



New Developments in NMR

Mobile NMR and MRI

Developments and Applications

Edited by Mike Johns, Einar O. Fridjonsson,
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Mobile NMR and MRI Developments and Applications

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Mobile NMR and MRI

Developments and Applications

New Developments in NMR

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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, cost 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

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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

Chapter 1	Introduction	1
	<i>Eiichi Fukushima</i>	
	Acknowledgements	9
	References	9
Chapter 2	NMR Well Logging	11
	<i>Martin D. Hürlimann and Nicholas J. Heaton</i>	
2.1	Introduction	11
2.1.1	General Technique of Well Logging	12
2.1.2	Overview of NMR Well Logging and its Challenges	14
2.2	Sensors for NMR Logging	15
2.2.1	Early Earth Field NMR Technique	15
2.2.2	Modern NMR Well Logging Technique: Pulsed NMR in an Applied Magnetic Field	16
2.2.3	General Considerations Governing the Tool Design	17
2.2.4	Configurations of NMR Logging Tools	18
2.3	NMR Measurement Techniques	22
2.3.1	Measurements in Grossly Inhomogeneous Fields	22
2.3.2	Relaxation Measurements	27
2.3.3	Diffusion Measurements	27
2.3.4	T_1 Measurements	28
2.3.5	Distribution Functions	29
2.3.6	Tool Motion Effects	30

2.4	NMR Log Calibration	31
2.4.1	Calibration Requirements and Challenges	31
2.4.2	Sensor Characterization/Engineering	32
2.4.3	Validation and Verification/Manufacturing	35
2.4.4	Periodic Calibration/Operations	35
2.4.5	Application of Calibration While Logging	36
2.5	Data Processing and Analysis	37
2.5.1	Inversion Challenges	37
2.5.2	Inversion with Regularization	38
2.5.3	SNR and Spatial Resolution	39
2.5.4	Robustness of Inversion	42
2.5.5	Alternative Inversion Approaches	48
2.6	Data Interpretation: Physics of Relaxation and Diffusion	50
2.6.1	Reservoir Properties	51
2.6.2	Amplitude	53
2.6.3	Relaxation	54
2.6.4	Diffusion	61
2.6.5	Diffusion–Relaxation Distribution Functions	63
2.7	Applications	67
2.7.1	Overview	67
2.7.2	NMR Amplitude-Based Applications	69
2.7.3	Applications Based on NMR Relaxation Measurements	72
2.7.4	Applications Based on Diffusion Measurements	75
2.8	Conclusion	79
	References	79

Chapter 3 Bench-top NMR—Food: Solid Fat Content Determination and Emulsion Droplet Sizing **86**

M. A. Voda and J. van Duynhoven

3.1	Introduction	86
3.2	Design of Commercial Benchtop NMR Equipment	88
3.3	Industrial Routine Benchtop Assessment of SFC	89
3.3.1	Acquisition and Processing	89
3.3.2	Tempering Protocols	90
3.3.3	Method Standardization	90
3.3.4	Application Scope and Performance of Routine SFC Methods	91
3.4	Industrial Routine Droplet Size Measurement by Pulsed Field Gradient NMR	93
3.4.1	Acquisition	93

3.5 Non-Routine Methodologies	100
3.5.1 Full Lineshape Analysis of Transversal Decay Curves	100
3.5.2 Rapid Single-Shot Relaxometric Measurements	100
3.5.3 On-Line Measurements	101
3.5.4 Rheo-SFC NMR	102
3.5.5 Model-Free Approaches for Droplet Size Distributions	102
3.5.6 Double Emulsions	103
3.6 Perspectives and Conclusions	105
3.6.1 Conclusions	105
3.6.2 Perspectives	105
Acknowledgements	106
References	106
 Chapter 4 Hardware Developments: Single-Sided Magnets	 110
<i>Peter Blümler and Federico Casanova</i>	
4.1 Introduction	110
4.2 Single-Sided Magnet Geometries	111
4.2.1 Basic Designs	111
4.2.2 Realized Devices	116
4.2.3 Magnets Generating a Uniform Gradient	117
4.2.4 Magnets Generating a Volume of Homogeneous Fields	121
4.3 Signal-to-Noise Ratio for Single-Sided NMR	126
4.3.1 The NMR Signal in a Single-Sided Setup	126
4.3.2 Rf Coils for External Noise Cancellation	128
4.4 Conclusions	129
Acknowledgements	130
References	130
 Chapter 5 Hardware Developments: Halbach Magnet Arrays	 133
<i>Peter Blümler and Federico Casanova</i>	
5.1 Concept and Theory	133
5.2 Practical Realization	135
5.2.1 Discretisation and Truncation of the Ideal Halbach	135
5.2.2 Achievable Flux Density	137
5.2.3 Achievable Homogeneity	137
5.3 Advanced Designs	139
5.3.1 Shimmed Magnets	139
5.3.2 Nested Rings	145
5.3.3 Force-Free Opening Magnets	147

5.4 Applications	149
5.4.1 Medical MRI of Living Organisms	149
5.4.2 Porous Media: Rocks, Soil, Construction Materials, Food	152
5.4.3 Chemistry and Process Control	152
5.5 Conclusions	154
Acknowledgements	154
References	155
Chapter 6 Hardware Developments: Handheld NMR Systems for Biomolecular Sensing	158
<i>Nan Sun and Donhee Ham</i>	
6.1 Introduction	158
6.2 Review of NMR Basics	161
6.2.1 Protons in Static Magnetic Field	161
6.2.2 Excitation Mode—NMR and Rabi Oscillation	161
6.2.3 Reception Mode	163
6.2.4 NMR-Based Biomolecular Sensing	163
6.2.5 Spin Echo Technique	164
6.2.6 Signal-to-Noise Ratio	167
6.3 System-Level Design Considerations	167
6.3.1 Magnet Miniaturization	167
6.3.2 Coil Miniaturization	169
6.3.3 Transceiver Miniaturization	170
6.4 Miniature NMR System—1st Prototype	171
6.4.1 RF Transceiver IC Architecture	171
6.4.2 Receiver LNA and Noise Matching	172
6.4.3 Digital Pulse Generator	174
6.5 Miniature NMR Systems—2nd and 3rd Prototypes	174
6.6 NMR and Biomolecular Sensing Experiments	177
6.7 Conclusion and Outlook	179
References	179
Chapter 7 Detection Using SQUIDs and Atomic Magnetometers	183
<i>Michelle Espy, Igor Savukov, and Petr Volegov</i>	
7.1 Introduction	183
7.2 Sensors	185
7.2.1 SQUID Basics	185
7.2.2 Atomic Magnetometers	188
7.2.3 Brief Overview of Hardware	192
7.3 Current Applications of ULF MRI	198
7.3.1 MEG and MRI	199
7.3.2 Unique Contrast and Anatomical Imaging	200
7.3.3 Materials	201

7.4	How to Model System Performance	201
7.4.1	How to Model an MRI System	201
7.4.2	What if We Just Used Coils?	216
7.5	Conclusions	221
	Nomenclature	221
	References	221
Chapter 8	Software Developments: Improvements in Data Analysis	225
	<i>Daniel J. Holland and Lynn F. Gladden</i>	
8.1	Introduction	225
8.2	Introduction to Data Processing in NMR/MRI	226
8.2.1	Discrete Fourier Transform	226
8.2.2	Filtering	229
8.2.3	Non-Cartesian Imaging	230
8.3	Compressed Sensing	235
8.3.1	Theory of Compressed Sensing	236
8.3.2	Applications of Compressed Sensing	241
8.3.3	Future Developments	246
8.4	Bayesian Analysis	247
8.4.1	Theory of Bayesian Analysis	247
8.4.2	Applications of Bayesian Analysis	252
8.5	Conclusions and Outlook	256
	References	257
Chapter 9	Emerging Applications: Surface NMR	263
	<i>Anatoly Legchenko</i>	
9.1	Introduction	263
9.2	Experimental Setup	264
9.2.1	Earth's Magnetic Field	265
9.2.2	Instrumentation	266
9.3	Theoretical Development and Modeling	270
9.3.1	Magnetic Field of the Surface Loop	270
9.3.2	Imaging Equation	271
9.3.3	Forward Modeling	273
9.4	Data Inversion	278
9.5	Experimental Verification	281
9.5.1	Detection of Groundwater	281
9.5.2	Aquifer Geometry	281
9.5.3	Aquifer Porosity and Hydraulic Conductivity	285
9.6	Conclusions	287
	References	288

Chapter 10	Rock Core Analysis: Metallic Core Holders for Magnetic Resonance Imaging Under Reservoir Conditions	290
	<i>Matthew Ouellette, Ming Li, Guangzhi Liao, Esam M. A. Hussein, Laura Romero-Zeron, and Bruce J. Balcom</i>	
10.1	Introduction	290
10.2	Imaging Techniques for Rock Cores	291
10.3	Magnetic Resonance Imaging and Metal Compatibility	292
10.3.1	Principles of MRI	292
10.3.2	Compatibility with Static Field	293
10.3.3	Compatibility with RF Excitation Field	293
10.3.4	Compatibility with Magnetic Field Gradients	293
10.3.5	Metal Selection	294
10.4	Design	294
10.4.1	Temperature Regulation	295
10.4.2	Stress Analysis	296
10.5	Fabrication and Testing	301
10.6	Imbibition Displacement Experiments	303
10.7	Conclusions	306
	Acknowledgements	308
	References	308
Chapter 11	Outlook: Quo Vadis, NMR?	310
	<i>Eva Paciok and Bernhard Blümich</i>	
11.1	Magnets	310
11.2	NMR-on-a-Chip: Miniature Magnets, Coils, Spectrometers and Microfluidics	316
11.3	Methods	318
11.4	Applications Beyond Spectroscopy	322
11.5	Summary	324
	References	326
	Subject Index	331

CHAPTER 1

Introduction

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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.

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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 subject² 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}

Strong⁵ described an unusual proton magnetometer developed by Wadsworth⁶ 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 magnetometers⁷ 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.

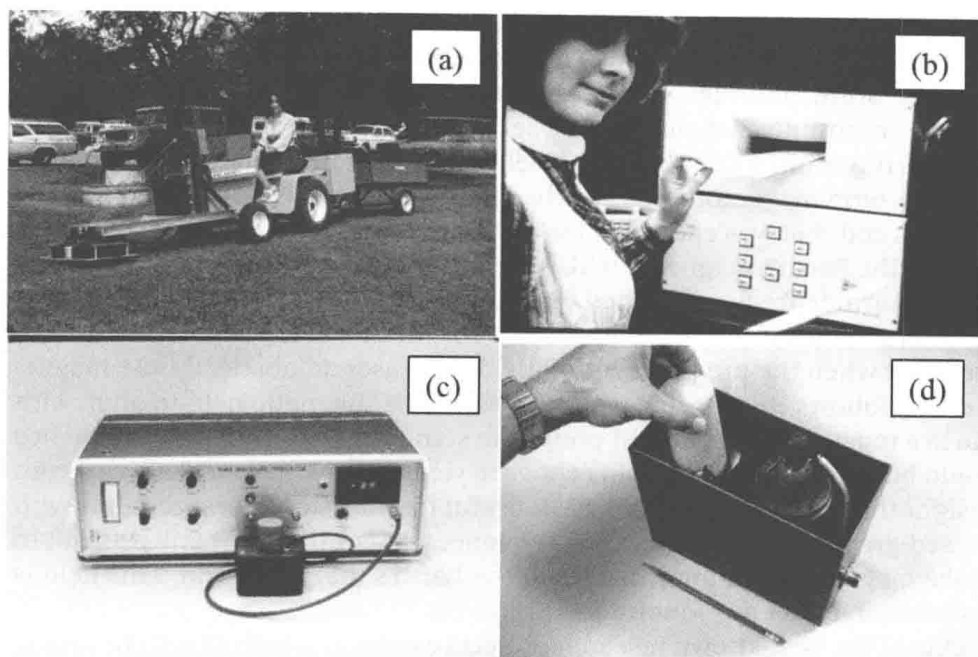


Figure 1.1 (a) Photo of a mine detector that is mounted in front of a tractor. The trailer carried the batteries. (b) Photo of a mail bomb detector based on ^{14}N nuclear quadrupole resonance (NQR). NQR is well-suited for mobile instrumentation because it requires no magnetic fields. (c) Photo of a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