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### Forthcoming NMR Meetings

- **Biennial Meeting of the Australian and New Zealand Society for Magnetic Resonance (ANZMAG2000)**, Mt. Buller, Victoria, Australia; **February 13-17, 2000**; Contact: Dr. Jenny Wilson, Victorian College of Pharmacy, Monash University, Parkville, Victoria 3052, Australia; E-mail: anzmag@edda.vcp.monash.edu;
- **PITTCON 2000**, New Orleans, LA, **March 12-17, 2000**; Contact: The Pittsburgh Conference, 300 Penn Center Blvd., Suite 332, Pittsburgh, PA 15235-5503; Phone: 412-825-3220; Fax: 412-825-3224; Email: expo@pittcon.org.
- **8th Scientific Meeting and Exhibition, International Society for Magnetic Resonance in Medicine**, Denver, CO, **April 1-7, 2000**; Contact: ISMRM, 2118 Milvia Street, Suite 201, Berkeley, CA 94704. Tel. 510-841-1899; Fax. 510-841-2340; E-mail: info@ismrm.org; http://www.ismrm.org.
- **Symposium on Advances in NMR Applications**, Monterey +/-, CA. Exact location to be announced. Shuttle service to and from Asilomar will be provided. **April 9, 2000**; Contact: Nalorac Corporation, 837 Arnold Drive, Suite 600, Martinez, CA 94553; 925-229-3501; Fax: 925-229-1651; Email: sales@nalorac.com; http://www.nalorac.com.
- **41st ENC (Experimental NMR Conference)**, Asilomar Conference Center, Pacific Grove, CA, **April 9-14, 2000**; Contact: ENC, 1201 Don Diego Avenue, Santa Fe, NM 87505; (505) 989-4573; Fax: (505) 989-1073; E-mail: enc@enc-conference.org. Web: enc-conference.org
- **15th European Experimental NMR Conference**, Leipzig, Germany, **June, 2000**. For information, see http://eenc.uni-leipzig.de.

*continued on inside back cover*
NMR Evidence for In-situ Modification of the Directing Agent in Zeolite Syntheses

Zeolite crystal size and morphology can be altered by varying the inorganic reagents in a synthesis mixture. The system investigated was the 1,6 hexamethylenediamine based ZSM-22 zeolite to reduce the crystal aspect ratio (length to width). Typically a synthesis mixture containing Ludox (colloidal silica) and KOH can produce ZSM-22. The presence of Na ions can produce ZSM-5. However, in this system replacing the Ludox/KOH combination with either Ludox/KOH/NaOH or with Na silicate/KOH produced zeolite offretite. The synthesis of offretite by a diamine is not unique. What was unusual was that the 13C CP/MAS NMR spectra of the as-synthesized offretite materials (Figure-top) show an unexpected carbonyl signal at 166.4 ppm in addition to four aliphatic resonances at 44.6, 41.5, 31.4 and 26.5 ppm. The peak at 166.4 ppm is characteristic of an amide or carbamic acid type carbonyl. The good cross polarization efficiency of the carbamate suggests that it is inside the pores of the zeolite rather than physisorbed on the surface. Spectral areas are consistent with the dicarbamate (i.e. "OOCNH(CH₂)nHCOO").

The observation of this carbonyl resonance stimulated our interest because it suggests the first example of "in-situ" formation of a structural directing agent in zeolite syntheses. Interestingly, offretites synthesized with 1,4-butanediamine, 1,6-hexanediame, and 1,8-octanediame all exhibit the carbonyl peak. However, the spectra of ZSM-5 and ZSM-22 synthesized with 1,6-hexanediame only possess resonances associated with the diamine. The spectrum of the ZSM-5, shown in the bottom of the Figure, consists of two main resonances in the ratio of 1:2 at 41.5 and 26.5 ppm from TMS. The chemical shifts and intensities of the aliphatic resonances are consistent with intact 1,6-hexanediame. The carbonyl signal was not observed in the as-received amine samples. Interestingly, no carbonyl signal was observed for a freshly prepared zeolite gel mixture. Only when the gel was heated to at least 100°C was there any evidence for the formation of the carbonyl species even though the gel was still amorphous. We speculate that the source of the carbonyl may come from the reaction of carbon dioxide preadsorbed in the basic sodium solution with the diamine to form a carbamic acid. A manuscript is in preparation that details the synthesis and analytical data of this study and a proposed mechanism for the formation of the carbonyl species.
### System Solutions and Precision Instruments from Bruker:

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Efficient Creation of Documents Containing High Resolution NMR Graphics on a PC

Dear Dr. Shapiro:

It is both convenient and economical to process NMR data on a computer that is not used to control a spectrometer. IBM PC compatible machines are an inexpensive and popular choice for NMR data processing. When using NMR processing software to prepare data for presentation and/or publication one often runs into problems. NMR processing applications usually provide limited annotation and graphics adjustment capabilities. This problem can be overcome by transferring spectra to a full-featured illustration application. Unfortunately data transfer from a NMR application to a drawing and/or document preparation application often degrades resolution. There are a number of solutions to the preceding problems. We will describe one that is easy to set up and use, has a relatively low cost, and provides high quality presentation material.

We use the Nuts program from Acorn NMR running on a PC to import and process NMR data collected with GE/Tecmag and Varian spectrometers. Nuts can read data from a wide variety of NMR spectrometers (see www.acornnmr.com for more information). After processing the data the bw command is used to make all spectra and axes black. If one wishes to make a graphic containing multiple spectra the buffer or stacked plot commands can be used to appropriately position spectra and axes. A printer-enhanced DC metafile is then copied to the Windows clipboard (see www.acornnmr.com/NutsHelp/copy.html for more). The contents of the clipboard are then pasted into Coreldraw 9 ($130 academic) using the edit > paste special > enhanced metafile command. One then has a Coreldraw graphic that has no visible reduction in resolution compared to the Nuts data. Each spectrum consists of a number of Coreldraw objects that can be readily grouped. As a result spectral features such as position, size, and line thickness can be easily modified. Also annotation and addition of other graphical objects such as chemical structures are readily accomplished. When it is complete the graphic containing multiple objects is exported to an encapsulated postscript file and this file is imported into a document preparation application (ie. MS Word). The above procedure was used to create this letter and the figure below. The figure contains $^2$H spectra taken at 55 MHz of hydrated 1-d31-palmitoyl-2-oleoyl-sn-
Position Available:

**NMR Operator/Researcher** with the NMR Facility at Clark University. Duties involve responsibility for maintaining instrumental operation of the Facility. Modern (recently installed) instrumentation including solid state (Varian Inova 400 WB) and high field liquid (Varian 4-channel Inova 600) is available. Opportunities for collaborative research in establishing programs in solid state NMR of polymers and/or high resolution NMR of biomolecular structure are available. The position requires a PhD with expertise in NMR operation, maintenance and good computer skills. The instrumentation is computer interfaced with a series of workstations for both host control and off-line processing. The position involves system management for the computers. Clark University is an EEO/AA Employer. Resume to: Paul T. Inglefield, Chemistry Department, Clark University, Worcester, MA 01610-1477

Glycero-3-phosphocholine (POPC) at different concentrations. The difference between spectra is due to the fact that the 0.05M POPC bilayers are more highly oriented than the 0.5M bilayers. For alternatives to using Coreldraw for presentation refinement of NMR spectra see [www.acornnmr.com/nut1.HTM](http://www.acornnmr.com/nut1.HTM).

Regards,

Valerie Cumbea

David Cafiso

Jeff Ellena
Dear Barry,

Apparently the color of this years ultimatum was not vivid enough to catch the eye on my overcrowded desk. As a result we missed the deadline, but we hope to put things right with the present contribution. Recently we have been using so-called double frequency sweeps to get a more efficient conversion of triple to single quantum coherence in MQMAS experiments of spin $I=3/2$ systems. These ideas originate from an early paper by Vega and Naor who demonstrated that amplitude-modulated pulses can be successfully used for 3Q$\rightarrow$1Q conversion in single crystals. In our case we use a time-dependent amplitude modulation so that our RF source is split into two sidebands that are swept over a certain frequency range to cover the satellite transitions of every crystallite in a powdered sample. We have found the method to be very efficient also for spin $I=5/2$ nuclei. This is demonstrated in the figure showing the $^{27}$Al sweep-enhanced MQMAS.

**Andalusite sweep-enhanced MQMAS**

![Diagram of NMR spectrum showing sweep-enhanced MQMAS results for Andalusite.](image)

**RF field $\sim 115$ kHz**

Nijmegen, September 23, 1999

----

Dr. B.L. Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303
U.S.A.

(received 10/4/99)

Double frequency sweeps in MQMAS of half-integer quadrupolar nuclei.

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National HF-NMR Facility, University of Nijmegen, Toemmooveld 1, NL-6525 ED Nijmegen, The Netherlands. FAX: +31-24-3652112
Dr. A.P.M. Kentgens, supervisor solid-state NMR, tel. +31-24-3652078 / 3652369 / e-mail: amk@solidmr.kun.nl
spectrum of the mineral Andalusite. This is a challenging case as one of the sites has a quadrupole-coupling constant of 15.3 MHz. In conventionally pulsed MQMAS experiments it is only possible to observe this site when a very large RF field strength (close to 300 kHz) is used. In the sweep-enhanced experiment we worked with 115 kHz. On top of that we get a significantly better signal to noise and the lineshape is close to the expected theoretical lineshape as is exemplified by the slice taken from the spectrum.

An important question is how to generate these clean amplitude modulated pulses, as our commercial spectrometers (Bruker and Chemagnetics) are currently not capable of performing this task. We use a commercially available arbitrary waveform generator from National Instruments (DAQArb PCI5411) which can be put in a PCI slot of a PC. This allows us to calculate any waveform that can be read out by the card in 25 nsec steps. We generate the amplitude modulation on a center frequency of 14 MHz. This signal is split in two as shown in the diagram. One part of the signal is fed into the low-power transmitter channel of the spectrometer. The spectrometer frequency is set to 14 MHz below the desired frequency used to irradiate the nuclei under study so that the sum frequency is the (modulated) Larmor frequency ($\omega_0$). This frequency is filtered and fed into the power amplifier in the usual way. The signal obtained from the sample is, after preamplification, fed into the right block where an unmodulated 14 MHz is subtracted before being fed into the receiver channel of the spectrometer. In this way all phase cycling capabilities etc. from the spectrometer are retained. A detailed description of the device will be submitted to the review of scientific instruments.

Sincerely yours,

Jan van Os
jaos@solidmr.kun.nl
Hans Jansen
haja@solidmr.kun.nl
Rieko Verhagen
rive@solidmr.kun.nl
Dinu Iuga
iuga@solidmr.kun.nl
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Dear Dr. Shapiro,

we describe here an imaging experiment, to solve an important problem of agriculture, which was faced to us by our colleagues of the faculty of agriculture of our university: Rain-induced cracking of sweet cherry fruit limits crop production and results from excessive water uptake through the fruit skin. The purpose of our study was to investigate water uptake locally by sweet cherry fruit using NMR imaging and D$_2$O as a probe.

**Experiment**

Mature sweet cherry fruit was incubated in D$_2$O for 1h at 20°C. Subsequently the loaded fruit was transferred into a custom-built cuvette inside a rf-double-turned saddle coil (32mm, see Fig.1). The deuterium NMR-signal (30.7 MHz; Fourier-Imaging with 64 phase increments) was scanned for 1h, 2h, and 5.5h (32, 64 and 176 scans, resp., 25°C).

The pulse sequence was a simple Hahn-echo procedure: Pulse(40 µs; c.17°) $\rightarrow$ 1.5ms $\rightarrow$ pulse (440 µs; 180°) $\rightarrow$ echo (acquisition).

The slice thickness was dependent on the unshaped pulse length and was estimated to 2 mm.

**Results**

To show the ability to give perfect $^2$H-images a longitudinal (72scans) and a cross-sectional (24scans) slice ($\approx$ 1mm) is shown in Fig. 2.

Water uptake increased linearly with time suggesting that uptake was a diffusion process. Initial studies established that water uptake during submersion was too slow (c. 1...2 mg/h) to allow online measurements. Hence, “loaded” fruit was scanned following removal of the incubation solution, thereby allowing extended accumulation periods. Increasing the number of scans from 32 to 176 markedly improved signal to noise ratio (Fig. 3).

Deuterium images of macroscopically perfect fruit revealed preferential absorption in stylar and stem cavity regions. However, microscopic cracks, detected by fluorescence light
microscopy following the NMR scans, have shown served the routes of preferential D₂O entry.

Fig. 2.
Longitudinal and cross-sectional view of a sweet cherry incubated for 12 h at 20°C in D₂O. For uniformity of D₂O distribution fruit was allowed to equilibrate for a further 48 h at 5°C and 95% r.h. prior to NMR imaging.

Fig. 3.
²H-images of two cherry fruits that were incubated in D₂O for 1 h at 20°C (upper and lower row). Fruit was scanned immediately after the incubation period. Number of scans was 32, 64 and 176 (from left to right). Upper row: Fruit with microscopic cracks in the cavity region. Lower row: Fruit with microscopic cracks in the stylar region.

M. Knörgen

Please credit this contribution to the subscription of Prof. H. Schneider, Department of Physics, Martin-Luther-University Halle Wittenberg, Halle/Saale, Germany
Title: Acyl-chain-length dependence of the $^{31}$P chemical shift of phosphatidylcholine

Dear Barry:

Variations in phospholipid molecular structure are critical to the functions of biological membranes. For some time our laboratory has been interested in the analysis of mixtures of phospholipids (PL) and related species in tissue samples by $^{31}$P NMR spectroscopy. Several years ago (1), John Pearce in my laboratory found that, by solubilization of the PL mixture in an aqueous bile-salt micellar solution under carefully controlled conditions, he could resolve the $^{31}$P NMR signals of phosphatidylcholine (PC) molecular species, which are PC molecules of differing acyl-side-chain unsaturation and/or length. In brain tissue, the major PC resonances could be assigned to species containing 0, 1, or 2 fully saturated acyl chains. Chain length was not an issue in this case because acyl side chains of less than 16 carbons constituted a small fraction of the total composition.

We previously reported (1) limited results on the dependence of the $^{31}$P NMR chemical shift of PC on disaturated acyl chain length in the aqueous sodium-cholate system. Recently we further investigated the chain-length dependence of the $^{31}$P chemical shift for a series of disaturated PCs of differing chain length, extending below 12 carbon atoms and over a range of temperatures. Some of the results are illustrated in the figure.

Figure. The $^{31}$P NMR spectrum of a mixture of synthetic n:0/n:0-PCs of varying acyl chain lengths in an aqueous sodium-cholate system at 121 MHz and 47 °C. The number of carbons n in the hydrocarbon chain is given above each resonance.

The previously observed trend to lower $\delta$ with decreasing chain length continued to $n = 7$, whereupon the direction of change reversed. Also, the largest relative variation with temperature was seen at $n = 7$.
(not shown), when \( \delta \) for \( n = 16 \) was assigned the same value of -0.510 ppm at all temperatures.

We do not know for certain the molecular origin of the observed chemical shift changes with chain length and temperature. Here spectra were acquired at high ratios of bile salt to PL. In that case, at least for longer chains, the system is a mixed micelle consisting of isolated PL molecules in a relatively small, globular, bile-salt aggregate. At the shortest acyl chain lengths (\( n \leq 7 \)), the PL molecules become increasingly soluble as monomers in aqueous solution, and probably are not fully incorporated into the micelles. At the longest chain lengths examined here (\( n \geq 16 \)), the PL molecules are completely solubilized in the detergent micelle. Thus the trend to lower \( \delta \) from \( n = 18 \) to \( n = 7 \) may primarily reflect structural changes in the micelle in the vicinity of the PL molecule in order to accommodate the shorter chain length. As the PL molecule becomes increasing soluble in the aqueous phase, the direction of \( \delta \) change reverses. It is also possible that direct electronic effects at the P atom are occurring as a result of the changes in molecular structure at the shortest chain lengths.


Sincerely,

Richard A. Komoroski

---

DEPARTMENT OF HEALTH & HUMAN SERVICES
Public Health Service

National Institutes of Health
National Heart, Lung, and Blood Institute
Bethesda, Maryland 20892

(received 10/12/93)

POSTDOCTORAL POSITION

A postdoctoral position is available in the Laboratory of Biophysical Chemistry at the National Heart, Lung, and Blood Institute. Our interests cover a broad range of NMR applications towards biomolecular structure determinations. A good background in magnetic resonance methodology and computer programming are required. The research project will be directed towards protocol development for structure determination and validation. Anyone who is interested in practical implementation of newly developed NMR techniques in structure determination are encouraged to apply. Please send a curriculum vitae and arrange to have two letters of recommendation sent to

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Laboratory of Biophysical Chemistry
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Baselines and Integration

Dear Barry,

Good baselines are critical for obtaining accurate integration. Baselines which appear to be acceptable are often revealed by a tilted integral line to be “distorted”. There are two techniques for correcting the integration: 1) correct the baseline before doing the integration and 2) adjust the zero and first order components of the integral to make the integral “appear flat”. Experience has proven to us that method 1 is the most reproducible and least subjective method. Further, it has been our experience that good integration results for different data sets can require application of different baseline correction methods. Since we believe in correcting baselines not integrals, we read with interest the letter about baseline corrections from Golotvin and Williams in the last issue of the Newsletter.

There are numerous sources of baseline distortions, often characteristic of the hardware or due to the nature of the sample, each resulting in a unique baseline shape. Specific hardware combinations often produce distinctive baselines shapes or “signatures”. Many approaches to correcting these baselines work well only for specific types of distortions. Correction of baseline distortion with an inappropriate tool can result in a poorly corrected baseline, corruption of integral values and/or spectral distortions including loss of peaks. While some methods lend themselves to automation, using a single approach in an automatic mode can result in unanticipated results. Also, even with an appropriate tool, automatic baseline corrections can often be improved by user interaction. This said, the baseline “signature” of one set of hardware often can be automatically corrected by using a baseline correction method optimized for that general signature.

The simplest correction method is removal of DC offset and/or linear tilt. This method is an example of a first order polynomial correction. When the distortion is of higher order, a higher order polynomial can be calculated to match the baseline roll and then subtracted from the spectrum. The baseline points from which the polynomial is calculated can be selected automatically or manually by the user to allow fine-tuning for optimal fit. One advantage of a polynomial correction of baseline is that it has a low probability of distorting integrations after baseline correction. An example of a least-squares fifth order polynomial correction is shown in Figure 1.
Often, the baseline roll is due to distortion of the first few points in the FID. This can result from non-linear responses in the instrumentation, such as: pulse break-through, preamp overload and/or recovery, probe ringdown, filter delays, etc. A traditional approach for correcting this type of distortion is linear prediction of the beginning of the FID’s early data points from FID’s later data points. Usually, only a few points need correction, but some severely distorted data can require prediction of several points, and some trial and error can be required to obtain good baselines. The user can vary parameters such as the number of points to correct, the number of points on which to base the prediction and the number of signals to use in the back prediction calculation. Figure 2 shows the effect of linear prediction of the first 2 data points of a high dynamic range sample.

Figure 2
Some undesirable baselines are the result of “real” NMR signal, such as a broad hump from exchangeable protons, poor water saturation, probe background or broad signal from a polymer component of the sample. While these broad peaks are not distortions of reality, they can interfere with extraction of the desired information from the spectrum, such as integration of small peaks superimposed on a hump. Figure 3 shows such a situation. A person can look at this spectrum and readily deduce where the “baseline” should be. The same process can be accomplished by software. The process involves automatically distinguishing regions of just baseline from regions containing peaks, interpolating where peaks exist, then subtracting this “deduced” baseline from the spectrum. This is similar to the approach described by Golotvin and Williams in the last issue of the Newsletter. The computer algorithms for “deducing” the baseline to be subtracted involve identifying what data points are peaks and what data points are baseline. As discussed in the letter from Golotvin and Williams, this process uses the RMS value of the spectrum’s noise, a user-defined number of data points and a user-defined multiple of the RMS noise value to determine whether a data point is noise or baseline. With care in the selection of these parameters, some very useful baseline corrections can be obtained. Figure 3 is a good example of an impressive and useful application of this method. Care in parameter selection is important to avoid distorting the low level lineshapes of peaks that can result in integration errors. This method has been found to be one of the best methods for correcting water saturation baselines.

Figure 3

![Figure 3](image)

Figure 4 shows one of the worst cases we’ve encountered. This is not a smoothly varying baseline, so cannot be corrected with a polynomial. The “deduced” baseline approach discussed in the previous paragraph results in elimination of the small peak at 6.7 ppm (which is real) even with careful parameter selection. The peak is lost because, due to its width and location at the top of a hump, the algorithm is unable to distinguish it from noise, and it is therefore “corrected” out of the data. This severe case can be addressed by dividing the spectrum into segments, selecting those segments that contain only noise and correcting each segment independently with a polynomial correction. This needs to be applied with care, as the selection of which segments do and don’t contain peaks is critical.
As is clear from these examples, the NMR user needs to select carefully from a variety of baseline correction tools and experiment with parameters to obtain the best result. However, this does not preclude automated processing. Some types of distortion result from hardware and give characteristic baselines. Especially with older instruments, data can often be immediately recognized as originating from a particular manufacturer’s spectrometer based on the shape of the baseline. Once the appropriate tool and its parameters have been determined, the same type of correction can be applied to similar spectra in an automated mode.

Sincerely,

Virginia W. Miner

Woodrow W. Conover
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<table>
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<th>Tube Length</th>
<th>Concentricity</th>
<th>Camber</th>
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<th>Price 100+</th>
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<td>0.0020&quot;</td>
<td>0.0020&quot;</td>
<td>5 mm</td>
<td>4.05</td>
<td>3.65</td>
</tr>
</tbody>
</table>

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Cautionary Note on Defining Gradient Specification

Dear Barry,

We had been waiting for our new Bruker Avance DRX600 spectrometer and the accompanying shielded magnet to be completely installed for quite sometime. Naturally when it was finally installed and met almost all of the required specifications we were very eager to start collecting data on the new machine. I am very happy to say that the machine is still functioning despite the abuse (so far) that we have given. Some of our colleagues here at NIH asked us about our new spectrometer and we had always been delighted to be able to say that it met the specifications that we asked for.

Indeed the spectrometer has been performing quite well and has turned into one of our workhorses. We are not sure whether it is a coincidence but as soon as you reminded us of our missing contribution to the newsletter we started to find a subtle problem with our new spectrometer. This problem is illustrated in the $^1$H-$^{13}$C correlation spectrum shown in Figure 1. It is a correlation spectrum of $^{13}$C labeled alanine in the methyl position. The shapes of the cross peaks of the quartet do show distinct asymmetry. We knew that it must be an instability of the spectrometer. On the other hand we also realized that the spectrometer has passed all of the stability tests for lock, temperature, etc that we required. This prompts us to ask around on campus to see whether anyone has seen a similar problem on other spectrometers. One of the suggestions that we received was to check for our gradient. I promptly replied that we have checked the recovery following gradient pulse and the system met the required recovery time. The same person reminded us that the amplitude recovery was not enough to specify a properly functioning gradient system. Indeed when we tested our system for gradient recovery it performed quite well as shown in Figure 2. However when we compared the signal acquired with a 1 ms rectangular gradient to the one acquired without gradient we clearly noticed the difference as shown in the difference spectrum in Figure 2. This is due to the shifting of
the peak position as well as the distortion in the shape of the peak. We could minimize the effect by using sine-bell shaped gradient pulse with substantially lower power.

Sincerely,

Eva deAlba

Nico Tjandra

Figure 1. $^1$H-$^{13}$C correlation of $^{13}$C labeled Alanine.

Figure 2. Series of spectra collected as a function of recovery delay with a 50 us increment after a 1ms gradient pulse at 25G/cm (A) and at 0 G/cm (B). The difference spectrum (C) is expanded 8 times with respect to the reference spectrum.
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Figure 1

Figure 2

A

B

C

8x
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PROMOTING RESEARCH AND DISCOVERY
Dr. B. L. Shapiro  
The NMR Newsletter  
966 Elsinore Court  
Palo Alto, CA. 94303

October 6, 1999

Providing adequate NMR support for our robotic synthesis group has proved very challenging for a variety of reasons not the least of which is the number of NMR tubes to be handled. Traditionally, analysis of final products generated by robotic synthesis has been done by mass spectrometry. However, reliance solely on MS for final product characterization has not been entirely satisfactory due to the lack of stereochemical information and the difficulty in assessing purity. Discussions with the Combi-Chem group resulted in the following requirements for NMR support: 1) NMR tubes would be too time consuming and deuterated solvent too costly; 2) Use of 96 well plate format to reduce sample handling and preparation; 3) Small scale synthesis required that the same sample be used for analysis and screening, thus requiring the use of non-deuterated solvents to eliminate screening problems; 4) Automated entry of sample information on the SUN workstation.

In order to meet the above requirements, we acquired a flow probe/Gilson 215 setup from Nalorac Corp for our Varian INOVA400 spectrometer. The flow probe utilizes a 120µL flow cell and Teflon transfer lines so that DMSO can be used as solvent. A separate PC controls the Gilson, allowing the Gilson to be used without interfering with normal NMR use. The effort required to enter the sample information on the SUN workstation is minimal: The information necessary to acquire the NMR spectrum, such as solvent, laboratory notebook number, NMR experiment, etc., is automatically created in an additional worksheet in the same EXCEL workbook the chemists use to submit samples to the screen. This worksheet is stored as a tab delimited text file on the SUN workstation using the network. MAGICAL macros were written which can then read this information to set up the experiment, create the text and save the FID to disk automatically. PRESAT or WET can be used for solvent suppression. Additionally, the chemists can specify which wells will be analyzed. When the spectrum has been acquired, the sample is recovered from the probe and returned to the proper well.
After very few teething problems, the results were quite satisfactory. Figure 1 shows a two spectra acquired in protonated DMSO using WET solvent suppression. The sample concentration is ~ 2mg/ml. Before suppression of the DMSO solvent peak, the solute signals were not observable. With WET suppression, the resulting spectrum is quite interpretable. Even though the portion of the spectra under the DMSO is obviously missing, protons close to the suppressed region are clearly visible at this solute concentration.

We would like to thank Ron Crouch of Nalorac Inc. for his help in making this work possible.

Sincerely yours,

D. J. Bowler
dbowler@pacbell.net

L. L. Chang
lydia.chang@agna.zeneca.com

Figure 1. NMR spectra of combi-chem samples acquired in protonated DMSO using 400 MHz Nalorac flow probe.
18 October 1999
(received 10/19/99)

B. L. Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303-3410

Re: Morphology and Spin Diffusion in a Fluoropolymer

Dear Barry:

We are in the throes of spectrometer installation which is my excuse for requiring the
"Ultimatum". We are replacing spectrometers and installing a 4 channel 600 MHz liquid system
and a 400 WB solid state system as well as a new analytical instrument, all from Varian. The
600 is completely installed, the others in progress. In this regard I am looking for an instrument
operator/manager (see attached ad).

We have been working for some time on the fluorocarbon polymer Nafion\textsuperscript{R} and I am enclosing
the results of some spin diffusion experiments taken under MAS conditions using chemical shift
as the gradient. The experiment involves a DANTE sequence and typical F-19 spectra are
shown. Two domains are present one composed of side chain groups (hydrophilic in nature) and
one composed of backbone groups (teflon-like). These are the resonances at -80 ppm and -120
ppm respectively. Length scales for the domains can be obtained by analysis of the spin
diffusion data. These are shown in the table for Nafion swollen by water and ethanol. This type
of experiment gives insights into materials of complex morphology such as this.

Best Regards,

\[\frac{\text{\footnotesize PTI/ECB}}{\text{\footnotesize Paul T. Inglefield}}\]
Table I: Domain Size Determinations from $^{19}$F Spin Diffusion Measurements

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<th>% Penetrant</th>
<th>$t_{sd}^{1/2}$ (ms) $^{1/2}$</th>
<th>$f_a$</th>
<th>L (nm)</th>
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<td>0.75</td>
<td>37.74</td>
<td>28.39</td>
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</table>
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AMT has a worldwide reputation as a leading supplier of high power, solid state power amplifier products that operate at frequencies between 1 MHz and 3 GHz and provide RF power from several watts to several kilowatts. Its products are noted for their exceptional performance, highest quality and superior reliability.

The company's products are sold to numerous major corporations, universities and research centers throughout the world.

AMT is located in Anaheim, California and occupies a 25,000 square foot facility allocated to engineering, manufacturing, quality assurance, marketing/sales, administration and finance.

Engineering areas include an R & D laboratory, a tool and die shop, mechanical design and drafting areas, an environmental testing laboratory and document control. The R & D laboratory is equipped with all of the latest design and testing equipment including intermodulation distortion simulators, network analyzers, spectrum analyzers, signal generators, noise figure meters and infrared (IR) scanners. The environmental testing laboratory includes equipment to simulate shock, vibration and thermal environments.

Manufacturing areas include a controlled access stock room, a 10,000 square foot assembly area and a production test area employing automatic testing. Also included is an environmental laboratory used for environmental stress screening of production products.

AMT's products vary in complexity from single modules, to rack-mounted amplifiers, to complete transmitter systems. The rack-mounted amplifiers and complete transmitter systems typically include detection/protection circuitry, built-in power supplies, front panel metering and digital and/or analog interface controls. Both forced air and/or water cooling are used, depending on the customer's requirements.

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These factors, along with computer driven automatic testing and environmental stress screening of the final product, ensure that the performance, quality and reliability meet AMT’s exacting standards.
Early Days of NMR in the Southwest:
Fifth Installment

Dear Barry,

As I mentioned previously, the petroleum industry in Texas was quick to perceive the possibilities of NMR to solve practical problems. In the fourth installment** of this history, I related the very early NMR research at Texaco in Houston, with roots that extended to Felix Bloch himself. Houston was (and still is) the hub of the petroleum industry in Texas, and I start this installment with another early NMR project in Houston.

SHELL OIL COMPANY

The early 1950's were a very active period for NMR research at Shell in Houston. There were two NMR research groups: the chemical group doing chemical shift NMR, and the petrophysical group doing NMR oil well logging research. J. D. Loren and J. D. Robinson headed the latter group. They constructed a pulse NMR machine that operated at a Larmor frequency of 28.7 MHz. It incorporated one of the earliest Varian magnets, that is still kept in storage for sentimental reasons. In 1960, they measured the proton T₁ of water in saturated cylinders of Selas porcelain (material having very narrow pore size distributions). The purpose was to investigate the shape of the spin-lattice relaxation curve of water in a porous medium of a given pore size, and to determine the effect of pore size on T₁.

Theory to interpret the data was developed later (1970), in collaboration with Stephen D. Senturia of MIT. This theory was also applied to data taken with a laboratory instrument that enabled measurement of signal intensities and relaxation times under the magnetic field conditions that prevailed in the commercial nuclear magnetism logging (NML) tools that were being developed by the oil field service companies to find petroleum.

** The fourth installment appeared in NMR Newsletter number 491, pages 17-22 (August, 1999).
The laboratory NML apparatus was constructed to measure the proton $T_1$ and $T_2$ in porous samples up to six inches long and three inches diameter. The sample was enclosed in a solenoid that served both to establish nuclear polarization and to measure the FID. Electric current was applied to the solenoid to establish a "steady" magnetic field of about 300 gauss. After the proton equilibrium magnetization was achieved, the field was rapidly reduced to about 5 gauss and held there for an adjustable period of time. Then the 5-gauss field was very rapidly turned off and the proton magnetization precessing in the earth's magnetic field (Larmor frequency of about 2 KHz) induced current in the solenoid and the FID was observed. This apparatus, like the commercial NML tool, was able to measure the $T_1$ at 5 gauss and the $T_2$ in the earth's field (from the FID decay time). However, the commercial NML tool would be lowered into the borehole of the oil well and the "sample" would be the porous rock that surrounds the borehole. With this laboratory apparatus, they did earth's field relaxation studies, $T_1$ studies of oils, $T_1$ studies in porous media as a function of oil and brine saturation, and paramagnetic relaxation studies.

The goal of many of these studies was to measure residual oil saturation in the oil well with a log-inject-log technique. In this technique, the NML would be run to measure signals from all the fluids in the rock (water and oil) to identify the porous formations that could contain petroleum. Water containing paramagnetic ions (so that the $T_2$ would be very short) was then injected into the rock. The NML was run again and the signal from the displacing water was not detected because the $T_2$ was too short to allow FID detection; the remaining signal was from the oil that was remaining in place.

In the early 1950's, they ran a set of ten logs in oil and gas wells of Shell fields using the Byron Jackson Company NML tool and did an extensive comparison of oil saturations determined from the logs with core saturations measured by other means. They also measured surface relaxivities and studied various models for determining rock permeability from $T_1$ measurements in sandstones and carbonates. Several published experimental and theoretical papers on relaxation in porous media and a patent on log-inject-log NMR logging for determining residual oil saturation resulted from this work. In addition, they collaborated with Schlumberger-Doll Research on optimizing the design of their NML tool.

PHILLIPS PETROLEUM COMPANY

Phillips Petroleum Company in Bartlesville, Oklahoma, had several people working in NMR research, both in the laboratory and in the oil field, in the 1960's. Don Lauffer and Morgan Waldrop built a pressure cell with rf coils inside and performed NMR analyses at elevated pressures. They also built and tested gradient coils and would have had an imaging system to image the location of liquids in rocks in 1973 if Phillips had bought a computer (pretty expensive in those days) for this purpose.

SANDIA NATIONAL LABORATORY

In 1959, Al Narath completed his Ph.D. in chemistry and was hired by Sandia to set up an NMR program. He developed an impressive NMR program in solid state chemistry/physics. Roger Assink came later (about the 1970's) and set up an imposing program on NMR of polymers.
TEXAS INSTRUMENTS

G. K. Walters joined Texas Instruments (TI) in Dallas in 1957 and started a project to use NMR as a probe of the properties of water and other hydrogen-containing molecules adsorbed on semiconductor surfaces. A 30 MHz pulse spectrometer with a Varian 12-inch electromagnet was constructed. Walters and C. G. McCormick obtained limited $T_1$ and $T_2$ data from adsorbates on powdered silicon. This research was along the lines of that being carried out at Mobil by Zimmerman and his group on silica gel surfaces. There was interaction with the Mobil group; seminars describing the fundamental, non-proprietary aspects of their research were held occasionally over many years. However, because the surface areas of silicon powders were much lower than those of silica gel, the signal-to-noise ratio of the adsorbate signals were insufficient for definitive studies and the project was abandoned. Walters left TI to go to Rice University in 1963. The other members of the TI NMR group left, or were reassigned to other projects within a few years later.

In a separate project around 1960, they used NMR as a diagnostic in studies of techniques for dynamical polarization of the rare isotope helium-3. This research was part of a successful R&D program that established TI as a major supplier of magnetometers for the military.

TEXAS A&M UNIVERSITY

Melvin Eisner, brother of Elmer Eisner of Texaco, started NMR at Texas A&M University in the physics department in 1951. He and his students designed and built a home-made NMR spectrometer. It incorporated a magnet that had been constructed by the electrical engineering department for a mass spectrometer. The magnet was rather poor and had a field of only about 3,000 gauss. The console incorporated parts donated by Western Electric Co. (they had no research budgets there in those days). They did their early work by detecting the spectral peaks with marginal oscillator circuits; then they shifted to rf bridge circuitry and a stable rf source.

The magnet was improved and, by 1956, they were doing some good research with it. However, most of this research was unpublished. Significantly, they measured the $T_1$ values as well as the chemical shifts of the various proton peaks in ethanol. This was described in a thesis by Al Hildebrandt and may have been the first $T_1$ measurement of the different protons in a molecule. They also developed a low field spectrometer; very high resolution spectra measured with it may have led to some publications.

In the 1960's, they acquired the magnet that had been used in the discontinued Texaco NMR well logging project (see the fourth installment) for Eisner's use and, with funding from the Robert A. Welch Foundation of Houston, acquired some Varian 40 MHz probes and other components. Using dilution of ordinary benzene with deuterated benzene, Eisner and his students separated the benzene intermolecular relaxation contributions due to molecular translational motion from the intramolecular contributions from molecular rotation. This research was reported in the 1966 Ph.D. thesis of R. Smith.

The Texaco magnet is still at A&M and is being used by Hans A. Schwessler of the physics department. (This is a very well-travelled magnet; the next installment will relate more of its wanderings.)
The chemistry department acquired high resolution NMR apparatus for analysis of liquids in the 1960's. They first acquired a Varian A-60 spectrometer and then a Varian HA-100. Ali Danti, affiliated with Bruno Zwolinski's API/MCA spectrum publication project, was the first to make any major, systematic use of NMR in the department. Barry Shapiro arrived in the summer of 1968 to run the department's NMR laboratory and had a mandate to choose a new machine and outfit a laboratory in the recently completed wing of the department. They acquired a 100 MHz JEOL FT spectrometer incorporating a Nicolet data system. This system was reliable and worked well. NMR in the chemistry department was used mainly for small molecule structure problems of the organic chemists.

The next installment will complete this history. I plan to include material from all of the installments in an historical article for publication in an NMR journal. Therefore, I invite comments (helpful or otherwise), suggestions, corrections, additions, etc., to these NMR Newsletter contributions.

Sincerely,

Donald E. Woessner
dwoess@mednet.swmed.edu

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**E-mail Addresses Wanted**

Please include your e-mail address on all correspondence, including technical contributions, or send me an e-mail message. This will make it more convenient - and economical - to contact you. Thanks.

BLS
shapiro@nmrnewsletter.com
A Simple Device for Inserting, Ejecting, and Positioning Samples in Bruker Widebore Spectrometers

Dear Barry,

We were recently faced with the need to insert, remove, and position samples for microimaging in our Bruker DMX400 NMR spectrometer without use of pneumatics. To allow a larger diameter for tissue perfusion apparatus, pH sensors, and other equipment in the magnet bore, we operate without an upper shim stack and therefore cannot insert or eject samples by compressed air in the customary way. Even with the upper stack in place, pneumatics alone could not permit accurate positioning of the microimaging samples at an arbitrary angle relative to the X and Y gradient axes. For this reason, we decided to build a tool which would attach to the standard Bruker widebore sample spinners and microimaging sample holders and extend above the top of the magnet bore to allow remote sample positioning.

My first thought, inspired by a suggestion from Mark Mattingly at Bruker, was to insert a piece of acrylic tube into the top of the sample spinner and rely on either friction or rubber O-rings to grip the spinner. Unfortunately, since the Bruker spinners were manufactured according to metric measurements and our acrylic tubes all had diameters in fractional inches, it would have been necessary to machine down the end of the tube to mate with the spinner. Since our machinists were very busy at the time, I asked them to simply cut a 1/2" slot down the length of an ordinary 1-3/4" diameter acrylic tube. Once this slot was cut, the plastic tube could be pushed with slight hand pressure into the top of the sample spinner. Thereafter, the spinner and sample would stay firmly held to the tube by friction. A slight squeeze of the acrylic tube would then release the spinner and sample. Thus, we had constructed a simple mechanical device which could grab and release a sample without any modifications to the sample spinner.

To allow reproducible radial positioning of the microimaging samples, we added a flange which bolted to the top closure flange of the magnet and had set screws to hold the acrylic tube firmly in place both axially and radially. The sample could then be aligned to one side of the slot and inserted into the magnet using a sample spinner and the acrylic tube. The side of the slot could then be aligned with the flange at the top of the magnet. The magnet documentation specified the orientation of the closure flange mounting holes relative to the magnet X and Y axes, so we could then position any sample at a known angle relative to these axes. Given the known orientation of the pulsed field gradients with respect to the magnet axes, we now had an accurate and reproducible microimaging sample positioner.

After building this positioning apparatus, we realized that it had two unplanned but handy additional applications. First, because the tube and flange were both slotted down their entire lengths, we could easily insert a closed-loop cell perfusion system such as a chondrocyte bioreactor or lymphocyte perfusion circuit into the positioning system without breaking the loop and therefore compromising sterility. Once the circuit was mounted into an NMR tube and sample spinner, we could then simply tape up the slot to create a closed environment surrounding the entire length of the perfusion circuit. This environment could be supplied with any required conditions of temperature,
Set screws at 90° and 270°

Socket cap screws to attach mount to magnet top flange

NMR tube

Calibrated mounting flange

Chamfers for easy tube insertion into flange

1.75" O.D. x 0.125" wall acrylic tube

Chamfer at end of tube for engaging spinner without squeezing tube

Bruker widebore spinner or microimaging sample holder

Cross Sectional View

Top View of Mounting Flange
humidity, or oxygen or carbon dioxide tension without exposing the magnet, probe, or room to these conditions. This arrangement has greatly simplified the setup of our bioreactor imaging and spectroscopy experiments, which require a humid, 5% CO2, 37°C environment around the perfusion loop. Finally, the slotted tube by itself makes a great emergency sample insertion and ejection tool when compressed air is unavailable for any reason. This is a much safer and reliable solution than pushing on the sample from below or connecting bottled gas to the spectrometer to run the pneumatics. Clearly, a slotted tube positioner could easily be built to accommodate narrow-bore sample spinners as well as some non-Bruker spinners. Best of all, the whole apparatus can be built for less than $10 in materials!

Please credit this contribution to Rick Spencer's subscription.

Best regards,

Ken Fishbein
Facility Manager, NMR Unit
NIH/NIA/GRC

Richard G.S. Spencer
Chief, NMR Unit
NIH/NIA/GRC

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Acrylic tube

1.75" OD X 0.125" wall acrylic tube with 0.5" wide slot
"NMR Spectroscopy: Modern Spectral Analysis"

by

Ursula Weber and Herbert Thiele

Translated from the German by Jack K. Becconsall


This book actually consists of a book and a CD-ROM. The stated goal of the book is to "(discuss) the strategies needed to efficiently and completely extract NMR parameters from the corresponding spectra." The CD-ROM contains versions of software for NMR spectral analysis, spectral simulation and dynamics calculation as well as all of the examples used to illustrate the lessons from the book. The book discusses general characteristics for analysis of first- and second-order spin systems, the effect of structure on spin-spin coupling, heteronuclear coupling, and time dependent phenomena, including relaxation times, NOEs and exchange effects. The text is liberally illustrated with example spectra, all of which are contained on the CD-ROM. The software is relatively powerful and easy to use, particularly if the reader is familiar with the Bruker suite of NMR software. Despite the many positives that the book includes, I believe that it falls somewhat short of meeting its own extensive goals.

It is obviously intended as a textbook. It starts out by explaining very simple AX spin systems. This would be acceptable for an introductory textbook. Unfortunately Weber and Thiele are not as consistent in their formalisms as they could be. In an effort to expose the student to all the formalisms used by NMR spectroscopists to describe spin systems, they use all of them at one time or another. This ends up by being confusing.

There are literally hundreds of examples used to illustrate the points in the text. What could be a very powerful teaching aid falls somewhat short of the mark. The need to continuously switch back and forth between the book and the PC has the effect of destroying the reader's train of thought. In fact it sometimes seems like the book is actually intended as an instruction manual for the software, rather than the computer examples being used to illustrate the text. Using this book in a formal course setting under the direction of an instructor and taking some period of time to cover the material could obviate some of these problems. Although the book is described as a self-paced, self-teaching text, I have some doubts that it would be very effective in this mode.

There is an enormous amount of information contained in this book. I do not know where I have seen so much information on analysis of spin-spin coupling in a single place. The problem is that the use of examples on computer with text in a book means that it is very difficult to move to a section in the middle of the book and be able to extract useful information. Each section is designed so that it builds on examples introduced and modified in earlier sections. This is an advantage if the book is studied from the beginning but is a problem if the plan is to try to use the book as a reference source.

If used carefully by an instructor in an introductory course on NMR spectroscopy, this book could have significant value. It is not a book I would recommend to an experienced NMR spectroscopist who wishes to become more expert on the analysis and use of NMR spin-spin coupling constants.

David Cochran
Wyeth-Ayerst Research
Princeton, NJ
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650-493-5971* - Please call only between 8:00 am and 10:00 pm, Pacific Coast time.

Deadline Dates

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* Fax: 650-493-1348, at any hour. Do not use fax for technical contributions to the Newsletter, for the received fax quality is very inadequate.

* E-mail: shapiro@nmrnewsletter.com

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Forthcoming NMR Meetings, continued from page 1:

Contact: Profs. Ivano Bentini or Lucia Banci, Chem. Dept., Univ. of Florence, Via G. Capponi 7, I-50121, Florence, Italy; Phone: +39-055-2757600; Email: icmrbs@irm.fi.cnr.it; Fax: +39-055-2756755; http://www.irm.fi.cnr.it//icmrbs.html.

Royal Society of Chemistry: 15th International Meeting on NMR Spectroscopy, Durham, England, week of July 8-13, 2001; Contact: Mrs. Paula Whelan, The Royal Society of Chemistry, Burlington House, London W1V 0BN, England; +44 0171 440 3316; Email: conferences@rsc.org.

Additional listings of meetings, etc., are invited.
The **Eclipse+** NMR Spectrometer can be operated anywhere there is a computer on the local network. The **Single Window Automation** pictured above can be used with a single mouse click to select the sample from the auto-sample changer, gradient shim on any probe, run the selected experiment, and plot the data on any network postscript printer. Need more data, click another button and the **Eclipse+** is off to do your work - and you have not left your office. Contact us at nmr@jeol.com or visit our web site at www.jeol.com.