ACADEMIC PRESS

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Magnetic Resonance 161 (2003) 204–209

JMR Journal of Magnetic Resonance

www.elsevier.com/locate/jmr

Degradation of historical paper: nondestructive analysis by the NMR-MOUSE☆

B. Blümich,[a,*] S. Anferova,[a,b] S. Sharma,[a] A.L. Segre,[c] and C. Federici[d]

[a] *Institut für Technische Chemie und Makromolekulare Chemie, RWTH Aachen, D-52056 Aachen, Germany*
[b] *Kaliningrad State University, 236041 Kaliningrad, Russia*
[c] *Institute of Chemical Methodologies of CNR, M.B. 10, 00016 Monterotondo Stazione, Rome, Italy*
[d] *Instituto centrale di patologia del libro, Via Milano 76, 00184 Rome, Italy*

Received 17 September 2002; revised 15 January 2003

Abstract

The NMR-MOUSE is a mobile sensor for single-sided NMR inspection of organic materials which takes advantage of the principles of magnetic resonance and inside-out-NMR. Historical books dating from the 17th century were measured at different points by positioning the NMR-MOUSE on the paper. Different degrees of paper degradation can be discriminated from the regularized inverse Laplace transform of the envelope of the acquired echo signals. For the first time the degradation of historical paper was characterized entirely nondestructively by NMR. As a contribution to current preservation efforts, NMR shows great promise for future use in damage assessment of historical documents.

Keywords: NMR-MOUSE; Unilateral NMR; Historical paper; Degradation; Cultural heritage

1. Introduction

The target of this work is to investigate, if unilateral NMR can be used for nondestructive analysis of paper degradation. For many centuries paper was the only material for recording cultural achievements all over the world. Antique paper is made essentially from cellulose and water in almost equimolar amounts. The art of making paper from fibrous plant matter begins in China in the 1st century BC. The manufacture of paper in Europe was first established in Islamic Spain in the middle of the 11th century. In the second half of the 14th century the use of paper had become well accepted in all of Western Europe. Prior to 1850 paper was made from cellulose and water using hemp, flax, and cotton fibers. Historical paper differs in many ways from contemporary paper. Antique paper was made entirely from rags, i.e., from linear long cellulose fibers, only with the addition of sizing compounds, whilst contemporary paper can be manufactured from short fibers, hemicellulose, and lignin, and may contain nonfibrous components including various coloring agents, fillers, and coatings. Originally an animal glue was used for sizing. It was substituted in the 19th century by rosin and alum, and more recently by other synthetic products.

Paper can be damaged to various degrees by different causes among which the more common ones include biological attacks by bacteria, fungi, and insects, while chemical attack is mostly due to oxidation and acidity. Moreover, a common risk factor is inadequate storage and careless handling which can lead to the presence of all the types of damage mentioned above. The longevity of documents is based on the physical preservation of the support material. In the past few years NMR methods have been shown to be valuable in assessing the quality of paper with regard to the early detection of enzymatic attack [1]. In standard NMR measurements [2] one of the most sensitive NMR parameters to measure is the transverse relaxation time T_2. Although only 10–20 mg of material are needed for investigation, the use of conventional NMR is destructive to the object in

☆ NMR-MOUSE is a registered trademark of Aachen University of Technology (RWTH).

* Corresponding author. Fax: +49-241-802-2185.
E-mail address: bluemich@mc.rwth-achen.de (B. Blümich).

1090-7807/03/$ - see front matter © 2003 Elsevier Science (USA). All rights reserved.
doi:10.1016/S1090-7807(03)00034-X

question. In fact any sampling of ancient historical paper must strictly be avoided. The so-called NMR-MOUSE probe [3] connected to a portable NMR spectrometer can measure proton T_2 relaxation in an entirely nondestructive way, maintaining the integrity of historical documents and books.

Nuclear magnetic resonance is usually performed within highly homogeneous and strong magnetic fields in order to obtain spectra which reveal well resolved resonance lines for structural chemical analysis. Recently, however, Pines and collaborators [4], disproved the common belief that the chemical shift can be resolved only in homogeneous polarization fields by an ingenious experiment generating NMR echoes with matched inhomogeneities in the polarization field $\boldsymbol{B}_0$ and the radio-frequency (RF) field $\boldsymbol{B}_1$. This experiment encourages the prospect of being able to measure NMR spectra from within objects by applying $\boldsymbol{B}_0$ and $\boldsymbol{B}_1$ to one side of the object, eliminating the restriction of the object size imposed by requiring the sample to fit inside the homogeneous region of a magnet. In fact, it has been attempted to overcome this restriction since the beginnings of NMR technology half a century ago, when so-called inside-out NMR started to develop with the intention of lowering NMR spectrometers down bore holes of oil wells [5]. The method became a commercial success about 10 years ago with the first use of a commercial instrument. Today, NMR well logging plays an integral role in oil well inspection. The NMR sensor consists of permanent magnets which incorporate a RF antenna for the excitation and reception of transverse magnetization generated in the inhomogeneous polarization fields outside the device in the fluids pervading the porous rock formation [6]. Echo trains of the transverse magnetization are generated following the ideas of Carr and Purcell [7] and Meiboom and Gill [8] to overcome the magnetization dephasing in the inhomogeneous $\boldsymbol{B}_0$ field by stroboscopically observing the transverse magnetization decay from the homogeneous field which passes through the echo maxima. Based on the the assumption of exponential signal decay dominated by wall relaxation in a pore of a given size, the observed echo envelope is analyzed by a regularized inverse Laplace transformation in terms of a distribution of relaxation times which translates into a distribution of pore sizes.

The same methodology is applied using the NMR-MOUSE [9], a *MObile Universal Suface Explorer,* which was developed at Aachen University of Technology (RWTH, Aachen) following the principles of inside-out NMR, but admitting much larger inhomogeneities of the polarization field $\boldsymbol{B}_0$ to obtain larger field strength for improved sensitivity [10,11]. Basically the NMR-MOUSE (Fig. 1) replaces the magnet and the probe of a regular NMR spectrometer. When operated with a small PC spectrometer, a mobile NMR unit is obtained which

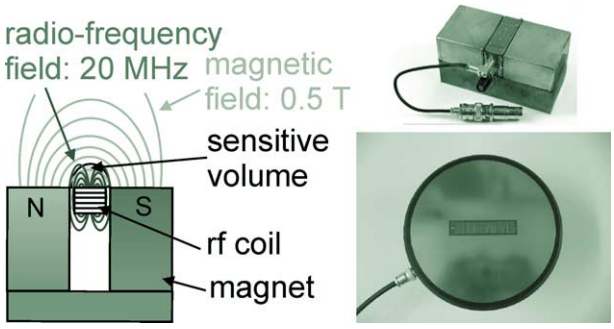

Fig. 1. Principle of the NMR-MOUSE, and photos of a figure-8-coil MOUSE (top) and a meander-coil MOUSE (bottom). A u-shaped magnet providing the polarization field $\boldsymbol{B}_0$ accommodates a RF coil in the gap, so that in a region above the plane of the NMR-MOUSE the magnetic polarization field $\boldsymbol{B}_0$ and the magnetic RF field $\boldsymbol{B}_1$ possess orthogonal components. This region defines the sensitive volume of the sensor.

can be transported to the sample. It turns out that the NMR-MOUSE sensor is well suited for nondestructive analysis of various materials, most notably soft matter like rubber in car tires and fittings [12] and organic tissues like skin and tendon [13], where material properties can be probed utilizing the same contrast principles which are exploited in magnetic resonance imaging [14,15]. In particular, relaxation times [16], self-diffusion constants [17,18], and multi-quantum coherences [19] can be measured. Closely related methodical developments of NMR in inhomogeneous fields are conducted in the context of well logging [20,21]. By improving the design of the NMR-MOUSE, the dead-time could be shortened to less than 10 μs and the sensitivity improved so that thin and rigid samples can now be analyzed as well. Using a figure-8 coil or a meander coil (Fig. 1) for the RF excitation [9] the signals from cellulose in paper can be measured with echo times of 60 μs and less, and sets of Hahn echoes from individual sheets of paper can be obtained within reasonable measurement times of a few hours.

2. Materials and methods

Historical paper is basically a two-component material made from cellulose and water, which includes some impurities [22]. EPR measurements have shown [23], that such paper exhibits a low content of paramagnetic impurities like copper and iron ions which act as relaxation reagents and shorten the relaxation times. In paper cellulose is 40–60% amorphous while the remainder is crystalline. Cellulose crystallizes in many polymorphous forms. Two of these polymorphs, monoclinic (I_α) and triclinic (I_β) constitute the crystalline part of paper. NMR measurements indicate, that the water molecules aggregate in small puddles and are

intimately mixed with the macromolecular cellulose domains [24]. NMR spin diffusion studies such as WISE and dipolar filtered ^{13}C CP-MAS spectra and also ^{1}H spectra measured as a function of temperature have shown, that the regions of crystalline and amorphous cellulose are also closely connected [25]. These results suggest, that cellulose forms a close-knit structure of water, amorphous, and crystalline regions on the nanometer scale. In good-quality well-preserved paper, that is, in paper in which the cellulose possesses a high degree of polymerization, the actual ratio of the spin densities of water to cellulose is always near 10/2, i.e., amorphous cellulose surrounds small water pools. Even a small loss of water from paper causes its full degradation [26].

Measurements on historical books were conducted at RWTH Aachen and at the Instituto Centrale di Patologia del Libro in Rome. The NMR-MOUSE used had a figure-8 coil etched on a printed circuit board. To reduce the background signal from the protons in the circuit board, Hahn echoes were measured instead of multi-echoes according to Carr, Purcell, Meiboom, and Gill (CPMG). The protons in the circuit board had a transverse relaxation time in the order of 20 μs, so that only the echoes at echo times shorter than 60 μs were contaminated by background signal. When using a multi-echo method like the CPMG method, the dipole–dipole interactions between the spins in the sample and in the coil-bearing material are partially averaged due to a distribution of flip angles from the inhomogeneous $\boldsymbol{B}_1$ field, and a separation of background signal and signal from the sample is more difficult, although different techniques could be employed. In addition, each echo other than the first one represents a superposition of a stimulated and a Hahn echo, so that the resulting echo envelope decays more slowly, and the apparent transverse relaxation is governed by the transverse relaxation under the influence of a partially averaged dipolar Hamiltonian and by longitudinal relaxation [27,28]. Therefore, the CPMG method was not used and successive Hahn echoes were measured using phase cycling. In this way the magnetization decay in homogeneous fields was stroboscopically probed in the echo maxima. The measurement frequency was 19.6 MHz, and the echo time was stepped from 60 μs to 1.3 ms with a recycle delay of 0.5 s. Using a Bruker Minispec-PC spectrometer (Fig. 2) 1600 averages were acquired per echo time in experiments carried out overnight.

3. Results and discussion

A typical echo envelope acquired from a 19th century German book made from good quality paper is shown in Fig. 3. From the logarithmic presentation it is obvious, that the decay is bi-exponential. The fast decaying component corresponds to the cellulose protons and does not vary much in different paper samples of good quality. Our investigations showed, that in different books it fluctuates around a mean value of 27 μs. The long component, which is known to be characteristic of the state of the paper, corresponds to water. For good quality paper it varies significantly between 0.4 and 1.8 ms for books printed between 1600 and 1870.

At the Instituto Central di Patologia del Libro two degraded books from the 17th century were investigated using the NMR-MOUSE. Different stages of degradation could be deduced from the NMR signals. In the case of one book only the upper half was still existing (Fig. 4). Measurements were obtained from the top part

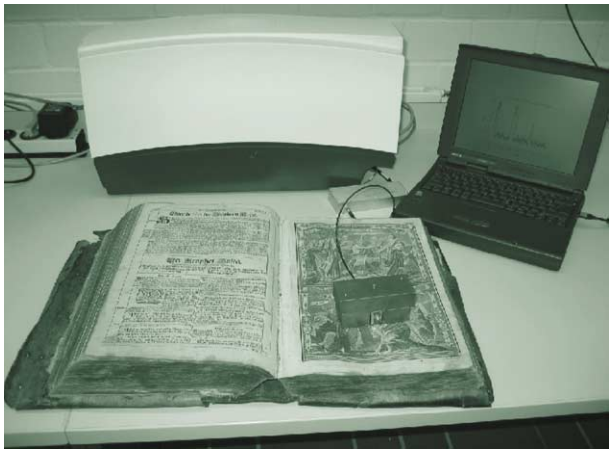

Fig. 2. PC-NMR spectrometer controlled by a notebook PC and NMR-MOUSE measuring the paper of a 17th century German bible. In principle the NMR-MOUSE can also be positioned in such a way that it does not touch the paper.

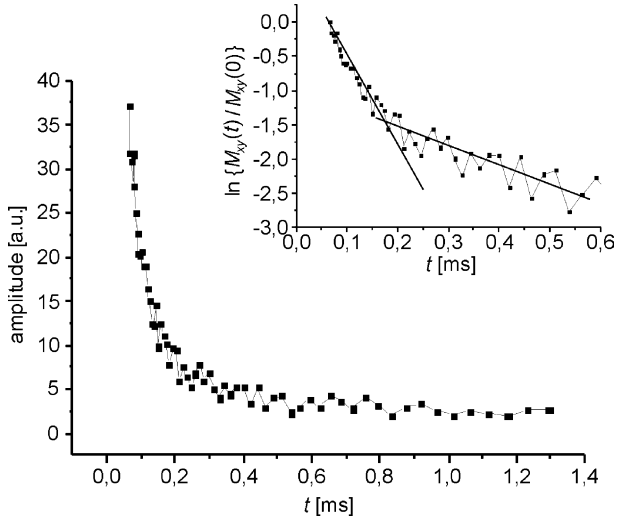

Fig. 3. Typical bi-exponential signal decay of good quality historical paper for a German book from 1867. Left: linear scales. Right: semi-logarithmic scales. M_{xy} is the transverse magnetization. $M_{xy}(0)$ is its value extrapolated to zero echo time.

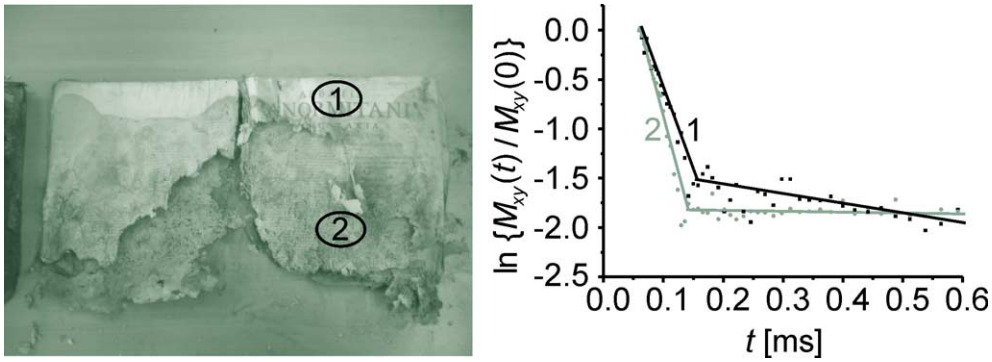

Fig. 4. Book from the 17th century with severe damage. The echo envelopes measured with the NMR-MOUSE at the top and the middle of the page are different. The slowly decaying component associated with water has disappeared in the middle of the page. The drawn lines serve as a guide to the eye. M_{xy} is the transverse magnetization. $M_{xy}(0)$ is its value extrapolated to zero echo time.

of the book where the paper was degraded medium and from the central portion where the degradation was high. The different degrees of degradation refer to evidence of biological attack and can be defined as follows: a high degree of degradation means that the paper is so fragile that it cannot be handled without the risk of disintegration; medium degradation means that the paper is very fragile, but handling remains possible; low degradation refers to paper that shows superficial traces of biological attack. A logarithmic presentation of experimental data reveals, that the decay of the echo envelope is bi-exponential for medium degradation. Therefore, the decay shows separate signals from the protons of cellulose and water. However, in the highly degraded part only the short component of the cellulose matrix was detected. Hence the loss of water is so high that the signal from water protons can no longer be measured.

Paper with an overall lower state of degradation was investigated in a second water damaged book from the same period (Ioannis Lorini, *In Acta Apostolorum Comentaria*, Lugdini apud Horatium Cardon, Paris, 1605) (Fig. 5). Unlike the first book studied, this book could still be opened and the state of degradation of the paper was medium on average. The bottom part of the sheets showed little to no degradation with a small area of paper in good condition. In the central portion of the sheets the paper was medium degraded, whilst the most damage was observed at the top of the sheets, where the paper was disintegrating.

In the logarithmic presentation of the NMR relaxation data the different degradation states of the sheets can be distinguished. All three relaxation decays are at least bi-exponential, and with increasing level of degradation, both the fast and the slow relaxation times decrease. The water loss coincides with a change in the state of the cellulose structure, that is to say, the paper becomes brittle. The change in the fast relaxation component can also be identified in a presentation which analyzes the decay of the echo envelope in terms of a distribution of relaxation times. Following the analysis established for the interpretation of well logging data,

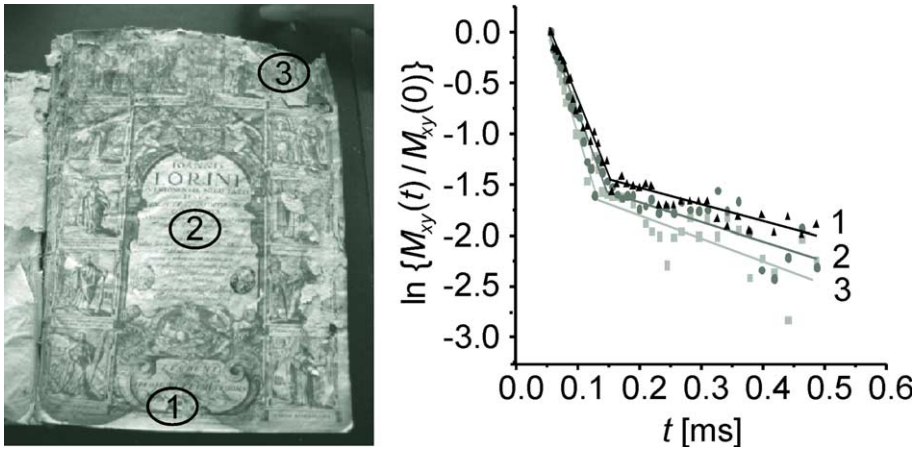

Fig. 5. Book from 1605 showing evidence of biological attack. The positions, where the NMR measurements were conducted are indicated. In the logarithmic presentation of the experimental NMR data the different degrees of paper degradation can clearly be distinguished. The degradation degrees are: 1, low; 2, medium; and 3, high. The drawn lines serve as a guide to the eye.

the echo envelope has been converted into a distribution of relaxation times $P(T_2)$ using the UPEN program. This program in effect performs a regularized inverse Laplace transformation by an algorithm which produces useful results with well-resolved peaks by fitting a distribution of decaying exponentials with positive amplitudes [29]. The algorithm works well for signal-to-noise ratios better than 20 [30]. While the slowly relaxing component from water is suppressed in the UPEN analysis due to low signal-to-noise ratio (Fig. 6), the signal from the rapidly relaxing cellulose protons is sufficiently indicative of the state of degradation.

For the relaxation data acquired from both damaged books it was observed that with decreasing paper quality the relaxation times from both, cellulose and water, decrease (Figs. 5 and 6). Given that the the paper degradation is associated with a loss of water, the unexpected decrease of the relaxation time from the cellulose protons is explained by magnetization exchange [31] between cellulose and water protons. The magnetization of the water protons exhibits longer relaxation times but slowly exchanges with that of the cellulose protons by spin diffusion and chemical exchange. Water loss reduces the replenishing of cellulose magnetization from the water reservoir, so that the magnetization of the cellulose protons relaxes faster upon water loss. In addition, the degradative attack on the cellulose chains is expected to start in the more mobile regions, which are the parts with a higher content of amorphous cellulose, while the more crystalline areas survive the attack. This type of behavior is consistent with chemical aging of semi-crystalline synthetic polymers, where the aging process starts in the amorphous regions [32].

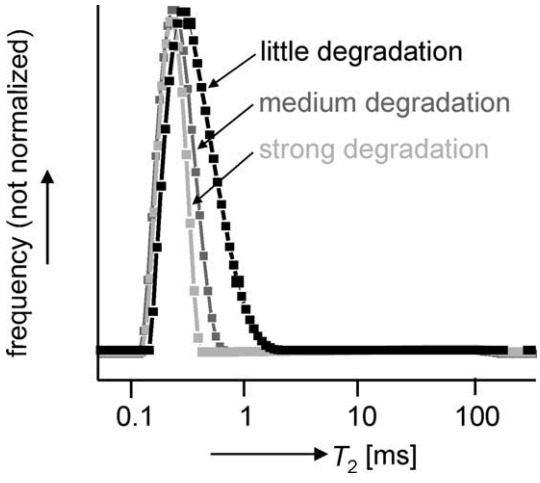

Fig. 6. Distributions of relaxation times obtained by inversion of echo envelopes measured with the NMR-MOUSE on a page in the middle of the book. The UPEN algorithm suppresses slowly relaxing signal from bound water because of bad signal-to-noise ratio. The distributions are scaled to the same maximum height. The different degrees of paper degradation can clearly be discriminated in this representation.

4. Conclusions

For the first time different degrees of paper degradation were analyzed entirely nondestructively by nuclear magnetic resonance relaxation. A mobile NMR sensor, the NMR-MOUSE was employed. Although the sensor works with strongly inhomogeneous polarization and RF magnetic fields, the quality of the experimental data is sufficient for discrimination of different states of paper preservation in the books investigated. Due to proton signal from the material supporting the coil, multi-echo sequences were abandoned in favor of more time-consuming Hahn echo measurements. Encouraged by the promising perspectives of these investigations for the assessment of the quality of historical documents and books, RF coils edged on glass or single-crystal wafers may provide a proton-free coil environment, and parallel operation of several sensors will further speed up the inspection process for the analysis of historical paper. Given the similar consistency, the analysis of historical and other precious objects made from wood, leather, and textiles is feasible as well. Nevertheless, further experiments on books and other materials are needed to establish a statistically relevant data base for reference, and hardware improvements are needed to increases the data quality. The nondestructiveness of the method as well as the potential to design the equipment and the measurement protocol for use by non-NMR experts should be appealing features to conservators.

Acknowledgments

This work was performed as part of the EUREKA project on Cultural Heritage *Eurocare* $\sum$!*2214-MOUSE* of the European Community in collaboration with Bruker Analytical in Milano (Dr. Giovanni Bizarro, Dr. Fabio Tedoldi) and Rheinstetten (Dr. Dieter Schmalbein) as well as the University of Rome La Sapienza (Prof. Franco de Luca, Dr. Cinzia Casieri).

References

[1] D. Capitani, M.C. Emanuele, A.L. Segre, C. Fanelli, A.A. Fabri, D. Attanasio, B. Focher, G. Capretti, Early detection of enzymatic attack on paper by NMR relaxometry, EPR spectroscopy, and X-ray powder spectra, Nordic Pulp Paper Res. J. 13 (1998) 95.

[2] R.R. Ernst, G. Bodenhausen, A. Wokaun, Principles of Nuclear Magnetic Resonance in One and Two Dimensions, Clarendon Press, Oxford, 1987.

[3] G. Eidmann, R. Savelsberg, P. Blümer, B. Blümich, The NMR MOUSE, a mobile universal surface explorer, J. Magn. Reson. A 122 (1996) 104–109.

[4] C.A. Meriles, D. Sakellariou, H. Heise, A.J. Moule, A. Pines, Approach to high-resolution ex situ NMR spectroscopy, Science 293 (2001) 82–85.

[5] G.R. Coates, L. Xiao, M.G. Prammer, NMR Logging Principles and Applications, Halliburton Energy Services, Houston, 1999.
[6] R.L. Kleinberg, Well logging, in: Wiley-Liss (Ed.), Encyclopedia of Nuclear Magnetic Resonance, Chichester, 1996, pp. 4960–4969.
[7] H.Y. Carr, E.M. Purcell, Effects of diffusion on free precession in nuclear magnetic resonance experiments, Phys. Rev. 94 (1954) 630–638.
[8] S. Meiboom, D. Gill, Modified spin-echo method for measuring nuclear relaxation times, Rev. Sci. Instrum. 29 (1958) 688–691.
[9] S. Anferova, V. Anferov, M. Adams, P. Blümer, N. Routley, K. Hailu, K. Kupferschläger, M.J.D. Mallett, G. Schröder, S. Sharma, B. Blümich, Construction of an NMR-Mouse with short dead time, Magn. Reson. Eng. 15 (2002) 15–22.
[10] G.A.A. Matzkanin, Review of nondestructive characterization of composites using NMR, in: P. Höller, V. Hauck, C.O. Ruud, R.E. Green (Eds.), Nondestructive Characterization of Materials, Springer, Berlin, 1989, pp. 655–669.
[11] P.J. Prado, NMR hand-held moisture sensor, Magn. Reson. Imag. 19 (2001) 505–508.
[12] V. Herrmann, K. Unseld, H.-B. Fuchs, B. Blümich, Molecular dynamics of elastomers investigated by DMTA and NMR-MOUSE, Colloid Polym. Sci. 280 (2002) 758–764.
[13] R. Haken, B. Blümich, Anisotropy in tendon investigated in vivo by a portable NMR scanner, the NMR-MOUSE, J. Magn. Reson. 144 (2000) 195–199.
[14] P.T. Callaghan, Principals of Nuclear Magnetic Resonance Microscopy, Clarendon Press, Oxford, 1991.
[15] B. Blümich, NMR Imaging of Materials, Clarendon Press, Oxford, 2000.
[16] B. Blümich, P. Blümer, K. Saito, G. Zimmer, The NMR-MOUSE: construction, excitation and applications, Magn. Res. Imag. 16 (1998) 479–484.
[17] G. Guthausen, A. Guthausen, F. Balibanu, R. Eymael, K. Hailu, U. Schmitz, B. Blümich, Soft-matter analysis by the NMR-MOUSE, Macromol. Mater. Eng. 276/277 (2000) 25–37.
[18] C. Casieri, F. de Luca, private communication.
[19] A. Wiesmath, C. Filip, D.E. Demco, B. Blümich, Double-quantum-filtered NMR signals in inhomogeneous magnetic fields, J. Magn. Reson. 149 (2001) 258–263.
[20] M.D. Hürlimann, Diffusion and relaxation effects in general stray field NMR experiments, J. Magn. Reson. 148 (2001) 367–378.
[21] M.D. Hürlimann, Carr–Purcell sequences with composite pulses, J. Magn. Reson. 152 (2001) 109–123.
[22] M. Paci, C. Federici, D. Capitani, N. Perenze, A.L. Segre, NMR study of paper, Carbohydr. Polym. 26 (1995) 289–297.
[23] D. Capitani, M.C. Emanuele, J. Bella, A.L. Segre, D. Attananasio, B. Focher, G. Capretti, ^{1}H NMR relaxation study of cellulose and water interaction in paper, Tappi J. 82 (9) (1999) 117–124.
[24] D. Capitani, A.L. Segre, D. Attananasio, B. Blicharska, B. Focher, G. Capretti, ^{1}H NMR relaxation study of paper as a system of cellulose and water, Tappi J. 79 (6) (1996) 113–122.
[25] D. Capitani, N. Proietti, A. Segre, F. Ziarelli, NMR study of water-filled pores of the most widely use polymeric material: the paper, Macromolecules 35 (2002) 5536.
[26] A.L. Segre, N. Proietti, The paper as observed by NMR spectroscopy, Quinio 1 (1999) 179–192.
[27] M.D. Hürlimann, D.D. Griffin, Spin dynamics of Carr–Purcell–Meiboom–Gill-like sequences in grossly inhomogeneous B_0 and B_1 fields and applications to NMR well logging, J. Magn. Reson. 143 (2000) 120–135.
[28] F. Balibanu, K. Hailu, R. Eymael, D.E. Demco, B. Blümich, NMR in inhomogeneous magnetic fields, J. Magn. Reson. 145 (2000) 246–258.
[29] G.C. Borgia, R.J.S. Brown, P. Fantazzini, Uniform-penalty inversion of multiexponential decay data, J. Magn. Reson. 132 (1998) 65–77.
[30] G.C. Borgia, R.J.S. Brown, P. Fantazzini, Examples of UPEN of multiexponential data, Magn. Reson. Imag. 16 (1998) 549–552.
[31] J.I. Kaplan, G. Fraenkel, NMR of Chemically Exchanging Systems, Academic Press, New York, 1980.
[32] L.C.E. Struik, Physical Aging in Amorphous Polymers and Other Materials, Elsevier, Amsterdam, 1978.