat gradiometer coil used in Earth's field NMR that is sensitive to a flat region parallel to the plane of the coil. Coils with length scales from 61 cm to 6 m have been used to detect proton signals from water without pre-polarization.

short-range interference that exists near man-made objects. Thus, a major topic of research in this area concerns mitigation of such interference by analog and digital means, often needing to use an extra coil to obtain a reference signal. There are several commercially available systems and the discipline will be described in Chapter 9.

Recent experiments at ABQMR demonstrated that it is possible to obtain NMR signals in Earth's magnetic field from shallower depths over smaller areas without prepolarization. Prototype two-dimensional coils obtained excellent signals from a ~10 cm deep water over an area of ~400 cm^2 in 32 scans. The essential components of these coils are: (1) a gradiometer configuration to attenuate long-range interference, (2) use of a sufficient amount of wire to enhance the sensitivity, and (3) geometry that fits the shape of the sample.[21]

Figure 1.4 shows a sketch of a flat gradiometer coil showing, for simplicity, only six turns of parallel wires in the center that form an array that is sensitive to a flat region that is parallel to the plane of the coil. An actual coil wound in this way has 992 turns of #18 wire in the 61 cm long, 10 cm wide, center array. The signal-to-noise ratio (S/N) depends on the coil parameters as:

$$\mathrm{S/N} \propto \frac{B_1/i}{\sqrt{r}} \qquad (1.1)$$

where B_1/i is the magnetic field strength at the sample element position per unit current flowing through the coil and r is the resistance of the coil.[22]

Because the numerator is proportional to the number of coil turns for a constant geometry, while the denominator is proportional to their square root, the performance will improve with additional turns. Low frequency NMR, such as Earth's field NMR, can take full advantage of this relation until the wire length becomes a non-trivial fraction of the wavelength, which is approximately 150 km! Additional improvements are possible by reducing the resistance of the coil wire, for example, by increasing the diameter of the wire, an avenue made easier in this situation simply by the large size of the coil. S/N was increased further by the use of adiabatic fast half-passage sweeps in order to cause B_1-independent nutation of magnetization into the transverse plane.

This arrangement has recently been scaled up to a coil that is 6 m across for detecting liquids 1 to 2 m away in less than a minute without pre-polarization. In order to keep the required transmitter voltage low with the increased current required to reach the sample element that is farther away, S/N was maximized not by maximizing B_1/i but by minimizing r. Therefore, the finished coil has only an 8-wire array in the center that is 1 m wide but each "wire" consists of 210 11-gauge aluminum magnet wires so that the total resistance with various connections is in the range of tens of milliohms. With the total impedance of ~4 ohms, it is possible to have an effective Q of ~100, which represents a bandwidth of 20–25 Hz. Although not portable in the usual sense, this coil can be moved around by a helicopter.

An early commercial compact NMR, aimed at industrial uses, was made by Tri-Valley Research using a Halbach magnet and was primarily aimed at examining rock cores. This is an ideal application for a compact NMR device without stringent field homogeneity requirements and has evolved into a viable field with companies such as Magritek marketing rock core analyzers, which are described in Chapter 10.

An exciting development is that of a bulk superconductor as a compact magnet that features field strength that is comparable to existing superconducting (wire) magnets and whose homogeneity is improving. The bulk superconductor is placed in a uniform field of another superconducting magnet and its temperature is lowered past the superconducting transition to trap the field. The strongest field strength attained so far is 4.74 T and the magnet operates at around 50 K, which requires only a standard cryogenic refrigerator.[23] Additional details are given in Chapter 11, but it is easy to conceive that this magnet could be configured as a desktop unit. It is also easy to imagine, because of its light weight, small size, and the relatively high operating temperature, that this magnet will be easy to transport while energized. This promising technology will join others involving permanent magnets to open the door to compact high resolution NMR. Other technological developments that may have beneficial effects on mobile and compact NMR/MRI include SQUID and atomic NMR, which are described in Chapter 7. Once again, the suitability of these techniques for mobile NMR is rooted in the lack of necessity of a large magnet although these methods must overcome some other barriers for them to be truly mobile. Specifically, the need for cryogens for SQUIDs and high temperature for atomic magnetometry plus significant shielding requirements must be overcome.

All in all, the field of mobile NMR and MRI is an exciting one with many potential applications, and significant additional progress should be forthcoming in the near future. The following chapters in this monograph offer ample evidence that the phrase "shrinking NMR" has become a distinct possibility.

Acknowledgements

The author is grateful to Armando De Los Santos of Southwest Research Institute and Daiki Tamada of University of Tsukuba for providing unpublished drawings and photographs. Discussions with colleagues Stephen Altobelli and Lana Chavez as well as editorial help from Janet Bench are acknowledged. Finally, the Earth's field NMR at ABQMR, briefly mentioned, was supported by Upstream Research Company of Exxon Mobile.

References

1. J. Mitchell, L. F. Gladden, T. C. Chandrasekera and E. J. Fordham, *Prog. Nucl. Magn. Reson. Spectrosc.*, 2014, **76**, 1–60.
2. G. S. Waters, *Nature*, 1955, **176**, 691.
3. C. M. Lerici, in *Expedition Magazine*, Spring, 1962, p. 4.
4. D. F. Brown, in *Expedition Magazine*, Winter, 1963, p. 40.
5. C. L. Strong, *Sci. Am.*, 1968, **218**, 124.
6. N. J. Wadsworth, *J. Sci. Instrum.*, 1967, **44**, 552.
7. S. Hollos and R. Hollos, in *Signals from the Subatomic World: How to Build a Proton Precession Magnetometer*, Abrazol Publishing, 2008.
8. J. Geller, *EDN*, 2012, August 12, 2012, available online at http://www.edn.com/design/analog/4392193/Geomagnetic-observatory.
9. J. A. R. Koehler, 2012, available online at http://members.shaw.ca/jark/ProtonPrecessionMagnetometers.pdf.
10. A. Mohorič and J. Stepišnik, *Prog. Nucl. Magn. Reson. Spectrosc.*, 2009, **54**, 166–182.
11. M. E. Halse and P. T. Callaghan, *eMagRes*, 2009, DOI: 10.1002/9780470034590.emrstm1025.
12. S. Appelt, F. W. Häsing, H. Kühn, U. Sieling and B. Blümich, *Chem. Phys. Lett.*, 2007, **440**, 308–312.
13. S. Appelt, S. Glöggler, F. W. Häsing, U. Sieling, A. G. Nejad and B. Blümich, *Chem. Phys. Lett.*, 2010, **485**, 217–220.
14. B. Blümich, *Sci. Am.*, 2008, **299**, 92–98.
15. Y. Geya, T. Kimura, H. Fujisaki, Y. Terada, K. Kose, T. Haishi, H. Gemma and Y. Sekozawa, *J. Magn. Reson.*, 2013, **226**, 45–51.
16. D. Capitani, F. Brilli, L. Mannina, N. Proietti and F. Loreto, *Plant Physiol.*, 2009, **149**, 1638–1647.
17. H. Van As, T. Scheenen and F. J. Vergeldt, *Photosynth. Res.*, 2009, **102**, 213–222.

18. T. Umebayashi, K. Fukuda, T. Haishi, R. Sotooka, S. Zuhair and K. Otsuki, *Plant Physiol.*, 2011, **156**, 943–951.
19. J. A. Jackson, L. J. Burnett and J. F. Harmon, *J. Magn. Reson.*, 1980, **41**, 411–421.
20. R. J. S. Brown, R. Chandler, J. A. Jackson, R. L. Kleinberg, M. N. Miller, Z. Paltiel and M. G. Prammer, *Concepts Magn. Reson.*, 2001, **13**, 335–413.
21. L. Chavez, S. Altobelli, E. Fukushima, T. Zhang, T. Nedwed, D. Palandro, L. Srnka and H. Thomann, *Near Surf. Geophys.*, 2015, **13**, DOI: 10.3997/1873.0604.2015023.
22. D. I. Hoult and R. E. Richards, *J. Magn. Reson.*, 1976, **24**, 71–85.
23. D. Tamada, T. Nakamura, Y. Itoh and K. Kose, *Phys. C*, 2013, **492**, 174–177.

CHAPTER 2

NMR Well Logging

MARTIN D. HÜRLIMANN*[a] AND NICHOLAS J. HEATON[b]

[a]Schlumberger-Doll Research, One Hampshire Street, Cambridge, MA 02139, USA; [b]Schlumberger HFE Center, 110 Schlumberger Drive MD-4, Sugar Land, TX 77478, USA
*E-mail: hurlimann@slb.com

2.1 Introduction

Well logging is the general technique of measuring physical properties of the subsurface using specialized sensors that are lowered into boreholes. NMR well logging is based on low field NMR measurements using NMR sensors. The measurements respond directly to the fluids in the subsurface and provide a unique tool for their characterization. Recent advances in the technique of NMR well logging have greatly enhanced the versatility and robustness of this measurement. Well logging provides a valuable tool in the exploration of hydrocarbon wells and has become a significant commercial application of NMR. The analysis of NMR well logging data enables the quantification of the fluids occupying the pore space and the prediction of the fluid flow properties through the reservoir. These are critical steps in the evaluation of hydrocarbon reservoirs and in the planning of production strategies. These tasks are not only important for the petroleum industry, but they lie at the heart of other applications based on the Earth Sciences. For example, hydrology focuses on the distribution, transport, and contamination of water in aquifers, and carbon sequestration deals with the deposition of carbon dioxide into earth formations. For these purposes, it is essential to

New Developments in NMR No. 5
Mobile NMR and MRI: Developments and Applications
Edited by Michael L. Johns, Einar O. Fridjonsson, Sarah J. Vogt, and Agnes Haber

Published by the Royal Society of Chemistry, www.rsc.org

understand the connectivity of the pore space and monitor the fluids inside the earth formations.

NMR measurements are of particular interest because they are able to directly detect, distinguish, and characterize both aqueous and hydrocarbon fluids *in situ*. There is no need to extract the fluids first from the formation, which is an expensive and time-consuming process. The *in situ* fluid characterization also avoids complications due to possible phase transitions induced by the process of fluid extraction. The unique value provided by NMR well logging for the characterization of subsurface earth formations can be best appreciated by comparing it to other available logging or surface measurements. The most widely used surface technique is seismic prospecting.[1] This provides large-scale information on the geometry of the geological structures deep into the earth, but yields limited information on the fluids contained in the pore space or on the flow properties of the formation. A number of surface-based measurements, including ground-penetrating radar, gravimetric measurements, electrical conductivity measurements, and the technique of surface NMR, can provide information on the fluids. While the typical resolution and range of depth accessible with these techniques is adequate for the investigation of shallow aquifers, it is clearly insufficient for the exploration of hydrocarbon reservoirs, which are often located 1 to 3 km below the surface, but can be as deep as 10 km.

Both the techniques of surface NMR and NMR well logging are based on the general concepts of nuclear magnetic resonance, but their implementations and operations are very distinct. The technique of surface NMR (see ref. 2 as well as Chapter 9 of this monograph) is based on earth field measurements using a large coil with a typical diameter as large as 100 m. The proton spins in the underlying earth formation are excited by passing an oscillating current at the relevant Larmor frequency through the large coil. The Larmor frequency is controlled by the strength of the local Earth's magnetic field and is therefore in the audio frequency range between 1 kHz and 2.8 kHz. The same coil is then used to detect the resulting free induction decay. From measurements with excitation currents of different strengths or durations, it is possible to infer a coarse one-dimensional image of the fluid distribution. The size of the sensitive region scales with the radius of the coil, which limits this technique to the exploration of the near surface region. To extend NMR measurements to greater depth, it is necessary to perform well logging measurements.

2.1.1 General Technique of Well Logging

The general method of well logging is a highly developed technique with many companies providing commercial services. In 2010, the logging industry generated total annual revenues in the range of tens of billions of dollars. Logging measurements are available with sensors based on many different measurement principles, including numerous electromagnetic, nuclear, acoustic, ultrasonic and NMR measurements. An overview of the various measurement principles can be found elsewhere, such as in the book by Ellis and Singer.[3] Here we focus on the technique of NMR well logging that allows the quantitative extraction of the relaxation and diffusion properties of the fluids. These measured properties can then be related to a wide range of other physical properties that are of direct interest to geoscientists and engineers, including porosity and fluid saturations, fluid compositions and viscosities, and estimates of the distribution of pore sizes and of flow properties.

There are a number of distinct modes of well logging. The two most important modes are *wireline logging* and *logging while drilling*, followed by the technique of *mud logging*. Wireline logging has traditionally been the dominant logging technique and has the longest history. In this mode, different sensors are connected into a so-called tool string that is lowered into the borehole at the end of a long armored cable. The cable acts simultaneously as a mechanical support, as a conduit of power, and as a link of communication to control the sensors and to retrieve the data to the surface. The assembly of sensors is typically first lowered to the bottom of the borehole. As the sensors are pulled back up to the surface at a controlled rate in the range of 2 cm s^{-1} to 30 cm s^{-1}, they are instructed to continuously perform measurements on the surrounding earth formation. The resulting data is referred to as log. Under special circumstances, it is also possible to perform so-called station measurements for a limited amount of time. Under typical borehole conditions, the duration of NMR stations has to be kept to less than 30 minutes to minimize the danger of getting stuck in the borehole and losing the sensor. While the tool string is stationary, it also becomes possible to use specialized sampling instruments that withdraw, collect, and analyze fluids directly from the formation.

The employment of the logging while drilling (LWD) method has grown rapidly in recent years and has now become of comparable importance to wireline logging in the oil and gas industry. In LWD operations, the sensors are directly integrated into the drill string and measurements are performed during the drilling operation. This has the advantage that the information from the sensor can be used to guide the direction of the drilling. This approach of directional drilling with LWD has enabled much higher accuracy in well placement at the desired geological location within the earth formation. Note that compared to wireline measurements, LWD measurements are less affected by fluid invasion (*i.e.* the replacement of formation fluid by borehole fluid) because the LWD measurements are performed shortly after the borehole is created.

Sensors for all forms of well logging have to be built to withstand the extreme conditions that can occur in a reservoir. The downhole temperatures and pressures can reach 175 °C and 140 MPa, respectively. The sensors have to be slim enough to fit into the boreholes with typical diameters in the range of 12 cm to 35 cm. Furthermore, LWD sensors have to be able to withstand high shocks and vibrations encountered during the drilling operation.

2.1.2 Overview of NMR Well Logging and its Challenges

Commercial services of NMR well logging are available for both wireline and LWD applications. There has been much progress in the development of this technique during the last two decades and advances continue at a rapid pace. Nevertheless, it is fair to say that NMR well logging is not yet as mature as other major logging techniques. A key reason is that NMR logging is not simply an adaption of a well-established laboratory measurement to downhole conditions. Important aspects of the NMR logging technique differ substantially from the traditional forms of laboratory NMR measurements, such as NMR spectroscopy and MR imaging. These differences include the configuration of the hardware, the dominant term in the underlying spin dynamics, data inversion, and data interpretation.

A fundamental difference between laboratory NMR and NMR well logging is that in the latter technique, the sample is located outside the sensor. Clearly, the earth formation cannot be placed inside the detection coil in a region of magnet field of high strength and homogeneity. NMR well logging tools therefore require an inside-out measurement scheme. The geometry of the magnet and radio frequency (rf) coil have to be adapted to this uncommon situation. As a consequence of the inside-out geometry, the applied magnetic fields across the sample are necessarily much weaker and less uniform than in standard NMR measurements. This leads to typical Larmor frequencies below a few MHz and inhomogeneities $\Delta B_0/B_0$ of order unity. This has to be compared to state-of-the-art high field laboratory NMR spectrometers where Larmor frequencies approach 1 GHz and $\Delta B_0/B_0 < 10^{-8}$. As a consequence, off-resonant effects play a key role in the spin dynamics for NMR well logging and they completely dominate chemical shift terms. This precludes the implementation of conventional NMR spectroscopy. Instead, NMR well logging relies on relaxation and diffusion measurements. The design of the sensor must also take into account that the apparatus is generally moving with respect of the sample during the measurement.

A number of different sensor configurations have emerged as solutions to these challenges. An overview of the various approaches is given in Section 2.2. In Section 2.3, we review the challenges posed by performing the NMR measurements in weak and grossly inhomogeneous fields and discuss the pulse sequences developed for well logging. Strategies to develop robust calibration procedures over the entire range of parameters are outlined in Section 2.4. There are often drastic changes in the environmental conditions (*e.g.* temperature and borehole salinity) during the logging operation that pose additional difficulties for NMR well logging. Issues related to data processing are covered in Section 2.5. The analysis of standard NMR measurements relies mainly on the technique of Fourier transformation, a robust and well-understood operation. In contrast, well logging deals with relaxation and diffusion data that require an inverse Laplace transformation. This is an ill-conditioned problem and poses many additional challenges. In Section 2.6, we give a brief overview of the relevant physics that control the relationships between the measured relaxation and diffusion properties, and the properties of the porous media and the complex fluids within. Finally, in Section 2.7, we present some representative applications of NMR logging.

2.2 Sensors for NMR Logging

2.2.1 Early Earth Field NMR Technique

Efforts to develop NMR well logging started early and began only a short time after the discovery of NMR by Bloch and Purcell in 1946. A historical overview of the activities up to the end of the 20th century can be found in.[4,5] The initial approach was based on an ingenious scheme using the earth magnetic field.[6] The logging apparatus consisted of a large solenoid with approximately 1000 turns. A 2 kW power supply was used to energize the coil with a large current that produced the strongest possible static magnetic field in the formation around the borehole and increased the magnetization of the nearby nuclear spins. To generate the maximum polarization, the field was applied for a time long compared to the longitudinal relaxation time (*i.e.* at least a few seconds). To detect the NMR signal, the current in the coil was then abruptly turned off in such a manner to result in a non-adiabatic removal of the applied field. This generated a free induction decay in the earth magnetic field that was detected by connecting the large coil to a sensitive preamplifier. The signal frequency corresponded to the Larmor frequency in the local earth magnetic field, *i.e.* 1.0 kHz to 2.8 kHz depending on the geographical location.

Despite the low detection frequency, the earth field approach was able to generate a signal with an adequate signal-to-noise ratio (SNR) as it was able to excite transverse magnetization in a relatively large volume. Nevertheless, the earth field method has a number of intrinsic shortcomings that limited its impact on formation evaluation. First, it was essential to eliminate any NMR signal that originates from the fluid inside the borehole. This was achieved by doping the borehole fluid with a sufficiently high concentration of paramagnetic salts. However, this procedure complicates the drilling procedure and increases the operation time, adding to the overall cost. Furthermore, it introduced a significant uncertainty in the calibration of the amplitude of the NMR signal in terms of the formation porosity because it requires the knowledge of the exact shape of the borehole and of the invasion profile of the paramagnetic ions into the formation, information that is generally not available. An additional challenge was posed by the sizeable dead-time of the receiver before the free induction decay could be recorded. Given the large initial current, the large inductance of the coil and therefore long intrinsic decay time, it took typically 25 ms before the current decayed to a sufficiently low level in the coil to detect the weak NMR signal. Signal components with relaxation times shorter than this dead-time could therefore not be detected. Such fast decaying components are often a significant fraction of the overall magnetization. As a consequence, it becomes impossible to relate the initial amplitude of the detected signal with this earth field NMR technique directly to the total porosity signal of the surrounding formation.

2.2.2 Modern NMR Well Logging Technique: Pulsed NMR in an Applied Magnetic Field

To circumvent the shortcomings of the Earth field approach, modern NMR well logging tools use externally applied B_0 fields and operate at a higher Larmor frequency. Conceptually, the overall architecture of modern NMR logging devices resembles those of standard laboratory NMR systems. They consist of a magnet system that generates the static magnetic field, and an rf coil that can be switched between an rf transmitter and a sensitive receiver. The rf coil is used to transmit strong rf pulses into the formation to generate net precessing magnetization, which is then detected with the same rf coil. Given the challenging environment for NMR logging, the static magnetic fields are not generated by superconducting magnets as in conventional NMR systems, but instead by permanent magnets. They are typically based on modern rare earth magnetic materials with a high Curie temperature such as SmCo. Pulsed NMR well logging using externally applied magnetic fields can overcome all the key limitations of the earth field based technique:

(i) Externally applied magnetic fields results in a strong spatial localization of the NMR signal with a well-defined volume of investigation. A signal is only generated in regions where the local Larmor frequency (proportional to the local field strength) is close to the rf frequency of the rf pulses used. This localization eliminates the need to dope the drilling fluid with paramagnetic salts. It also avoids the calibration uncertainties associated with the details of the borehole size and invasion profiles of the paramagnetic ions that were encountered in the earth field technique. However, the challenge now becomes designing a sensor with a sufficiently large sensitive volume that can generate signals with adequate signal to noise ratio.

(ii) The detection frequency is up to three orders of magnitude higher than in earth field measurements. In current logging instruments based on modern permanent magnets, the operating frequencies range from about 150 kHz to 2.3 MHz. As a consequence, the electronic recovery times are much shorter compared to earth field operation and it becomes feasible to detect fast relaxing components and to determine the total porosity.

(iii) The pulsed NMR technique allows flexibility in the type of measurements to be performed. The pulse sequence and pulse parameters can be tailored to the specific application of interest. As discussed below, measurement schemes are available to measure not only porosity, but also relaxation and diffusion properties quantitatively in grossly inhomogeneous fields. In addition, it is possible to vary the spatial location of the volume of investigation by changing the carrier frequency of the rf pulses, similar to the technique of slice selection in MRI.

2.2.3 General Considerations Governing the Tool Design

A fundamental challenge in designing a sensor for pulsed NMR is to find a configuration of magnets and rf coils that creates a sufficiently large resonant volume that leads to a resulting NMR signal with an adequate signal-to-noise ratio. All the possible designs are controlled by a number of general considerations. Given that the sample is outside the NMR apparatus, it is not possible to apply uniform B_0 and B_1 fields to the sample. This leads to a large distribution of the local Larmor frequency $\omega_L(\vec{r}) = \gamma B_0(\vec{r})$ and nutation frequency $\omega_L(\vec{r}) = \gamma B_{1,\perp}(\vec{r})/2$ across the entire sample. In inhomogeneous fields, the signal S generated by the normalized magnetization $m_\perp(\vec{r})$ is given by:[7,8]

$$S = \phi \frac{2\chi}{\mu_0} \int d\vec{r} \; B_0^2(\vec{r}) \frac{\omega_1(\vec{r})}{I} D(\omega_0(\vec{r})) \left[m_x(\vec{r}) + i \; m_y(\vec{r}) \right] \tag{2.1}$$

Here ϕ is the porosity, χ is the MKS susceptibility of the relevant nuclei, which is typically hydrogen, I is the current in the antenna, and $D(\omega_0)$ is the frequency response of the detector, including the tuned coil. We use the standard notation $\omega_0(\vec{r}) \equiv \omega_L(\vec{r}) - \omega_{RF}$ to indicate the offset of the local Larmor frequency from the applied rf frequency, ω_{rf}, in the rotating frame. The factor of ω_1/I is the detection efficiency of the antenna according to the reciprocity theorem.

Inspection of eqn (2.1) reveals a number of required design principles for the generation of a large NMR signal. The equation contains the term B_0^2, which is a combination of the Boltzmann factor, which describes the polarization effect, and the detection efficiency based on Faraday's law. This strong dependence on the magnetic field strength implies that magnet assemblies should be used that generate the highest possible static field B_0 in the formation. It is also important to generate transverse magnetization over the largest possible volume. The exact results depend on details of the field profiles and pulse sequences, but to first order the resonant volume can be approximated by the region in space where the local Larmor frequency deviates from the nominal Larmor frequency (*i.e.* the applied rf frequency ω_{RF}) by less than the nutation frequency, ω_1, In other words, the resonant region is approximately the region of space where $|\omega_0(\vec{r})| < \omega_1$. This implies that the static field generated by the magnet assembly in the earth formation should not only be as large as possible, but also be as uniform as possible. Earnshaw's theorem states that it is impossible to generate field profiles with a maximum outside the magnets.[9] Nevertheless, it is possible to generate fields that are sufficiently uniform and to create sensitive regions that extend either along a line or a plane. The first category includes magnet configurations that create field profiles with saddle points where the local gradient vanishes along a line, while the second category consists of magnet configurations that create gradient fields.

The resonant volume depends on the rf power. An increase of the instantaneous rf power results in larger values of ω_1, which increases the acceptable deviations of the static magnetic field from its target value. For this reason, an effort is made to maximize the peak rf power in commercial NMR well logging tools. Typical values are of the order of kW.

There is a long list of additional requirements for the successful design of an NMR logging tool. It is essential that the resonant region is completely localized within the earth formation surrounding the borehole and that it does not intersect the borehole. In addition, it is desirable that the resonant region is as far away from the borehole wall as possible to minimize the impact of possible formation damage induced by the drilling operation on the measurement. A large depth of investigation also reduces the fraction of the sensitive region that is contaminated with invaded borehole fluid. There is obviously a trade-off between the design criteria for a large depth of investigation and the goal of maximizing the signal-to-noise ratio of the measurement. Current commercial logging tools are able to achieve a depth of investigation of up to 15 cm from the borehole.

The sensor design also has to take into account the motion of the apparatus during the measurements. The resonant region has to extend along the direction of the motion. For wireline applications, the resonant region should extend along the length of the apparatus, whereas for LWD applications, the resonant region should have azimuthal symmetry to account for the rotational motion of the drill-string.

2.2.4 Configurations of NMR Logging Tools

The first practical solution of this optimization problem was described in 1980 by J. Jackson and collaborators at Los Alamos National Laboratory.[10–12] This group also presented the first experimental demonstration of the feasibility of a pulsed NMR logging tool based on permanent magnets. Since this pioneering work, a number of other suitable configurations have been identified and developed into commercial logging tools. The different configurations of the magnet and rf coils can be generally classified according to two overall properties:

(1) The azimuthal symmetry of the resonant volume: azimuthally symmetric *versus* one-sided.
(2) The radial profile of the magnetic field across the sensitive region: saddle-point *versus* gradient.

Logging tools with azimuthally symmetric resonant regions probe the formation all around the borehole. Such devices have to be operated while being centralized in the borehole. They are designed for a given borehole diameter. Logging tools with one-sided sensitivity patterns are pushed against the borehole wall during the logging operation. In this case, the depth of investigation is independent of the diameter of the borehole and the same tool can be used in a range of borehole sizes. This is an attractive feature that lowers the overall asset cost and simplifies service maintenance.

The radial profile of the magnetic field across the sensitive region controls another set of tradeoffs. A saddle point profile generates a relatively wide resonant region that makes the measurements less sensitive to lateral motion than in a tool based on a gradient design. Measurements in a gradient tool are generally more affected by diffusion effects. Depending on the application, this can be considered either an advantage or a disadvantage. In a gradient tool, it is straightforward to change the depth of investigation by changing the rf frequency. In a saddle point design, quantitative measurements require the setting of the rf frequency precisely to the Larmor frequency at the saddle point. In such tools, it is important to track and compensate any drifts in the Larmor frequency due to possible changes in the magnet temperature or accumulation of magnetic debris on the magnets.

Commercial logging tools have been developed with all four possible combinations of azimuthal and radial field profiles. We now present illustrative examples for each possibility.

2.2.4.1 Centralized Logging Tool with Saddle-Point Magnetic Field Profile

The magnet configuration introduced in the pioneering work by Jackson *et al.*[10–12] consists of two cylindrical magnets, polarized in opposite directions along the axis of symmetry, that are spatially separated along the axis. In the plane of symmetry perpendicular to the axes of the magnets, this magnet array produces a purely radial field with azimuthal symmetry. In the radial direction, the field strength starts at zero in the center, rises to a maximum, and then falls off at larger distance. By adjusting the magnet spacing, it is possible to achieve a relatively uniform saddle-point-like field profile in a toroidal region. An efficient way to generate an rf field perpendicular to the static field in the resonant region is to place a tuned solenoid coaxially between the magnets. The resulting resonant region has the form of a toroid with azimuthal symmetry, but without a large extent along the sensor axis. Therefore, this configuration is suited for LWD applications where the dominant sensor motion is circular, but not suited for wireline logging where the sensor moves along the borehole. Several commercial logging-while-drilling devices[13–15] are based on variations of this basic tool configuration. A schematic drawing of the device described in[13] is shown in Figure 2.1.

2.2.4.2 Centralized Logging Tool with Gradient Magnetic Field Profile

Taicher and Shtrikman[16] developed an alternative tool configuration that is based on two-dimensional dipole profiles for both the static and rf magnetic fields. The static field is created by a long cylindrical magnet that is magnetized perpendicular to its axis. Neglecting end effects, the resulting magnetic field lies in the transverse plane and has a magnitude that depends

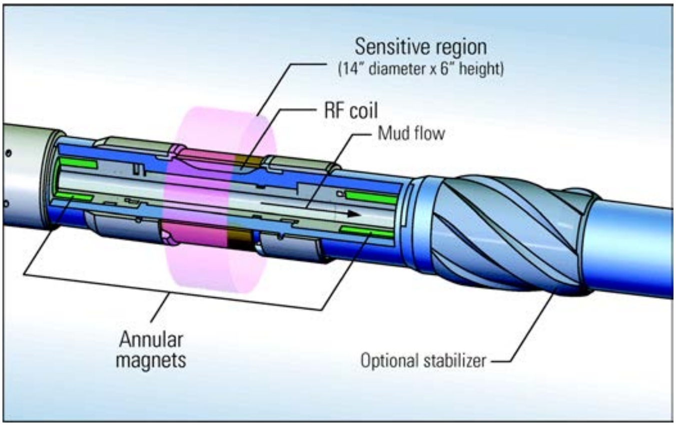

Figure 2.1 Schematic view of the NMR logging-while-drilling device with an azimuthally symmetric sensitive region described in ref. 13. The two permanent magnets, shown in green, are magnetized along the tool axis in opposite directions and generate a magnetic field that is radial in the sensitive region. Illustration copyright Schlumberger. Used with permission.

only on the distance from the tool. The direction of the field varies along the azimuth. This static field is matched by an rf field generated by a coil that is wound around the magnet and oriented in such a way that it produces a two-dimensional dipole rf field that is everywhere perpendicular to the static field. The magnets are built from non-conducting ferrite magnets to make them transparent to the rf fields. This elegant design results in an azimuthally symmetric resonant region that consists of a thin cylindrical shell extending along the tool. The diameter of the shell is controlled by the operating rf frequency. In practical implementations, the magnets extend beyond the rf coils to attenuate the impact of the end effects on the field profiles in the sensitive zone and to help polarize the spins before they enter the measurement zone. The symmetry of this design (see Figure 2.2) makes it suitable for both wireline and logging-while-drilling applications, and commercial devices have been developed for both applications.[17,18] In these devices, the operating frequencies are in the range of 500 kHz to 750 kHz, and the corresponding radii of the resonant regions are in the range of 17 to 21.5 cm. Within the resonant region, the field profile is characterized by a well-defined gradient that falls in the range of 14 G cm^{-1} to 21 G cm^{-1}. This leads to thin shells with a typical thickness of about a millimeter.

2.2.4.3 Single-Sided Logging Tool with Saddle-Point Magnetic Field Profile

Kleinberg and Sezginer[19] introduced a single-sided design with a magnetic field profile characterized by a saddle point that extends along the tool direction. This field profile is achieved with the use of two SmCo magnets that

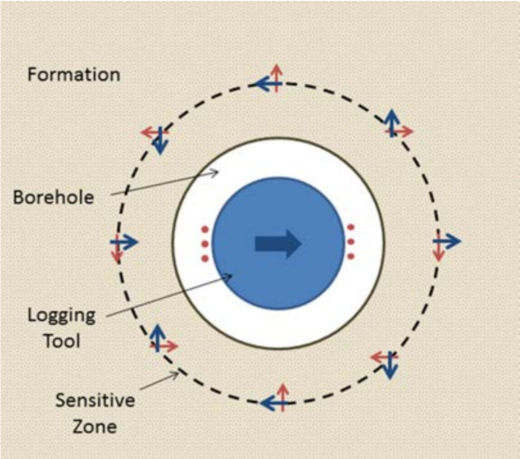

Figure 2.2 Centralized logging tool with a gradient field profile. Schematic cross section of a wireline NMR logging tool[17] based on the design by Taicher and Shtrikman.[16] The tool consists of a long cylindrical permanent magnet, shown in blue, magnetized perpendicular to its axis, as indicated by the arrow, and an rf coil shown in red. The sensitive region consists of thin cylindrical shells (indicated by the dashed line). By symmetry, in these shells the static magnetic field (shown as blue arrows) and the rf magnetic field (shown as thin red arrows) have a constant magnitude and are everywhere perpendicular to each other.

are both magnetized transverse with respect to the sonde axis. The resulting magnetic field is predominantly radial into the formation and its profile has a saddle point about 2.5 cm inside the formation. The field strength in the resonant region is 55 mT, corresponding to the Larmor frequency of 2.3 MHz. The rf coil occupies a semicircular cylindrical cavity on the face of the sonde. It can be thought of as half a coaxial cable 15 cm long that irradiates the formation with a field transverse to the static field. It is loaded with ferrite to improve the reception of weak signals from the nuclear spin system. This device, shown in Figure 2.3, has been commercialized for wireline applications.

2.2.4.4 Single-Sided Logging Tool with Gradient Magnetic Field Profile

When a single-sided logging tool with a saddle point is operated at an rf frequency that does not correspond to the saddle point, the sensor becomes a one-sided logging tool with a field profile characterized by a gradient. More generally, any sensor that has an rf coil located on one side operates as a single-sided gradient tool, unless special care is taken to design it as a saddle point tool. This configuration has the advantage that the sensitive region can be easily moved to a different depth away from the borehole by changing

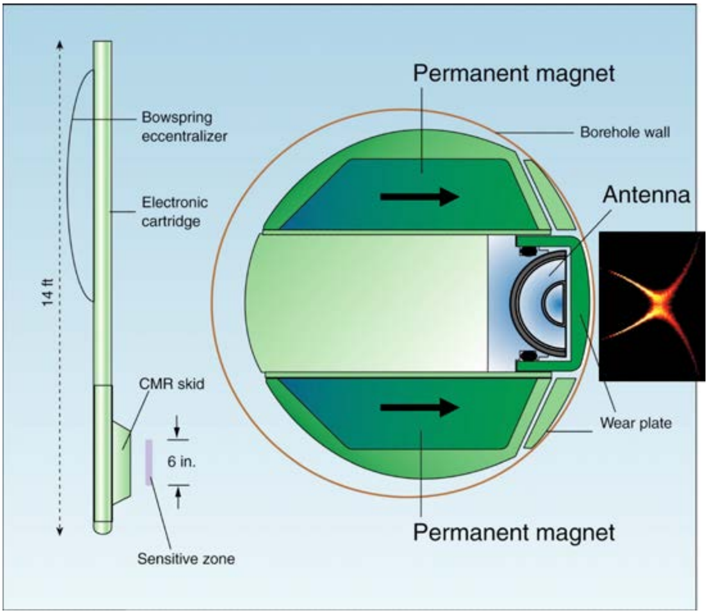

Figure 2.3 Single-sided logging tool with a saddle point field profile. Schematic view of the NMR logging tool designed by Kleinberg *et al.*[19] The permanent magnets are magnetized in the direction of the arrows. The sonde is pressed against the borehole wall. The magnitude of the magnetic field forms a saddle point about 25 mm inside the formation. The resulting sensitive region is shown in the insert. The color intensity indicates the local signal sensitivity. Illustration copyright Schlumberger. Used with permission.

the rf carrier frequency of the pulses. Examples of such sensors used in commercial wireline operations are described in.[20,21] As an illustration, Figure 2.4 shows the wireline NMR logging tool of[20] that can be operated at different rf frequencies between 1000 kHz and 500 kHz, corresponding to depths of investigations ranging from 2.5 to 10 cm. In each case, the field profile is well characterized by a uniform gradient in the range between 38 G cm^{-1} and 12 G cm^{-1}.

2.3 NMR Measurement Techniques

2.3.1 Measurements in Grossly Inhomogeneous Fields

It is a general feature of inside-out measurements on extended samples, such as those encountered in NMR well logging, that the range of Larmor frequencies across the entire sample is much larger than the amplitude of the rf field. Therefore, all pulses act as slice selective pulses. As a consequence, the T_2* dephasing time of the free induction decay is very short and

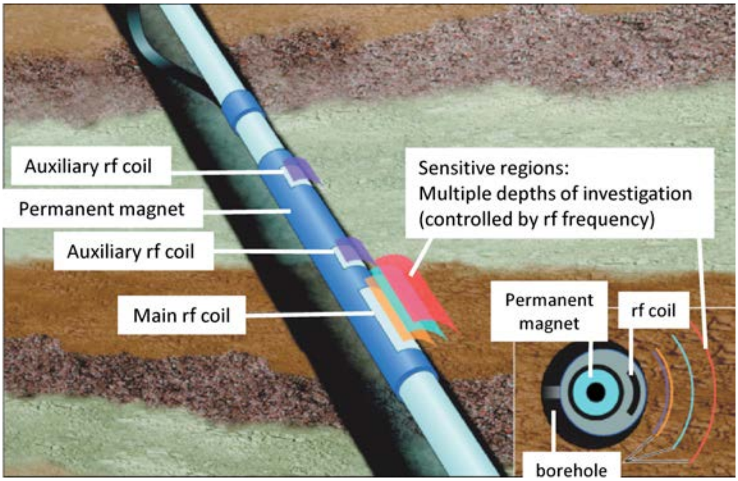

Figure 2.4 Single-sided logging tool with a gradient field profile. Schematic view of the NMR wireline logging device described in.[20] The magnet (shown in blue) generates a gradient field in the formation. The main rf coil can transmit and receive at different rf frequencies, which correspond to different sensitive regions as shown by the differently colored surfaces. In addition, there are two auxiliary rf coils that are operated at a higher rf frequency and are associated with a shorter sensitive region. The sensor is pushed against the wall of the borehole by the bow spring placed on the opposite side of the tool, indicated on the top left of the figure. Illustration copyright Schlumberger. Used with permission.

only of the order of the pulse duration. This makes it difficult to acquire the signal of the free induction decay, especially at these low Larmor frequencies where in all practical cases T_2* is shorter than the dead-time of the electronics. It is therefore essential to use multi-pulse sequences to generate echoes that can be more readily detected. However, the detailed NMR response of such multi-pulse sequences and the extraction of quantitative information is complicated by the grossly inhomogeneous fields of logging tools as all pulses act as slice selective pulses. In particular, it is critical to use sequences that are robust against the rapid accumulation of the large resonance offset effects.

The prototypical multi-pulse sequence for moderately inhomogeneous fields widely used in conventional NMR applications is the Carr–Purcell–Meiboom–Gill (CPMG) sequence[22,23] shown in Figure 2.5. It consists of an initial 90° excitation pulse, followed by a long series of 180° refocusing pulses that are phase shifted by 90° with respect to the excitation pulse. Echoes appear at the mid-points between successive refocusing pulses. In the practical implementation, a simple two-step phase cycling scheme of the first pulse is used to eliminate baseline offsets and ringing effects. This basic sequence and modifications thereof form the basis of all pulsed NMR logging measurements. It allows the determination of the overall amplitude and the

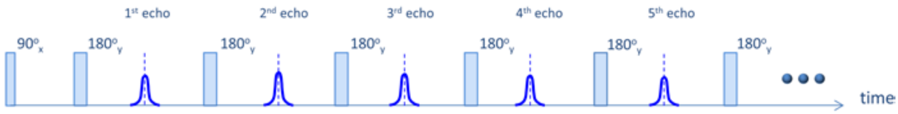

Figure 2.5 Basic Carr–Purcell–Meiboom–Gill (CPMG) sequence used to measure amplitude and transverse relaxation time. The dashed lines indicate the nominal echo times.

decay time of the magnetization. As long as the echo spacing is shorter than any intrinsic relaxation time, the measured amplitude of the early echoes is proportional to the initial longitudinal nuclear magnetization of the sample, which in turn can be related to the porosity, as is further discussed in Section 2.4. The decay time of the echo amplitudes, T_2, is related to the pore size or viscosity of the fluid, as discussed in Section 2.6.

In conventional applications, the inhomogeneities in the applied B_0 field are typically much smaller than the strength of the rf field, B_1. In this case, the refocusing pulses in the CPMG sequence are able to compensate the dephasing caused by the field inhomogeneities and the magnetization forms echoes that are all in-phase, as shown in the top row of Figure 2.6.

When the inhomogeneities in B_0 approach or exceed B_1, dephasing during the application of the pulses becomes significant. As a consequence, the phase of the magnetization generated by the CPMG sequence becomes highly dependent on the offset frequency and the echo number, as illustrated in Figure 2.6. The simulation demonstrates that the resulting magnetization at the time of the nominal echo can lie anywhere on the Bloch sphere. At first sight, this appears to rule out the CPMG sequence as a suitable sequence for quantitative measurements in NMR logging.

Fortunately, the situation is not as dire as suggested by the results shown in Figure 2.6. In fact, the CPMG is surprisingly well suited for robust measurements in grossly inhomogeneous fields.[8] This is evident from the experimental results shown in Figure 2.7. The top panel shows the traces of the first ten CPMG echoes on an extended sample of doped water in a gradient field, while the lower panel shows the decay of the amplitudes of all the echoes. After the first few refocusing pulses, the echoes quickly approach a constant shape that is in phase with the refocusing pulses.

To reconcile the apparent contradictions between Figures 2.6 and 2.7, we have to consider that the detected echo signal is the sum of the contributions from all positions in the inhomogeneous field. Even though the local magnetization can point in any direction on the Bloch sphere, there is a net excess of magnetization along the axis of the refocusing pulses. The experimental results show that this excess magnetization is a quantity that is robust from echo to echo and gives rise to the characteristic echo shape. After the first few echoes, the overall amplitudes of these echoes decay exponentially. The CPMG sequence therefore allows the robust extraction of relaxation times even in grossly inhomogeneous fields.