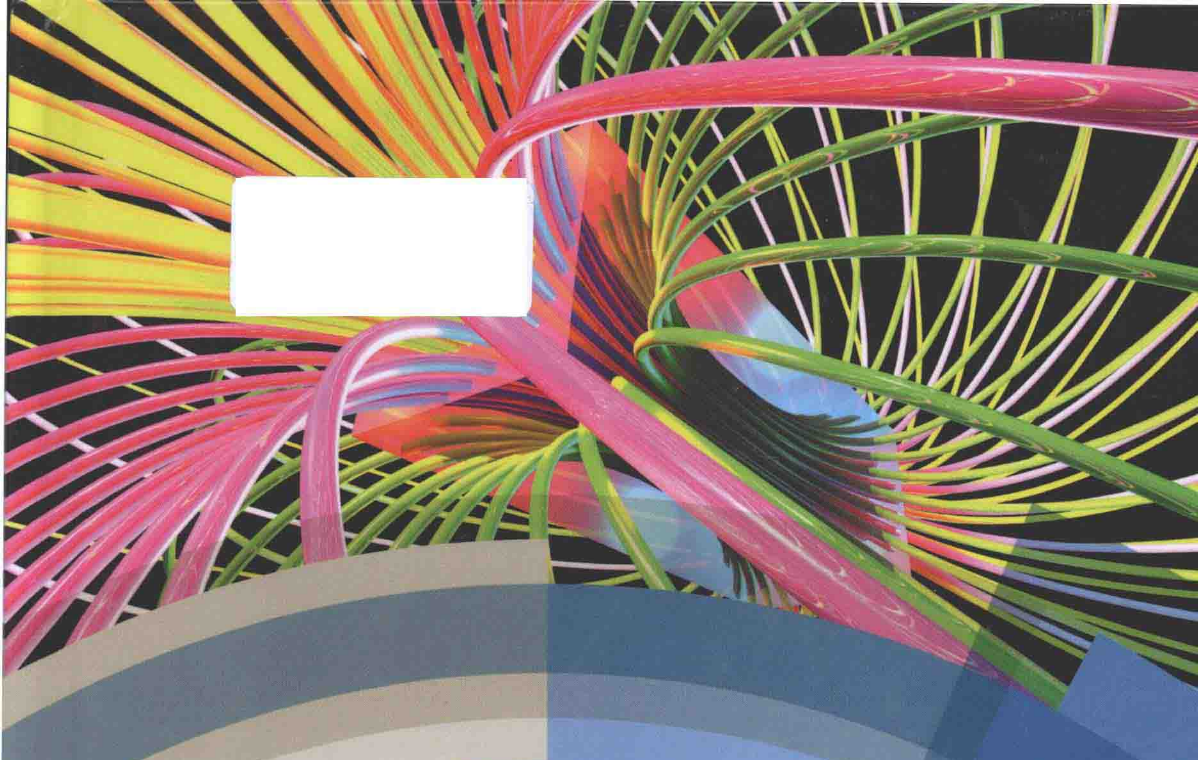

New Developments in NMR

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

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

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

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

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.

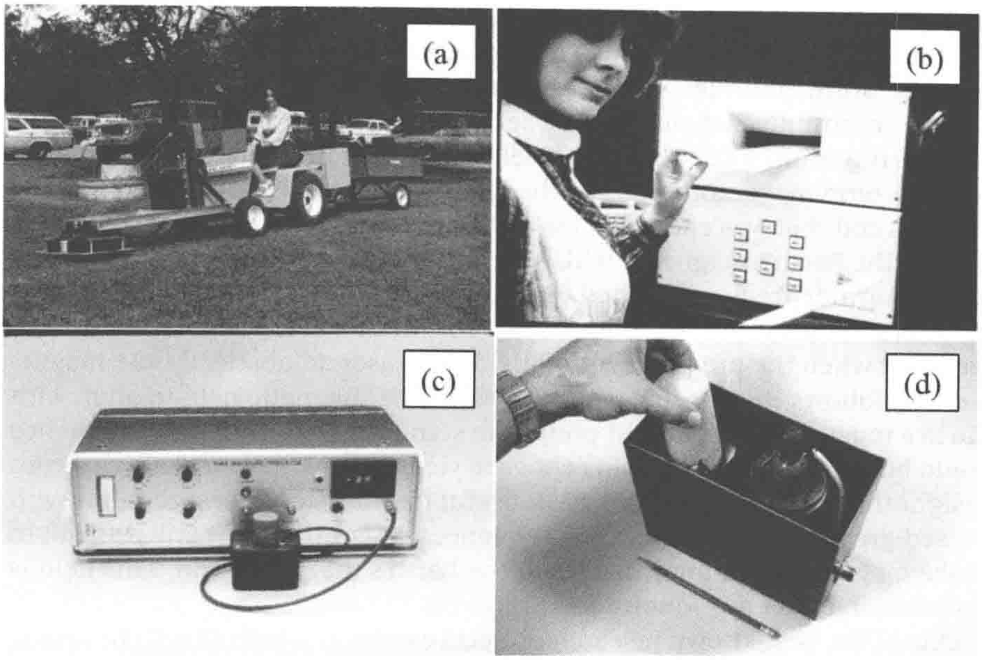

Figure 1.1 (a) Photo of a mine detector that is mounted in front of a tractor. The trailer carried the batteries. (b) Photo of a mail bomb detector based on ^{14}N nuclear quadrupole resonance (NQR). NQR is well-suited for mobile instrumentation because it requires no magnetic fields. (c) Photo of a 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]