TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 431

August 1994

Continued on inside back cover

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Resolution: 0.1Hz-100KHz (opt)
Switching: 1-20μs

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Spurious Outputs: – 70dBc
Phase Noise: – 63dBc (0.5Hz-15KHz)

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Range: 1-620 MHz
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Switching: 1-20μs

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Spurious Outputs: – 70dBc
Phase Noise: – 63dBc (0.5Hz-15KHz)

Freq. St'd: OCXO, TCXO, Ext.
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Switching: 5-10μs

Output: +3 to +13dBm; 50ohm
Spurious Outputs: – 70dBc (0.1-500 MHz), – 65dBc (500-1000 MHz)
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Switching: 1-5μs
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Spurious Outputs: – 65/ – 60dBc (typ/spec)
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FORTHCOMING NMR MEETINGS

Ampere Summer School on Magnetic Resonance with Spatial Resolution, Eichstätt, Bavaria, Germany, **September 2 - 8, 1994**; Contact: L. D. Hall or B. Blümich - See TAMU NMR Newsletter 426, 56.

FACSS XXI (21st Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies, St. Louis, Missouri, **October 2 - 7, 1994**; Held jointly with the MMRS-5 meeting *(v.i.)*. Contact: FACSS National Office, 198 Thomas Johnson Drive, Suite S-2, Frederick, MD 21702-4317; Phone: (301) 846-4797. See TAMU NMR Newsletter 428, 28.

5th Missouri Magnetic Resonance Symposium, St. Louis, Missouri, **October 5 - 6, 1994**; Held jointly with the FACSS meeting *(v.s.)*. Contact: FACSS Natl. Office, 198 Thomas Johnson Dr., Suite S-2, Frederick, MD 21702-4317; Phone: (301) 846-4797. See TAMU NMR Newsletter 428, 28.

Symposium on "NMR as a Structural Tool for Macromolecules: Current Status and Future Directions, Indianapolis, IN, **October 30 - November 1, 1994**; Contact: Ms. Padmini Nallana, Coordinator, NMR Symposium, Dept. of Physics, Indiana University Purdue University Indianapolis, 402 N. Blackford St., Indianapolis, IN 46202-3273; Tel. (317) 278-1263; E-mail: PADMINI@INDYVAX.IUPUI.EDU; Fax: (3172) 274-2393. See TAMU NMR Newsletter 425, 31.

36th ENC (Experimental NMR Conference), Boston, MA, **March 26 - 30, 1995**; Contact: ENC, 815 Don Gaspar, Santa Fe, NM 87501; (505) 989-4573; Fax: (505)989-1073

Keystone Symposia on Molecular and Cellular Biology, Frontiers of NMR in Molecular Biology - IV, Keystone, Colorado, **April 3 - 9, 1995**; Organizers: S. W. Fesik, T. L. James, and G. Wagner; Contact: Keystone Symposia, Drawer 1630, Silverthorne, CO 80498; Phone: (303) 262-1230; Fax.: (303) 262-1525..

12th International Meeting on NMR Spectroscopy, Sponsored by the Royal Society of Chemistry, Manchester, England, **July 2 - 7, 1995** [sic]; Contact: Dr. J. F. Gibson or Ms. G. B. Howlett - See TAMU NMR Newsletter 415, 5; Phone: (44-71) 437-8656; Fax: (44-71) 437-8883.

ISMAR 1995, Sydney, NSW, Australia, **July 16-21, 1995**; Contact: Dr. Les. Field, Dept. of Organic Chemistry, Univ. of Sydney, Sydney, NSW 2006, Australia. Phone: +61-2-692-2060; Fax: +61-2-692-3329; Email: ismar-95@biochem.su.oz.au Also, see TAMU NMR Newsletter 419, 26.

ZENECA

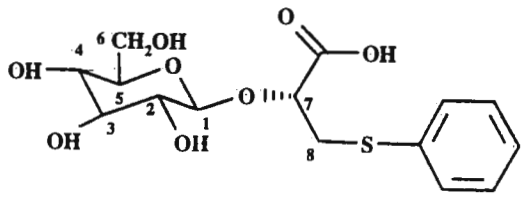
Dr. B.L. Shapiro, Editor
T.A.M.U. Newsletter
966 Elsinor Court
Palo Alto, CA 94303

(received 7/14/94)

Re: Chemical Shift Assignments of a Glucopyranoside

Dear Barry,

We recently have been interested in determining the anomeric configuration of a glucopyranoside, as well as the absolute configuration of the aglycone. The glucopyranoside of interest is a metabolic product of a commercial compound of ours. The name of the metabolic product is 2-(ß-D-glucopyranosyloxy)-3-(phenylthio)propanoic acid,(R) and the following is its structure:



During the synthesis of this compound it was necessary to also synthesize the other remaining isomers i.e, the ß-(S), the α-(R) and the α-(S). We have collected NMR data on all these isomers and in addition, their protected acetyl derivatives. A full paper is being written. The NMR data for the above structure are presented in the table below. The ^{1}H NMR assignments were accomplished mainly by coupling constants and 1D TOCSY experiments. The ^{13}C chemical shifts were determined by a 2D HETCOR experiment.

H1	H2	H3	H4	H5	H6	H6'	H7	H8	H8'	A	A	A
4.32	3.24	3.31*	3.39*	3.25	3.75	3.61	4.27	3.24	3.18	7.23	7.28	7.40
C1	C2	C3	C4	C5	C6	C7	C8	C=O	IPS	O	M	P
104.5	75.8	78.5*	72.0	78.3*	63.3	81.3	39.5	179.9	137.4	132.4	131.8	129.4

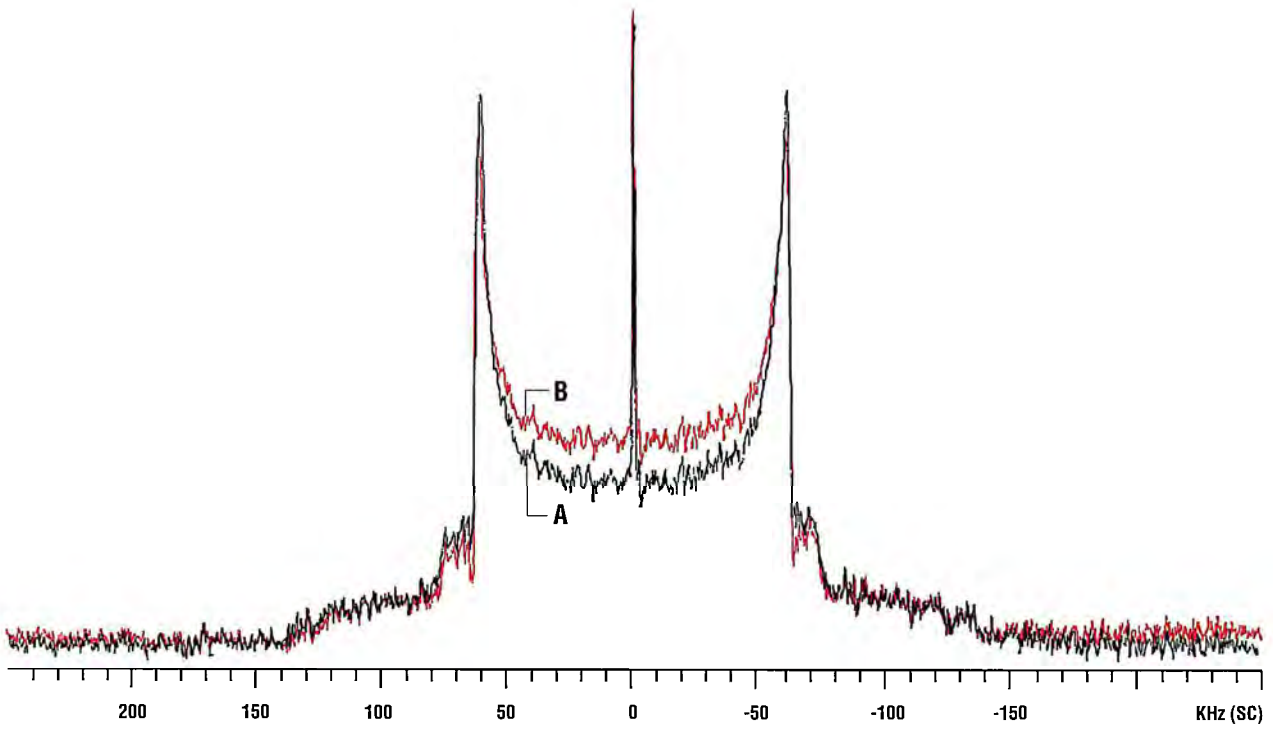
*may be reversed.

Barry, please change the name on the subscription to Dr. Lydia L. Chang. Thank you.

Sincerely,

Joseph R. Snyder Donald J. Bowler Nancy Kerlinger Bryan Eya

Digital Signal Processing for Wideline Applications



*Wideline spectra of malonic acid-d_4, acquired using a Wideline•nmr probe and a UNITY*plus *400 system, demonstrating the effect of data sampling rates on wideline bandshapes. The data were acquired at 5 MHz, left shifted to the echo maximum provided by a) 5 MHz sampling rate and b) 2 MHz sampling rate, downsampled and digitally filtered to a 500 kHz spectral width.*

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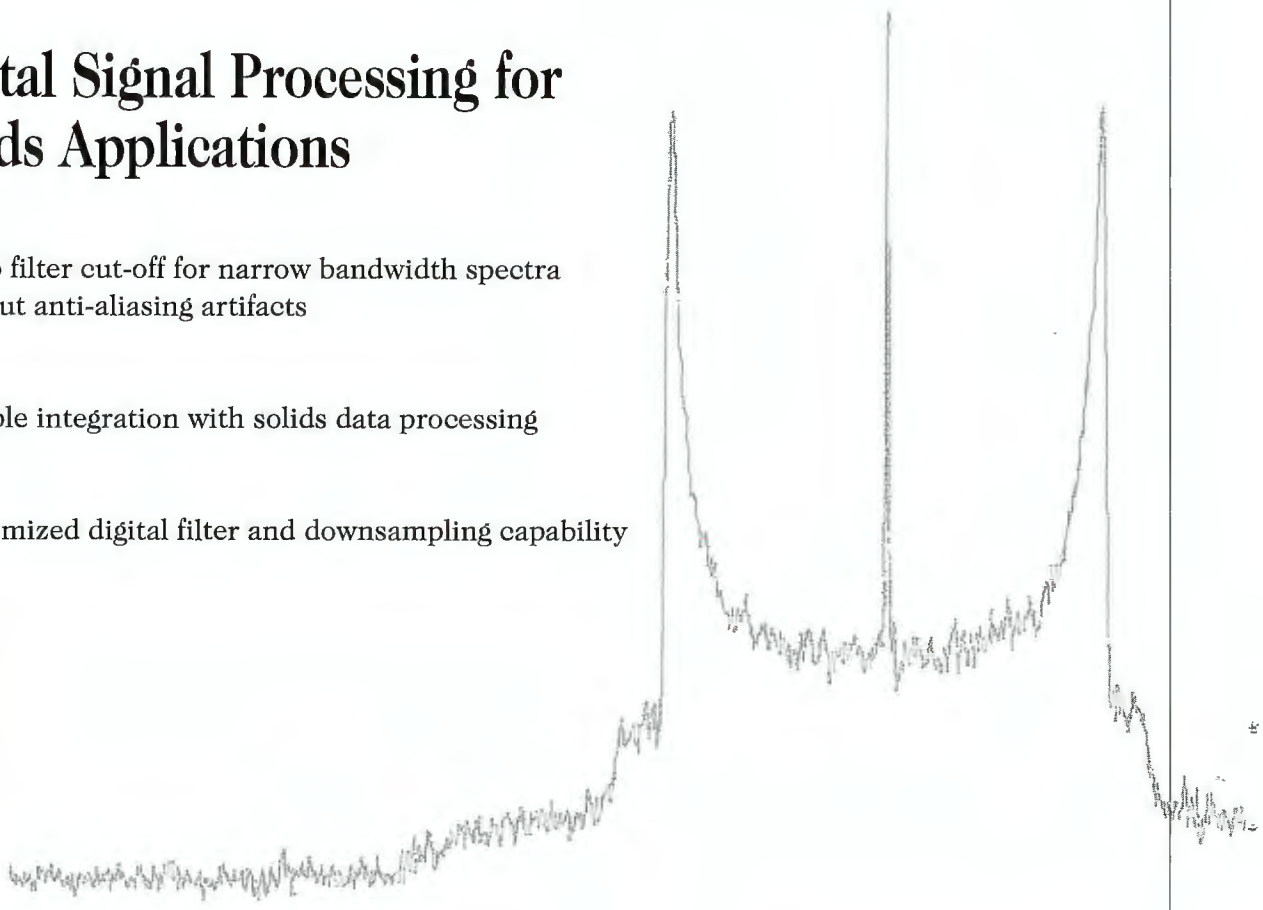

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July 16, 1994 (received 7/21/94)

Professor Bernard Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303
U.S.A.

"Helix-sense Inversion in Poly(β-*n*-propyl L-aspartate)"

Dear Professor Shapiro,

Poly(L-aspartates) take on various conformations in solution as well as in solid, depending on the temperature, the solvent, and the intrinsic properties of the different ester side chains. We investigated the temperature dependence of the NMR spectra of poly(β-*n*-propyl L-aspartate) (PnPLA) in $CDCl_3$, in which PnPLA forms an α-helical conformation. ^{13}C spectra of PnPLA show broad resonances, due to the slow-tumbling motion and the molecular aggregation for rod-like molecules, as shown in Figure 1. The main resonances at 27°C are characteristic of the right-handed α-helical conformation (R), and, on the other hand, minor resonances are characteristic of the left-handed α-helical conformation (L). With increasing temperature the intensities of the latter grow up while those of the former decrease. This shows the thermally induced helix-sense transition from the right-handed to the left-handed α-helical conformation. The mid-point is about 50°C. All the chemical shifts for both conformations are different, showing that the main chain conformation affects on the longer side chain conformation. T_1 and T_2 are different between both conformations, suggesting that the molecule in the left-handed helix is more mobile than that in the right-handed helix. The quantitative analysis of the relaxation times is in progress.

Sincerely,

T. Hiraoki

Toshifumi Hiraoki

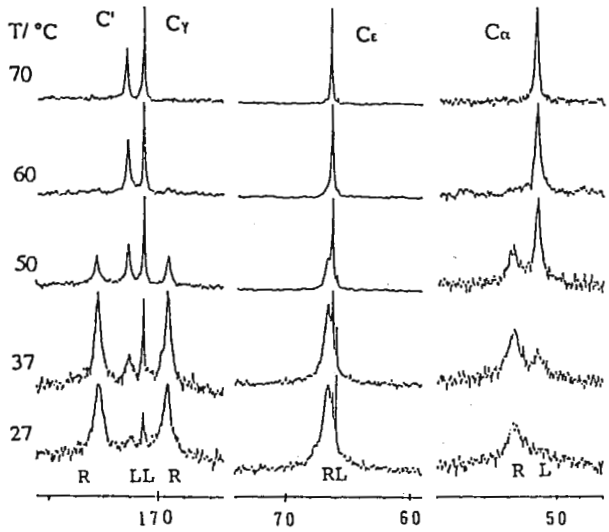

Fig. 1. Temperature dependence of ^{13}C NMR spectra of PnPLA in $CDCl_3$.

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Centre RMN, bât. 308
43, boulevard du 11 novembre 1918
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To : Dr. B. L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303
(received 7/13/94)
July 4, 1994

HSQC WITH MULTISITE PROTON HOMODECOUPLING

Professor Shapiro,

In the field of high resolution NMR, homo decoupling is yet largely used for attribution of the protons of small organic compounds when only a few number of irradiation is necessary. For more complex problems, the use of 2D homo and hetero nuclear experiments with pulsed gradients is a faster and more efficient approach. In some cases, it is of great interest to combine the two techniques.

Considering a compound containing several ABMX spin systems where all the AB parts of the ^1H spectrum are concentrated in a small region but all carbons are resolved. Because of overlapping, it may be impossible to evaluate the coupling constants of the AB part. In this case, a high resolution 2D HSQC focused on the corresponding carbon region allows to visualize each AB parts of the ^1H spectrum. Moreover, if the acquisition is done without carbon decoupling, the AB systems become AX systems. As a matter of fact, the ^1H_A-$^{13}C_A$ doublet with $^1J_{CH}$ is nearby a ^1H_B-$^{12}C_A$ which is a singulet roughly situated at the center of the doublet. The second order effect is very attenuated and vanishes out in practice. For one carbon, with the simultaneous homo decoupling of H_M, H_X, the 2D HSQC exhibits a doublet ($^1J_{CAHA}$) of doublets ($^1J_{HA\text{-}HB}$) which allows a very precise measurement of the coupling constant between H_A and H_B.

This technique can be implemented on new spectrometers in two different ways.

The first one, requires as much RF channels as protons to be decoupled. It is the easiest way, but the number of channels available on the spectrometer limits the number of homo decoupling positions. This experiment has been run on a DMX 500 of the BRUKER Application Laboratory of Wissembourg (FRANCE) equipped with 4 channels. One channel was used for ^{13}C, the three others for ^1H homo decoupling and observation.

The second way uses the shifted pulses technique. It requires only 2 channels if the excitation and the demodulation frequencies are available at the same time, and one waveform generator (amplitude and phase modulation). After the carrier frequency has been set, the relative decoupling frequencies are determined. A composite signal containing all these frequencies is generated, stored in the waveform generator, and used to modulate the transmitter during the decoupling process. To avoid cross talking between the homo decoupler and the receiver, the two process have to be synchronized and done in time sharing. This experiment has been run on a UNITY Plus 500 of the VARIAN Application Lab of Darmstadt (GERMANY).

Both techniques give very nice results and their choice will mainly depend on spectrometer configuration.

We thank Marcial PIOTOT (BRUKER) and Peter SANDOR (VARIAN) who spent time to implement these experiments on their spectrometers during and after our visit in their laboratories.

B. FENET

J.M. VATELE *

* Laboratoire de Chimie Organique I, URA 467 CNRS
Please, credit this contribution to the "Laboratoire de Resonance Magnetique Nucleaire" (Pr A. BRIGUET)

FIRST CUSTOMER INSTALLATION OF AN *AVANCE™* DMX 750 IN JAPAN

In March 1994, Bruker Japan delivered the first 750 MHz NMR spectrometer in Japan in the laboratory of Dr. Katsura at the National Institute of Agrobiological Resources in Tsukuba. We are looking forward to exploring the research capabilities and benefits of this new technology together with the leading high-field NMR scientists in Japan.

The first 750 MHz NMR system installed successfully in a customer's laboratory in Japan is an *AVANCE™* DMX 750, incorporating a superstabilized, cooled 750 MHz 54 mm superconducting magnet built by Bruker. In a previous application note, entitled *750 MHz NMR Spectroscopy at Bruker: RESULTS IN THE FIRST YEAR*, dated February 1994, we have described the data quality which was obtained in Bruker's own laboratory. However, successful customer installations clearly are more meaningful as a "yardstick" to measure the success and impact on NMR research of this new high-field NMR technology.

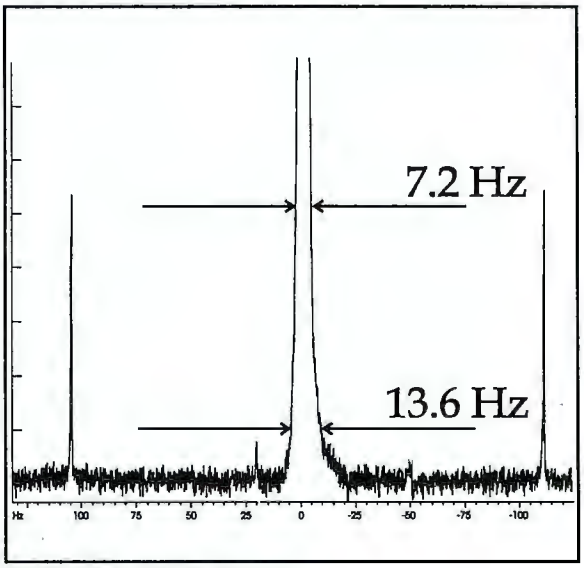


Figure 1: non-spinning lineshape;
5 mm GRASP II broadband inverse probe

The drift, homogeneity and short-term stability of the superstabilized, cooled magnet design is evident from certain key numbers: The ***drift*** has come down below 3 Hz/hr, 4 weeks after energization and cryoshimming. The ***homogeneity*** is demonstrated by the non-spinning lineshape on *all* four 5 mm water suppression probes (proton-only, GRASP II broadband inverse, GRASP II triple-resonance, and GRASP III broadband triple-resonance) well within 8/16 Hz.

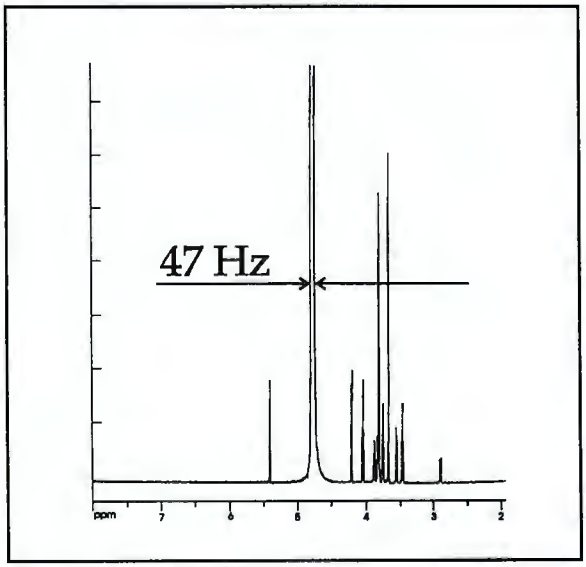
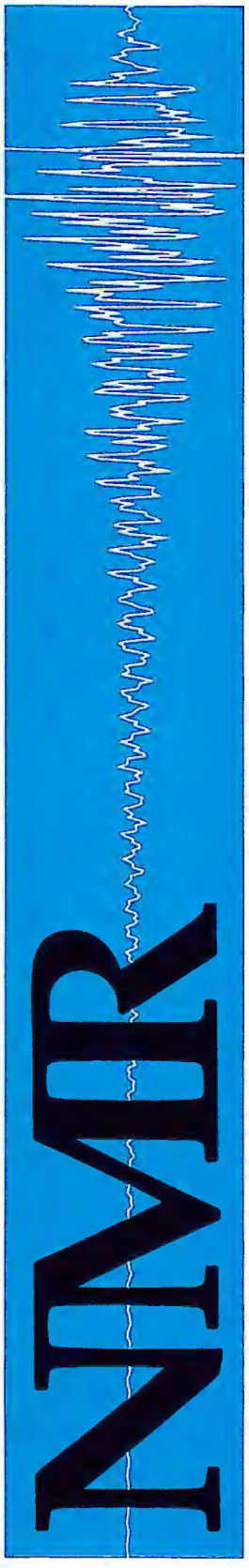


Figure 2: water suppression test;
5 mm GRASP III broadband triple-resonance probe



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Similarly, the magnet passed the <0.25 Hz ODCB resolution test (Fig. 3). Presaturation water suppression tests on 2 mM sucrose exhibited linewidths well below the specification of 100 Hz at 50% of the DDS signal (Fig.2). The first increment of a presat-NOESY on 2 mM lysozyme in 90% H_2O showed a very narrow water peak (Fig. 4). The two-scan spin-echo difference test on 3% chloroform was passed easily, evidencing the outstanding ***short-term stability*** of this superstabilized magnet technology.

The new *AVANCE*™ DMX 750 spectrometer with "on the fly" real-time oversampling and digital filtering, a digital lock, and real-time 3-channel gradient calculations, also features some of Bruker's latest preamplifier, probe and gradient designs: the latest generation of 750 MHz preamplifiers and probes yield very high sensitivity (Fig. 5). GRASP III probes with 3 gradients each >35 G/cm are available on 5 mm 750 MHz probes (Fig. 2 and 6). Finally, Bruker's innovative 5 mm broadband triple-resonance inverse probe (Fig. 2 and 6) provides significant additional flexibility for various triple-resonance applications on the same probe, such as for instance $^{1}H/\{^{13}C/^{15}N\}$, $^{1}H/\{^{13}C/^{31}P\}$, etc. while retaining excellent short pulse widths and sensitivities for each nucleus.

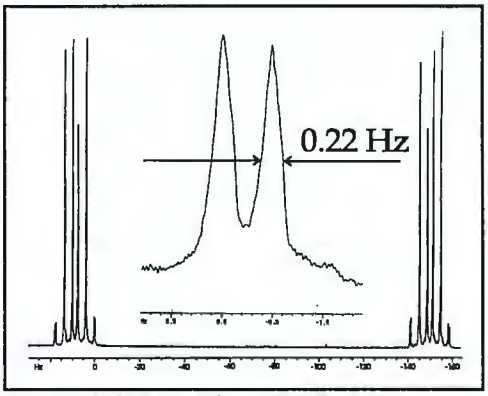

Figure 3: ODCB resolution <0.25 Hz;
5 mm proton probe

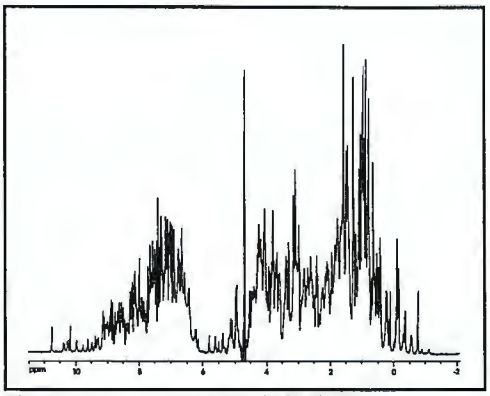

Figure 4: 1D presat NOESY in 90% H_2O;
5 mm GRASP II broadband inverse probe

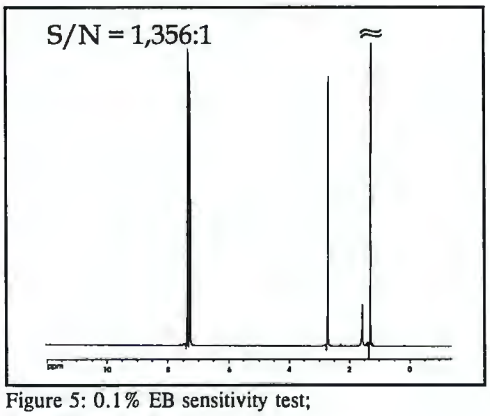

Figure 5: 0.1% EB sensitivity test;
5 mm proton probe

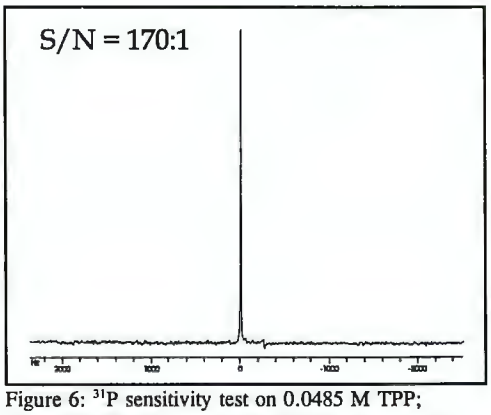

Figure 6: ^{31}P sensitivity test on 0.0485 M TPP;
5 mm GRASP III broadband triple-inverse probe

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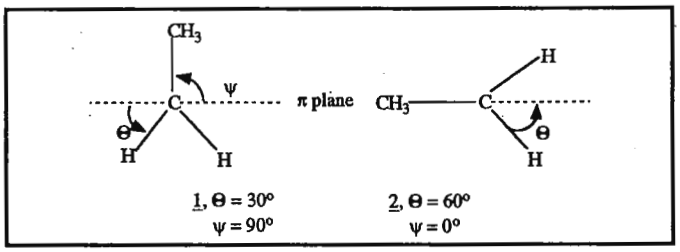
June 23, 1994
(received 6/29/94)

B.L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA. 94303

Dear Barry,

ETHYLBENZENE ONCE MORE

For such a simple molecule, there exists an amazing variety of theoretical and experimental estimates of the shape and magnitude of the barrier to rotation about the Csp^2-Csp^3 bond. The height of the barrier appears to lie somewhere between 4.2 and 9.2 kJ/mol; the potential is probably mainly twofold in nature, with perhaps a minor fourfold component. All but one of the investigations agree that 1 lies at the potential minimum, 2 at the maximum; that one, for the 3,5-dibromo derivative, has Ψ as 60° for the minimum.



As any avid reader of the literature no doubt knows, long-range, σ-π electron mediated spin-spin coupling constants between sidechain and para ring nuclei display a simple dependence on θ and Ψ; in consequence, their measurement yields expectation values of $\sin^2\theta$ and $\sin^2\Psi$. The latter are directly related to the internal potential barrier. Complete analyses of the ^1H nmr spectra of ethylbenzene and its β-^{13}C derivative, together with ^{13}C, ^{13}C splittings, yield such expectation values. Our conclusions are, a) if the internal potential is purely twofold and 1 sits at the minimum, then the magnitude is 5.0 kJ/mol and is solvent - independent; b) if the minimum in the potential occurs at Ψ = 60°, then the twofold height is 22.6 kJ/mol; c) if a significant fourfold component exists, then one has V_2/V_4 as 4.9 ± 0.7/0.9. There exist fairly high-level MO computations which imply that b) is unreasonable and that c) is somewhat favored over a).

Other, indirect, methods in theis laboratory suggest, furthermore, that the maximum hyperconjugative contribution to the barrier is 1.2 ± 0.3 kJ/mol and that, energetically, C-C is larger than C-H hyperconjugation. All these things are discussed in detail in Can. J. Chem. later this year; early preprints are available.

We here in the Canadian midwest, out from under the snowdrifts at this time of year, never cease to be amused, mystified and sometimes frightened, by the extraordinary behaviour in your part of the continent. Is it catching?

Stay well.

Yours sincerely,

Ted Schaefer

TS/tl

431-10

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Skokie, Illinois 60077
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June 22, 1994
(received 6/27/94)

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

THREE FOLD SENSITIVITY INCREASE FOR CARBON-13 SPECTRA USING A MICROTUBE

Dear Barry:

SEARLE

Recently, I have evaluated the potential of increased 13C sensitivity using a symmetrical NMR microtube. The unique feature of that microtube is that it is made of a special glass which has a magnetic susceptibility that matches that of water. In a TAMU private communication dated May 20, 1994, I showed the 13C spectrum of a 400 µg sucrose sample in D2O using a SHIGEMI BMS-005V microtube. Since then I have tested this microtube for Proton NMR with a sample of chloroform, using our VXR-400 NMR spectrometer. The difference in the magnetic susceptibility of chloroform and that of the glass of the microtube caused line-shape distortions that were unacceptable for most Proton NMR studies.

Since the criteria for 13C NMR is primaririly centered on sensitivity, I decided to explore the use of this microtube for 13C using a sample in chloroform. An 11 mg sample of an available steroid in 220 µl CDCl3 in the microtube was compared with an 11 mg sample of the same material using the usual 700 µl of CDCl3 in a standard 5 mm sample tube. The molar concentration in the microtube is a factor of 3.18 greater, and all of the sample is contained within the volume of the probe coil. Also, there is no loss in filling factor due to this tube.

For each sample, the data was collected in 30 minutes using 900 pulses with identical parameters with our VXR-500 NMR spectrometer. Only Z1, Z2, and Z3 shims were adjusted. The Z1 shim required the largest change, but this change was only 12.5 percent of the available adjustment range.

The S:N of the 13C NMR spectrum from the sample in the microtube was 3.05 times greater than the S:N from the sample in the standard sample tube.

Sincerely,

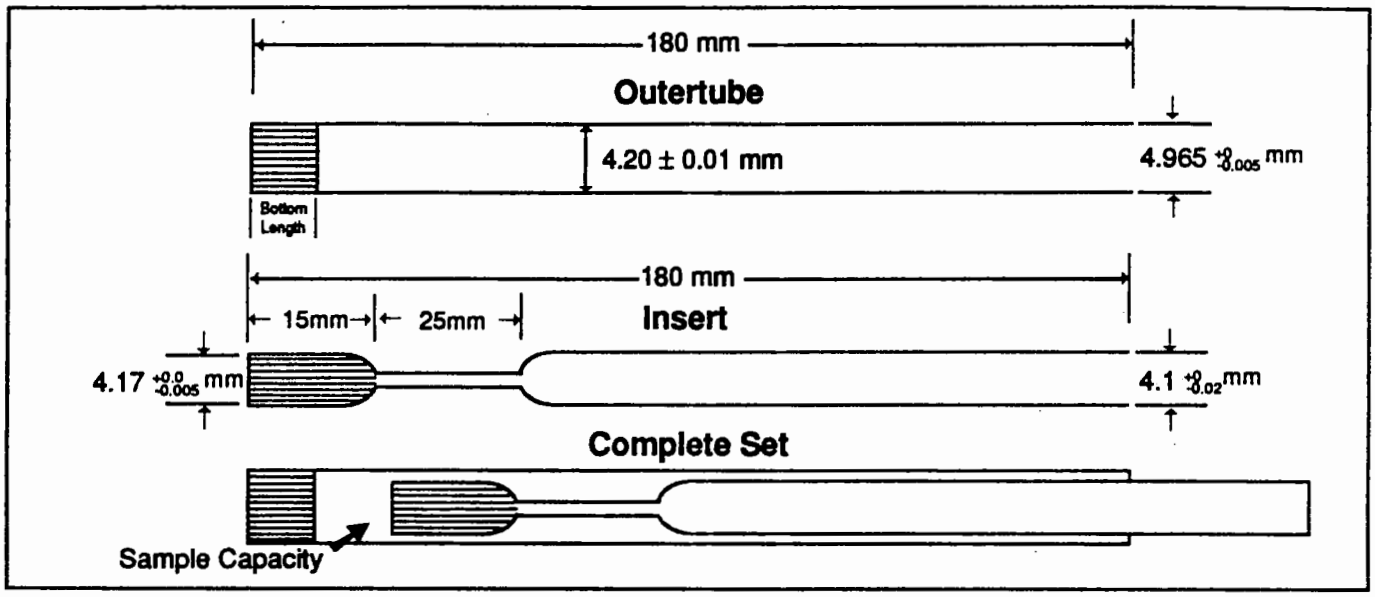
Robert W. Dykstra

Specially designed

SYMMETRICAL NMR MICROTUBES

for Aqueous samples

This unique NMR microtube is made of a special type of hard glass which has an excellent chemical durability and **a magnetic susceptibility which matches that of D_2O.** Therefore, the best resolution of a sample can be obtained in a D_2O or H_2O solution.



SHIGEMI SYMMETRICAL 5mm NMR MICROTUBE SYSTEM

Complete Set	Insert length (mm)	Insert ID (mm)	Insert OD (mm)	Outertube length (mm)	Outertube ID (mm)	Outertube OD (mm)	Bottom* length (mm)
BMS-005B	180	2.6	4.1	180	4.2	4.965	8
BMS-005V	180	2.6	4.1	180	4.2	4.965	15

***For best results, choose the one that matched your probe coil height most closely.**

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Shigemi's high precision thin wall NMR sample tube has a unique construction. The wall thickness of this particular tube is reduced only around the position of the detection coil. The result of this new invention allows an increase in the sample volume and higher sensitivity without sacrificing its mechanical strength. Therefore, there is no need for special handling during routine usage of our Shigemi NMR tubes.

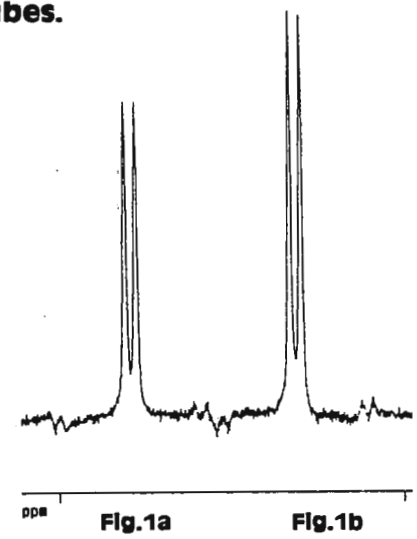
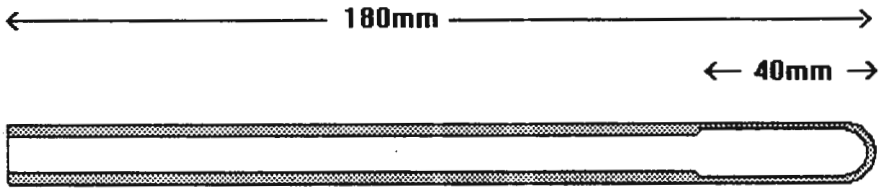
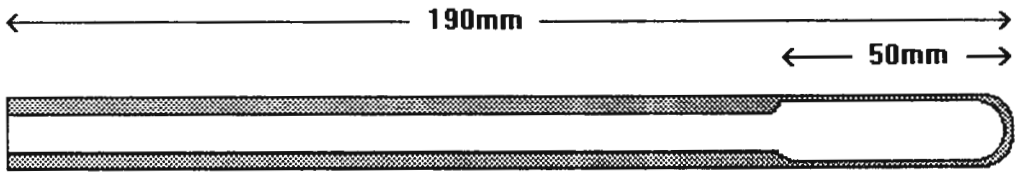


Fig.1a Fig.1b

The spectra of 20mm sucrose in D_2O were obtained with a single scan without apodization prior to Fourier transformation on a Bruker AMX-600 spectrometer at 298 K. By using Shigemi high quality 5mm standard tube (Fig.1a) and the Shigemi highly sensitive thin wall 5mm tube (Fig.1b), the spectra confirms a sensitivity enhancement of about 10%.



PST-001 and PST-002



ST8-001,ST8-002, ST10-001, and ST10-002

O.D. (mm)	Product Number	Wall (mm)	Concen-tricity/Camber (μ)	OD (mm)	ID (mm)	Price Each 1-99	Price Each 100+
5	PST-001	0.21	20/ 8	4.96 + 0.00 - 0.01	4.54 ± 0.01	$15.00	$13.50
	PST-002	0.21	40/15	4.96 + 0.00 - 0.01	4.54 ± 0.01	$13.00	$12.00
8	ST8-001	0.25	40/ 8	8.00 + 0.00 - 0.01	7.52 ± 0.01	$31.00	$28.00
	ST8-002	0.25	50/15	8.00 + 0.00 - 0.01	7.52 ± 0.01	$27.00	$25.00
10	ST10-001	0.25	40/ 8	9.98 + 0.00 - 0.01	9.52 ± 0.01	$36.00	$32.00
	ST10-002	0.25	50/15	9.98 + 0.00 - 0.01	9.52 ± 0.01	$32.00	$28.00

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Acorn NMR

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Fremont CA 94538-6491
Telephone: (510) 683-8595
FAX: (510) 683-6784

Re: A cure for our Achilles' heel

July 8, 1994

Dear Barry,

The weak link in keeping our vintage NT360 alive and functioning (and generating revenue) has always been its CDC Phoenix disk drive. Repairs following a head crash 3 years ago cost us about $1,500 and a week of down time. Aside from its tempermentality, the drive is very noisy, requires regular maintenance such as filter changes and is extremely difficult to work on due to its size. The idea of a disk drive which measures 30"x18"x10", weighs nearly 200 lb. and holds a whopping 32 Mbytes seems ludicrous given today's technology.

After 3 years of essentially constant use, we figured we were running on borrowed time. Sure enough, about a month ago, the lab was filled with that stomach-churning, screeching sound and distinctive burning smell. We were reluctant to shell out the estimated $2K to fix it, with the certainty of a repeat performance down the road, so explored alternatives.

One option is a replacement which uses solid state memory with either tape or disk back-up, available fom Vermont Research Corp. (802-886-2256). This can replace CDC Phoenix, CDC Hawk and Diablo drives, among others.

We chose a different option which was less expensive. It consists of a PC-type ESDI disk drive and a PC board with the "smarts" to fool the computer on the other end of the cables into thinking it is an SMD drive. The disk substitute simply plugs in using the same cables.

We ran SMDbuster on the 1280 to map out the new drive, then transferred the NMR programs onto it from a floppy. *Voilà*, up and running in a few hours. We now have a 200 Mbyte drive which needs no maintenance, isn't prone to head crashes, fits into a 19" rack, is blessedly QUIET and doesn't require Arnold Schwartzenegger to lift it. It's been in use for a month without a hitch.

We got our disk replacement from:

Magnetic Resonance Services, Inc.
(512) 388-7355
(512) 388-7356 FAX

Gina

Woody

Gina Miner

Woodrow W. Conover

P.S. Anyone interested in a Phoenix or Hawk drive in need of repair?

Oklahoma State University

COLLEGE OF ARTS AND SCIENCES

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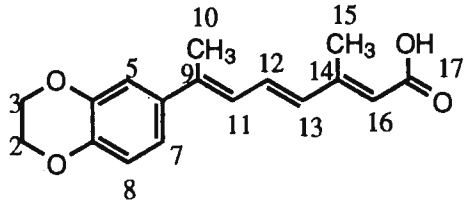
405-744-5920
FAX 405-744-6007

Dr. B. L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CALIFORNIA 94303

July 1, 1994
(received 7/11/94)

Dear Barry:

As our contribution to the newsletter, please accept the following. It is not often that one can assign with some confidence *most*, but not all, of the proton signals in a polyene chain in retinoid mimics as shown below. The values are:



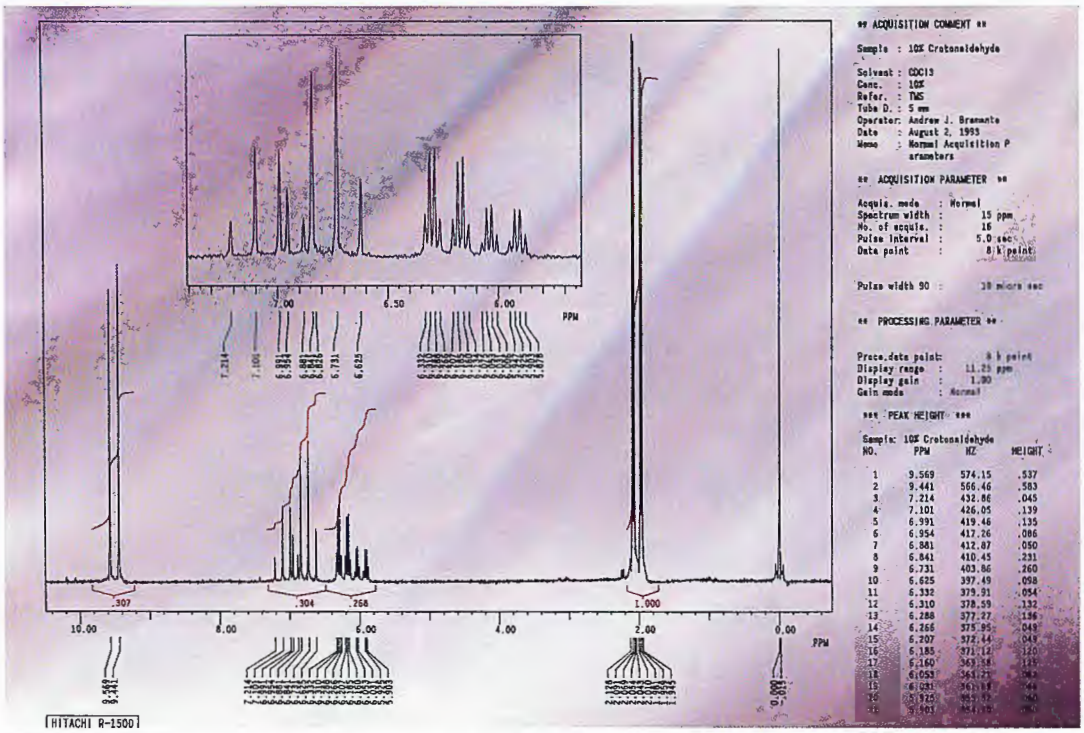
Position	^{1}H Shift (δ)	Position	^{1}H Shift (δ)
H(2,3)	bs, 4.27	H(11)	d, 6.53
H(5)	m, 6.83-7.09	H(12)	m, 6.83-7.09
H(7)	m, 6.83-7.09	H(13)	d, 6.38
H(8)	m, 6.83-7.09	H(15)	s, 2.39
H(10)	s, 2.21	H(16)	bs, 5.83

The resolution at 399.99 MHz was simply not adequate to "pull out" the signals for H(12) from those of H(5,7,8). The assignments shown are based upon comparisons with the spectra from simple relatives.

We trust this will serve as our contribution to the Newsletter. Best regards.

Sincerely yours

K. Darrell Berlin
Regents Professor



This R-1500 FT-NMR spectrum of crotonaldehyde represents a 16 pulse acquisition; each pulse was 10 µsec with a pulse interval of 5 seconds.

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CITY: _____ STATE: _____ ZIP: _____

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IF YES, PLEASE LIST MANUFACTURER AND MODEL: _____

APPLICATION(S): _____

ARE YOU CONSIDERING AN NMR SPECTROMETER FOR PURCHASE? YES ❑ NO ❑

IF YES, AT WHAT FIELD STRENGTH? _____

IF YES, WHEN DO YOU NEED IT? _____

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Prof. Dr. B.L. Shapiro
966 Elsinore Court
Palo Alto
CA 94303
U.S.A.

Nijmegen, july 18 1994
(received 7/25/94)

Dear Prof. Shapiro,

Through-Bond Sequential Backbone Assignment in ^{13}C Labeled RNA.

Multi-dimensional triple resonance experiments have revolutionized the structure determination of isotope labeled proteins by NMR. Of particular importance is the sequential backbone assignment developed by Bax and coworkers based on through-bond instead of through-space interactions. The former do not suffer from the inability to distinguish inter- and intra-residue interactions.

The recent advent of biochemical enrichment techniques for RNAs, allows to develop such methods for RNAs as well. In this vain we have recently demonstrated (1,2) a three-dimensional triple-resonance experiment, termed HCP, which allows sequential backbone assignment in ^{13}C labeled RNAs based through-bond interactions. To fully use the higher resolution in the H1' part of the proton spectrum we have developed (3) an off-spring of the HCP experiment, termed P(CC)HTOCSY, which also allows to make a complete sequential walk along RNA backbone, but now in the well resolved H1' region the resulting two-dimensional ^{1}H-^{31}P spectrum. In the pulse sequence (Fig. 1) coherence is transferred from ^{31}P via ^{13}C to H1' in three steps. First a refocussed-INEPT transfers coherence from P_i to C2', C3', and C4' of residue i-1 and to C5' and C4' of residue i. Thus connecting the residues along the RNA backbone. This transfer step is quite efficient since it is governed by the ≈ 10 Hz $J_{PC4'}$ -couplings. Subsequently, the ^{13}C coherence is transported through the system of J-coupled ^{13}C spins of the ribose ring (J_{CC} ≈ 10 Hz) via DIPSY mixing on ^{13}C to C1', after which the transfer to H1' is realized via J-cross-polarisation (J_{HC} ≈ 150 Hz). The sequence is demonstrated on a ^{13}C labeled RNA hairpin (1mM). The experiment is quite sensitive since the resulting ^{1}H-^{31}P spectrum (Fig. 2) could be recorded with good signal to noise in only 12 hours. As can be seen (Fig. 2) a complete sequential walk can be made from the first residue G1 through the sequence including the tetraloop to the final residue U12.

In summary, the P(CC)HTOCSY is a simple and efficient two-dimensional triple resonance NMR experiment which allows unambiguous sequential backbone assignment of the H1' and ^{31}P resonances in ^{13}C-labeled RNA oligonucleotides.

1). Heus, H.A., Wijmenga, S.S., van de Ven, F.J.M. and Hilbers, C.W. (1994) *J. Am. Chem. Soc.*, **116**, 4983-4984; 2). Wijmenga, S.S., Heus, H.A., van de Ven, F.J.M. and Hilbers, C.W. (1994a) *NMR of Biological Macromolecules* (NATO ASI Creta, ed.: Stassinopoulou, C.I., Springer Verlag:

Berlin) in press; 3. Wijmenga, S.S., Heus, H.A., Leeuw, H.A.E., Hoppe, H., van der Graaf, M., and Hilbers, C.W. (1994) *J. Biomol. NMR*, to be published.

Fig. 1

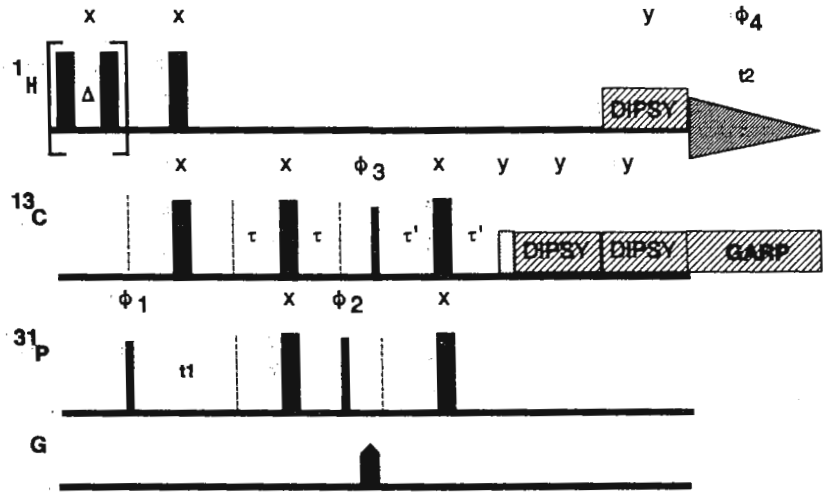
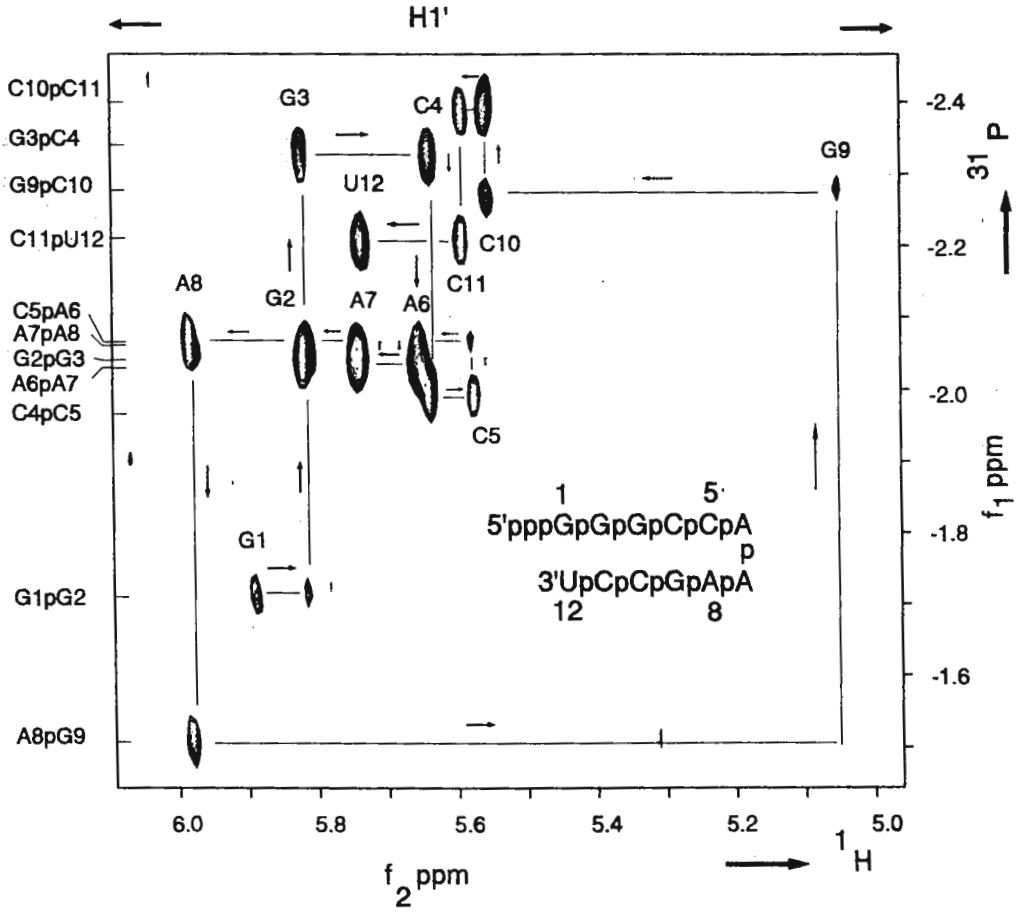


Fig. 2



Sincerely yours,

Sybren Wijmenga Hans Heus Cees Hilbers

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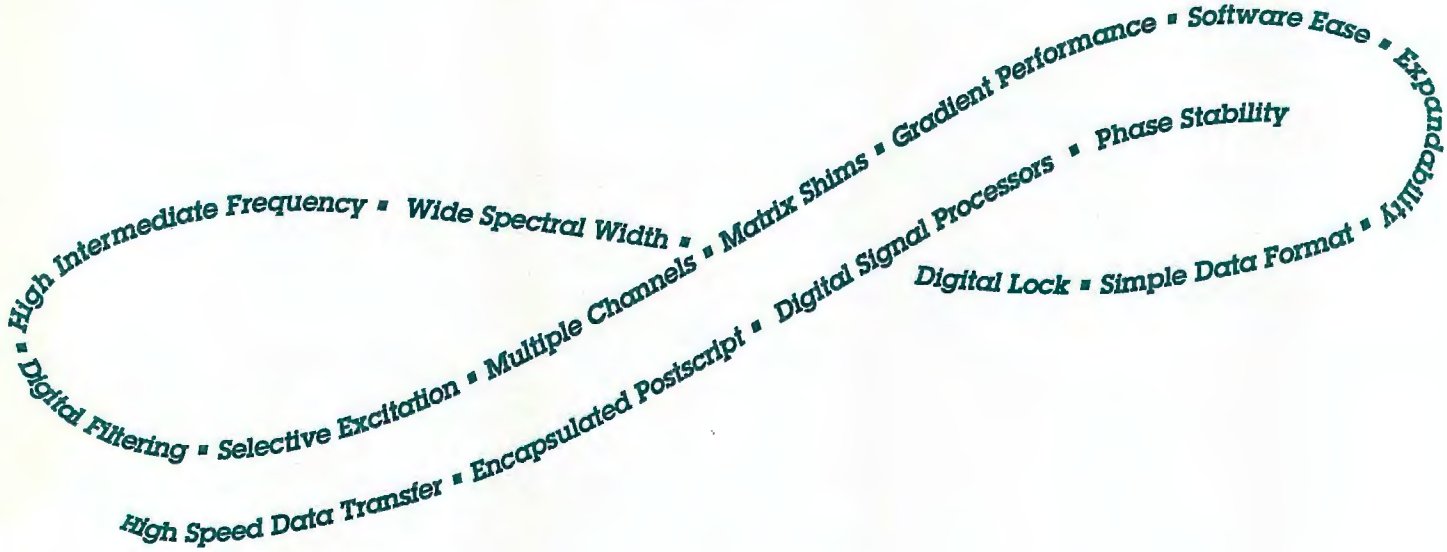

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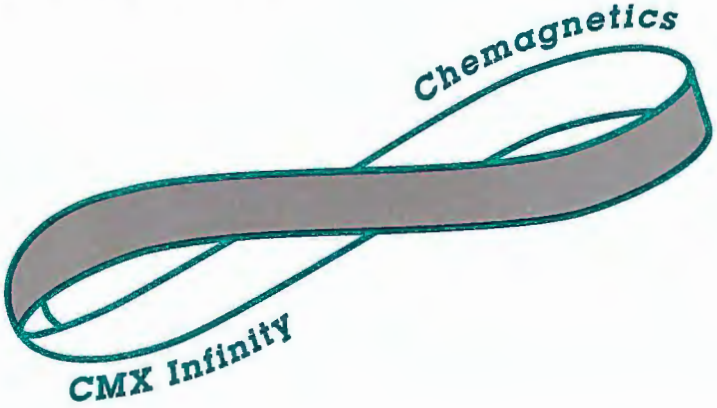

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Fax-Nr. (089)3209-3473
June 28, 1994
(received 7/7/94)

Dr. B. L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303
USA

"Socks" for Broad NMR Signals

Dear Dr. Shapiro,

the ususal application of solenoidal probeheads lies in the field of solid-state NMR (wideline NMR of powders with high power operation). In this letter we want to show, that the beneficial characteristics of solenoidal probes can also be used for measurements of liquid and especially paramagnetic samples. The main advantages of solenoidal probeheads are:

1. They display short ring-down delays with a maximum of 10 μs. This is extremely important for paramagnetic samples, since they give broad signals due to short T_2 and T_1 (with $T_1 \approx T_2$) values. The latter exclude the application of Quadrupolar-Echo techniques; even with τ delays of 30 μs too much of the initial FID is lost, leading to poor signal intensity and problems with first order phase correction. On the other hand, the small T_1 values allow a pulse repetitition time of ca. 100 ms.
2. 90 ° pulses as short as 2 to 4 μs are a prerequisite for quantitative measurements of paramagnetic species, whose ^{13}C spectral range, for example, spans from about +1500 to -800 ppm [1,2]
3. Solenoidal probeheads provide a signal-to-noise ratio that is about a factor of three better than the one obtainable with a saddle-coil arrangement [3]. Additionally, the sensitivity is improved, because every frequency range has its own insert. Optimal S/N is especially important for dilute samples of unsymmetric, strongly paramagnetic species, because in this case the signal intensity is split into many broad resonances.
4. The shimming of solenoidal probeheads is easy, because the sample is positioned horizontally in the homogeneous zone of the magnet. With diamagnetic samples, linewidths of about 2 Hz can be obtained without an extended shimming procedure. The resonances of paramagnetic samples are usually rather broad anyway [1,2]. It is important to note that the sample tube as described below does not have to be filled completely. Gas bubbles do not disturb the shim and even a half-filled sample tube will do.

For our measurements we use home-made sample tubes as shown in Fig. 1. They are affectionately called "NMR socks" in our lab. These socks are made from ordinary glass (no quartz because of the acoustic ringing!) and are equipped with a ground glass joint and stopper. With regard to reopening and reusing the tube we find this more convenient than sealed tubes. The stopper is fixed with rubber band which is necessary for temperature dependent measurements and because our paramagnetic substances are usually highly air sensitive. The socks fit very well into the common commercial teflon inserts available form BRUKER; only part of the upper rim has to be removed. In order to avoid background signals, special inserts were built by BRUKER for ^{1}H, ^{13}C and ^{19}F measurements.

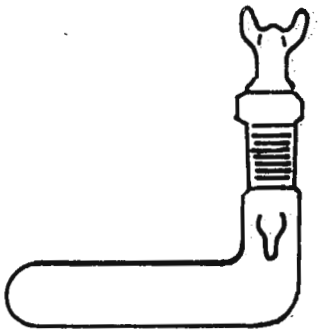
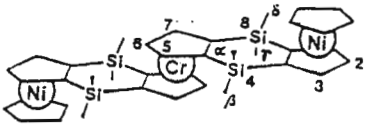
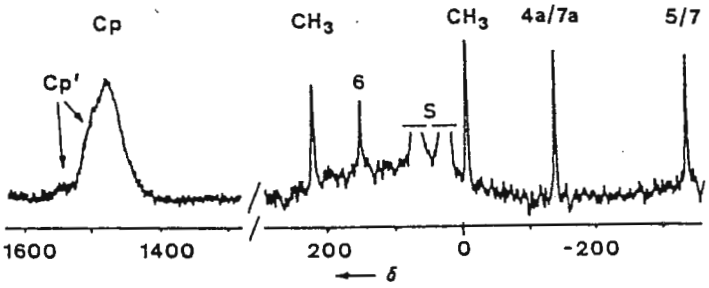


Fig. 1: Sideview of an airtight glass sample tube ("NMR sock"; original size) for measurements of liquids in solenoidal probeheads

A minor disadvantage of solenoidal probeheads is that they must be removed from the magnet for sample change, but this usually happens just once or twice a day anyway.

Fig. 2 shows a typical 75 MHz ^{13}C NMR spectrum of a paramagnetic trinuclear metallocene dissolved in THF-d_8 (signals S) at 25 °C.





Finally, it should be noted, that the solenoidal sample tubes are equally applicable for conventional wideline NMR spectroscopy of air sensitive powders. Furthermore, little socks with 5 mm sample diameter also proved successful.

J. Blümel

(Dr. J. Blümel)

(Prof. Dr. F. H. Köhler)

[1] J. Blümel, N. Hebendanz, P. Hudeczek, F.H. Köhler, W. Strauss, J. Am. Chem. Soc. 114(1992)4223-4230.

[2] P. Bergerat, J. Blümel, M. Fritz, J. Hiermeier, P. Hudeczek, O. Kahn, F.H. Köhler, Angew. Chem., Int. Ed. Engl. 31(1992)1258-1260.

[3] D.C. Hoult, R.E. Richards, J. Magn. Reson. 24(1976)71-85.

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Phase error overpulse	4° to 20 ms duration, typ.	
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Blanking delay	< 1 µ s on/off, TTL signal	
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(AMPX00HV) 02/94

May 29, 1994
(received 7/15/94)

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

A "short cut" to determine transport mechanism and kinetics by NMR.

Dear Dr. Shapiro,

In recent years we have studied extensively the kinetics of metabolic processes in perfused cell cultures and organs. Since a large number of metabolic processes are dependent on the supply and uptake of precursors from the external environment, we have decided to extend the use of NMR and determine also the rate(s) and mechanism(s) of transport processes. To that end we have utilized the approach of the zero trans transport procedure (Stein W.D., *Methods in Enzymology* **171**, 23, 1989) which measures the kinetics of uptake processes. This method was applied to study the mechanism and kinetics of transport of cyclocreatine (c-Cr) into uterine cells, and of choline into MCF7 human breast cancer cells.

The velocity of metabolite movement into the cells was determined from the change with time in the integrated intensity of the metabolite signal. For c-Cr we have monitored the ^{31}P of its phosphorylated product after confirming by magnetization transfer studies that the phosphorylation step (by creatine kinase) is fast and the rate determining step is the transport. For choline we have monitored simultaneously the deuterons of choline (trimethyl-D_9) and the ^{31}P of its phosphorylated product. This parallel measurement enabled us to show that the conversion of external choline to intracellular phosphocholine is rate limited by choline transport into the cells and to determine the transport mechanism and kinetics.

The uterine system included 22 excised immature rat uteri prepared and perfused in the NMR spectrometer at 37°C as previously described (Kaye A.M., Shinkarenko L., Waisman A., Victor T. and Degani H., *J. Steroid Biochem.* **34**, 289, 1989). MCF7 cells were cultured on microspheres and perfused in the spectrometer at 32°C as previously described (E. Furman, E. Rushkin, R. Margalit, P. Bendel and H. Degani, *J. Steroid. Biochem. Molec. Biol.* **43**, 189, 1992), using for cultivation choline-free growth medium. During the NMR measurements, increasing amounts of the transported substrate (c-Cr or choline) were added sequentially to the perfusion medium. The NMR recordings were performed on a Bruker AM-500 spectrometer. The external inorganic phosphate signal (0.9mM) and the natural abundant water deuterons signal (16.4 mM) served to calibrate the concentrations of metabolites in the ^{31}P and ^{2}H spectra respectively.

Cyclo-creatine transport was measured by monitoring the increase in the ^{31}P signal of phosphocyclo-creatine (Pc-Cr) and determining the initial rate of increase in this signal for each c-Cr concentration S. These concentration dependent results were analyzed by plotting the initial rate (V), k (k=V/S) and 1/k vs. S as shown in Fig. 1. The specific patterns in these three plots indicated that two mechanisms: Michaelis-Menten and diffusion kinetics were both contributing to c-Cr transport. Thus the data was fitted to the equation: $V=k_d \cdot S + V_{max} \cdot S/(K_m + S)$ yielding k_d of $6 \cdot 10^{-6}$ sec^{-1}, K_m of 1.4 mM and V_{max} of 0.36 mM/h.

The transport of choline into MCF7 cells was characterized from the increase in the ^2H signal of deuterated choline. Concentration dependent studies of the initial rate of transport of deuterated choline showed a classical Michaelis-Menten kinetics (Fig. 1) with K_m of 0.042 mM and V_{max} of 0.045 mM/h. It is clear that this method can be applied to measure a wide range of transport processes. We are also extending this approach to measure transport processes *in vivo* in the whole animal.

Please credit this contribution to the account of Dr. Raphy Poupko.

Hadassa Degani Leonid Shinkarenko Rachel Katz-Brull,

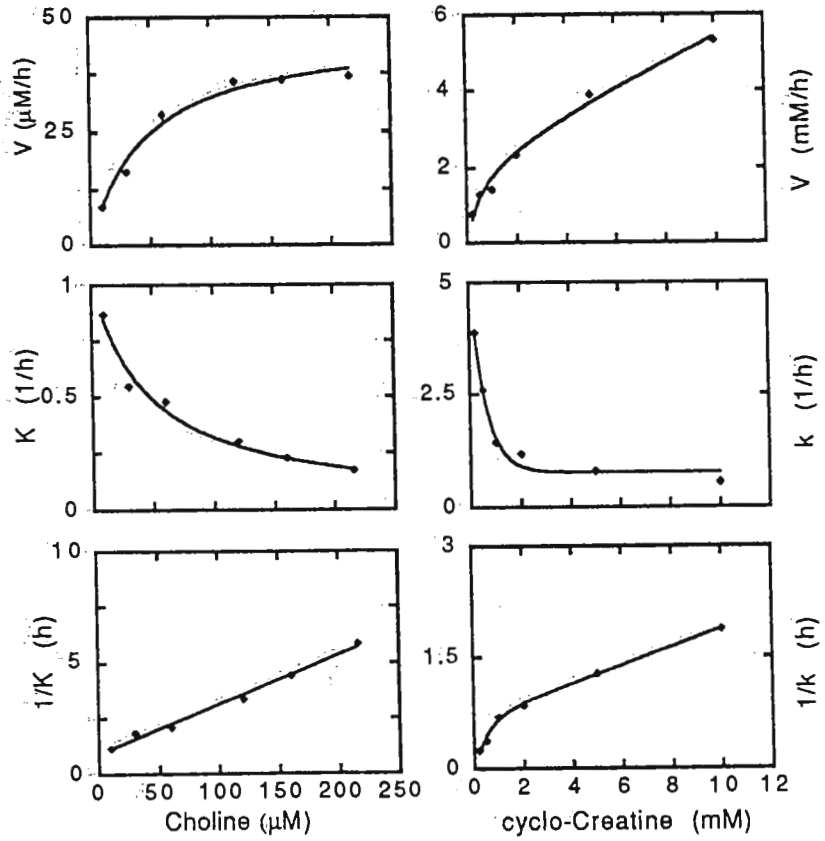
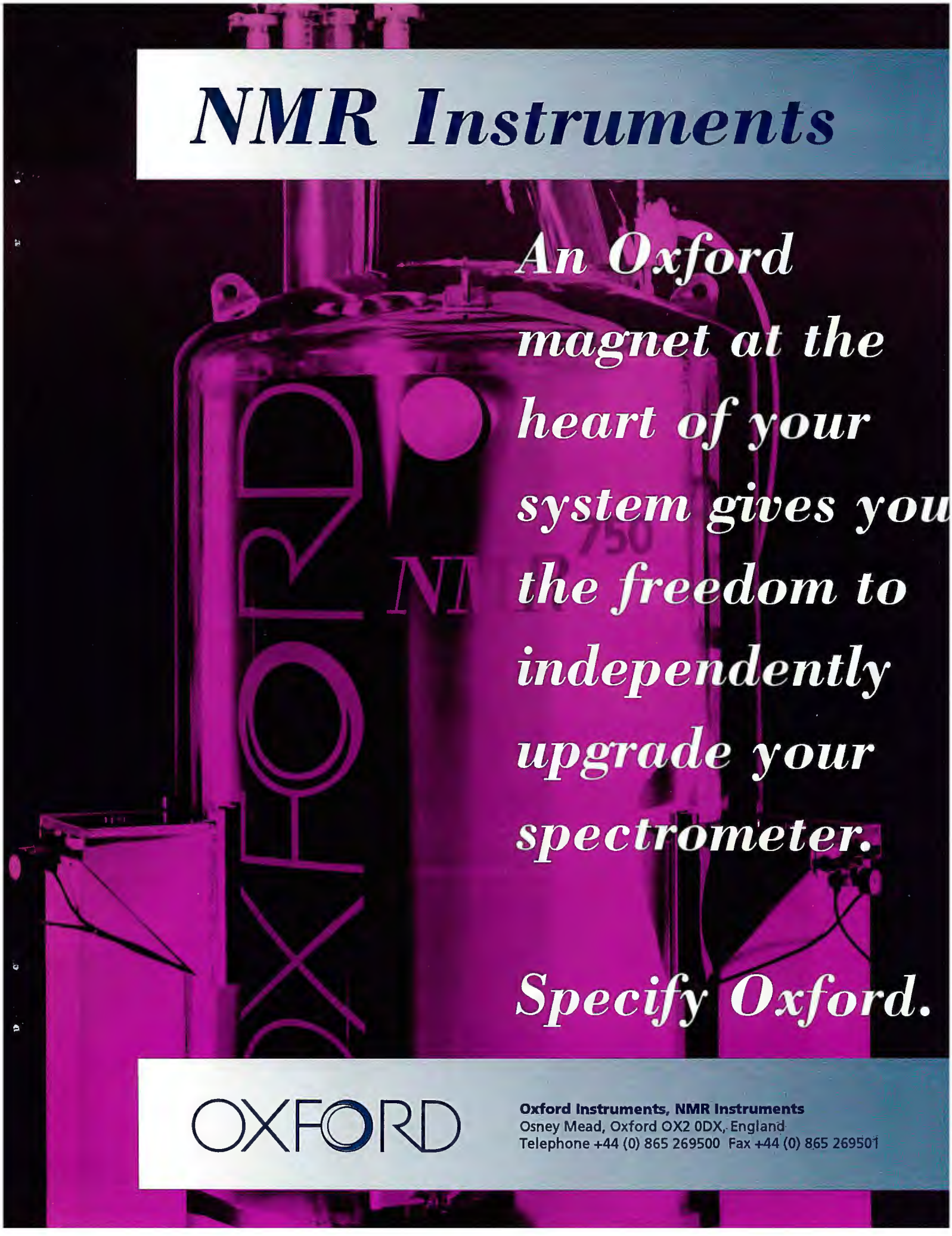


Fig. 1. Variation with substrate concentration in the kinetic parameters of choline transport into MCF7 human breast cancer cells (left) and of cyclocreatine transport into immature rat utreri (right).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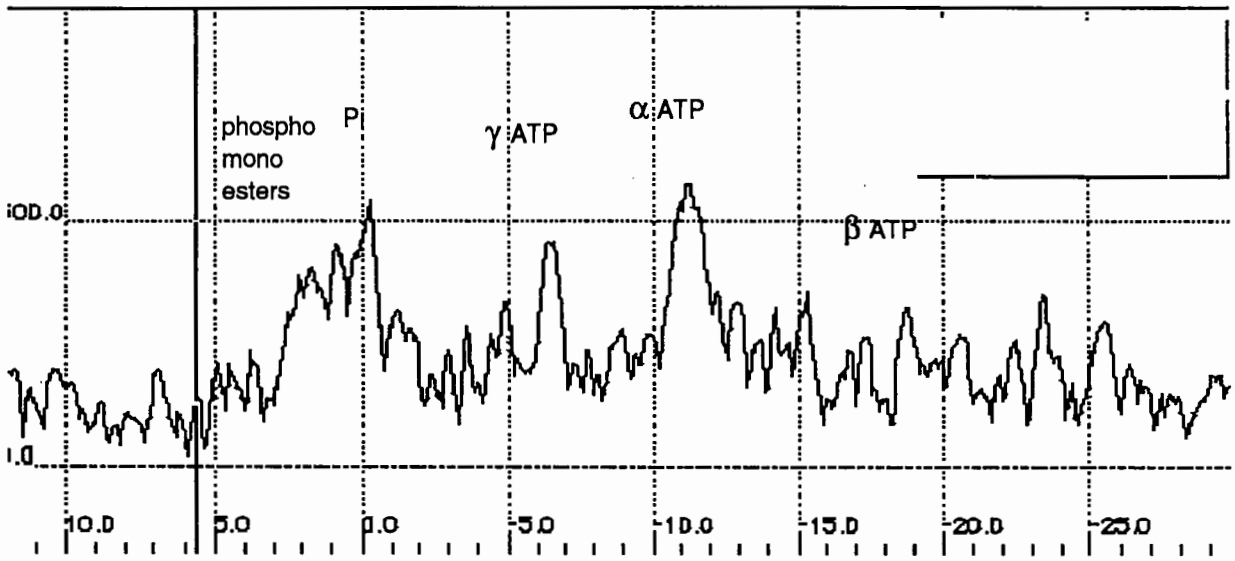
Dr. Bernard Shapiro
TAMU Newsletter
966 Elsinore Court
Palo Alto, CA 94303

July 15, 1994
(received 7/18/94)

^{31}P NMR of Live Paramecia

Dear Barry,

Thanks for the reminder. How about ^{31}P NMR of free-swimming unicellular organisms? In a slight departure from our routine of NMR on agarose-imbedded cells we modified our perfusion apparatus to accommodate paramecia. In lieu of the agarose threads, we used an 8 micrometer pore-sized filter to enclose the paramecia. Fresh media was continuously supplied from an inlet tube placed above the bottom of the usual perfusion insert within the NMR tube. The following ^{31}P spectrum was taken from 2 ml of media containing a half million lively swimming paramecia!



Sincerely,

Kirsten Berghmans Lisa Theisen Bruce McConnell

431-30

United States Department of Agriculture | Agricultural Research Service | Midwest Area U.S. Dairy Forage Research Center | 1925 Linden Drive West University of Wisconsin Madison, WI 53706

(608) 264-5407
E-Mail JRALPH@FACSTAFF.WISC.EDU
July 13, 1994
(received 7/18/94_

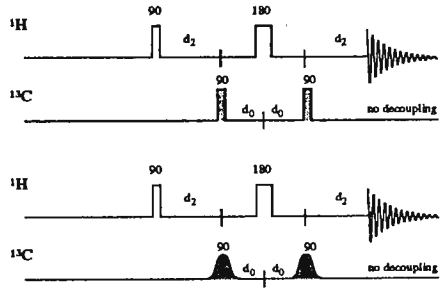
Dr. B.L. Shapiro
966 Elsinore Court
Palo Alto, CA 94303

Dear Dr. Shapiro,

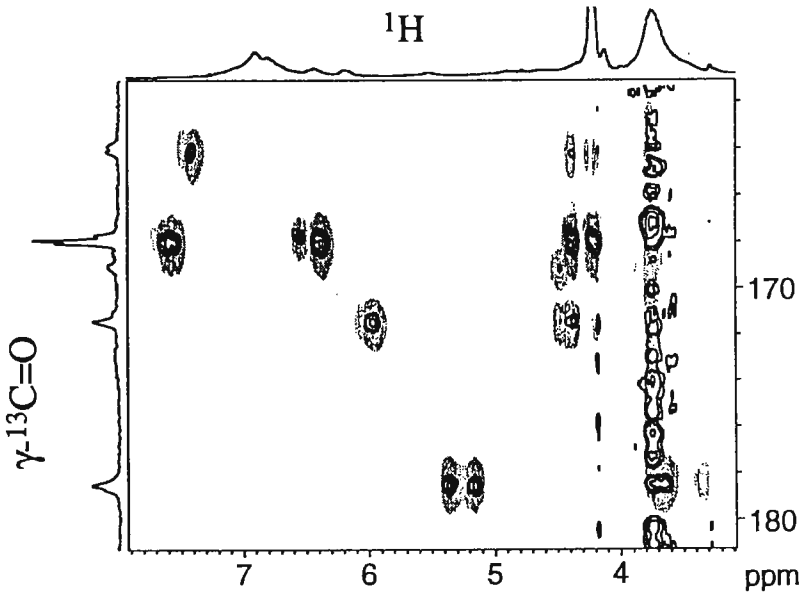
Soft-Pulse Carbonyl Selection

We have recently been getting excellent results applying inverse-detected C—H correlation experiments (HMQC and HMBC) to some nasty polymers, lignins. It is amazing how useful the 2D spectra are when the 1D proton spectrum is all but worthless.

Application of the HMBC experiment to a carbonyl-labeled ferulate arabinose derivative actively incorporated into a synthetic lignin proved that ferulate undergoes coupling at all the expected sites to form a variety of structures that had been ignored to this point in the literature, but I won't bore the NMR community with those details. It was really only the carbonyl region that was of interest — it contained all of the valuable correlative detail. Acquiring the entire carbon frequency range was wasteful. Obviously, semi-selective pulse variants could be useful here.



We wish to report how effective simple square pulses are in this case. The experiment is trivial to set up if you simply use the basic HMQC experiment with a long-range delay and, for reasons of not wishing to calibrate phase relations between hard and soft pulses, use soft pulses for both carbon pulses. The figure shows the result of the semiselective experiment using 500 µs square carbon pulses centered over the carbonyl region with the underlying (dotted) contours from the full HMBC experiment.



Only one significant correlation near the edge of the spectrum is missing in the restricted soft-pulse experiment. We are pursuing more elegant pulse-shaping now but the wham-bam approach is surprisingly useful.

Sincerely,

John Ralph

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I have further funding available for a good Ph.D. student with strengths or interests in Organic Synthesis, Plant Cell Wall Chemistry and, of course, NMR to do an exciting project in the area of plant cell wall cross-linking mechanisms. Please contact me at (608) 264-5407, FAX (608) 264-5275, or E-Mail at JRALPH@FACSTAFF.WISC.EDU if you have an interest, want lots of easy-access NMR time, and enjoy cold winters. The Center is an equal opportunity employer.

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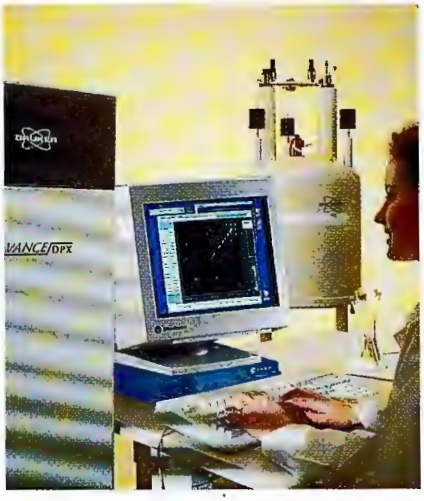

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June 15, 1994
(received 6/25/94)

Dr. B.L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Dear Barry,

Multi-frequency solvent suppression

Currently available water-suppression schemes tend to be based on differences in chemical shift δ, relaxation time ,T1,T2, or coupling constant J between solvent and solute. PFG exploits other physical properties of the nuclei[1], in particalar the diffusion constant, and allows suppression of solvent with the following advantages:

1. Independence of chemical shift difference between solute and solvent.
2. No role of water line width or shimming (B0 homogeneity).
3. Spins resonating at the water frequency can be studied.
4. The intensity profile in the spectrum is frequency independent.
5. Transmitter offset is not necessary set at water resonance.
6. Exchangeable protons can be studied.

Recently, we have used a FT Pulse-Field-Gradient stimulated echo method, Fig.1, to simultaneously suppress the very large resonances from H_2O and urea, in 2 mM Cyano-metmyoglobin in 90/10 H_2O/D_2O in the presence of 2 M urea(Fig.2). Transmitter offset was set at 9.88 ppm. There is no necessity to set either on the water peak(4.8ppm) or the urea peak(5.79ppm). There is no phase and baseline distortion in the spectrum. Since the method is based on the diffusion constant difference of solvent and solute, it can be used to suppress multiple-frequency small molecular resonances in biopolymer aqueous system.

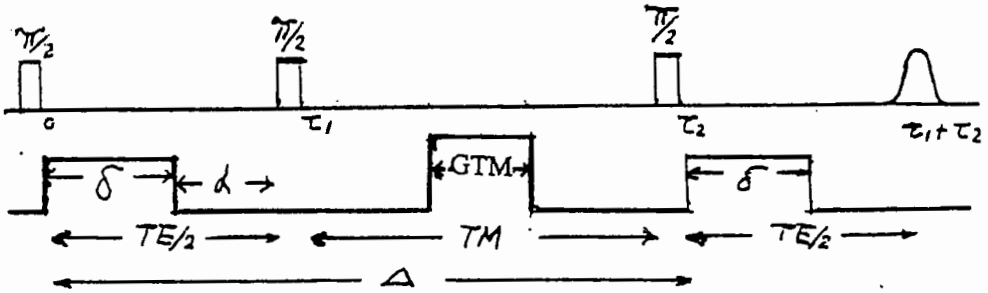

Fig. 1. Schematic representation of the fundamentals of PFG NMR stimulated echo (STE). Sequence employing gradient pairs to become diffusion sensitive. The gradient GTM in the STE serves to destroy non stimulated echoes.

1, P.C.M. van Zijl, and C.T. Moonen, J. Magn. Reson. 87, 18 (1990)

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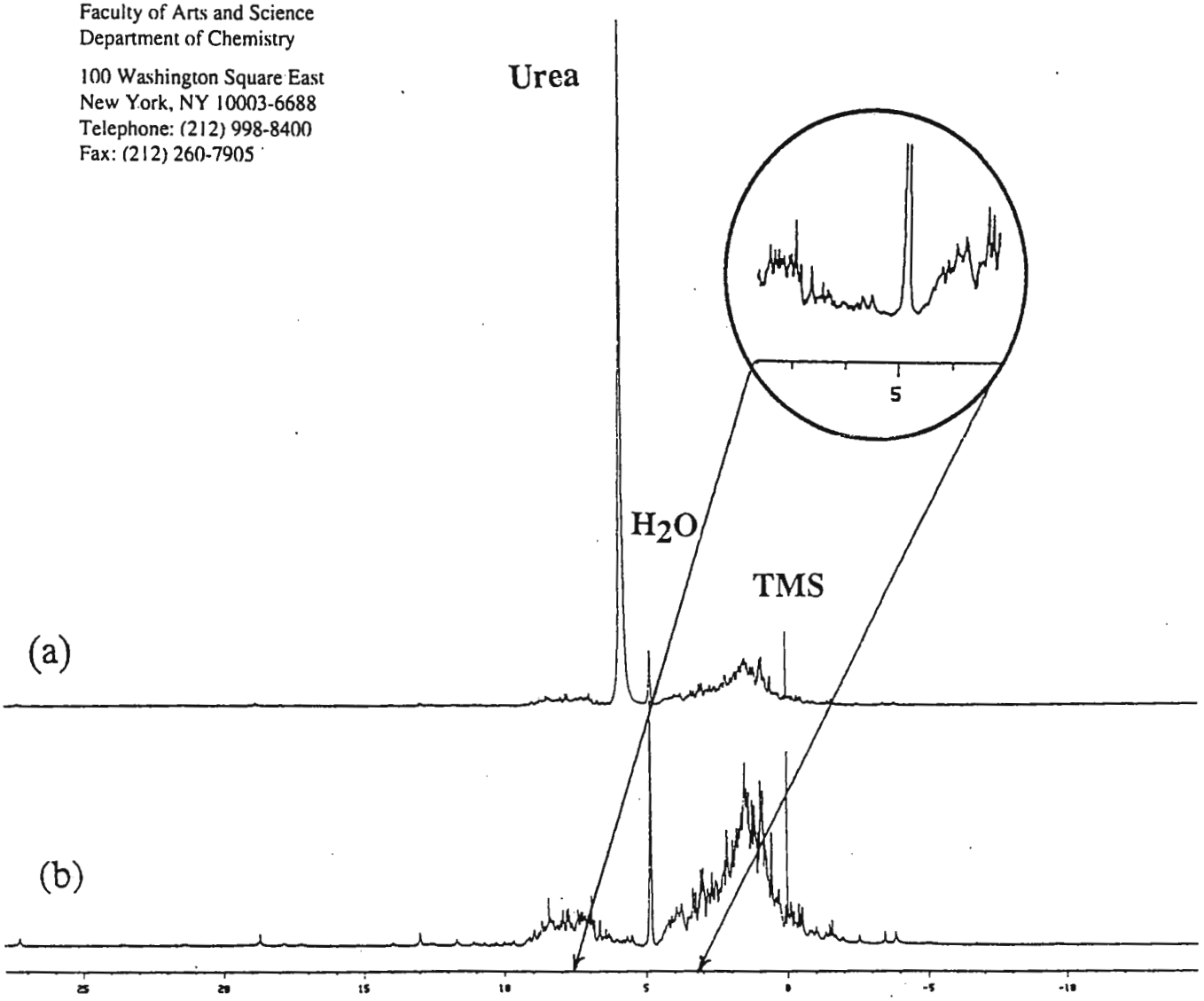

Fig. 2 Water suppressed NMR spectra, recorded on a Varian Unity 500 spectrometer, of 2 mM Cyano-metmyoglobin in 90/10 H_2O/D_2O in the presence of 2 M urea. (a) Presaturation method, with only the water resonance suppressed. (b) PFG stimulated echo method, with G=32G/cm, δ=5.5 ms, 90° pulse width=9.2 μs, TM=25 ms, TE=11 ms. Both water and urea resonances were suppressed simultaneously. The αH proton resonances near the huge urea resonance(5.79 ppm) appear.

Sincerely,

Mingming Guo Neville R. Kallenbach

Mingming Guo and Neville R. Kallenbach

HARVARD MEDICAL SCHOOL
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July 25, 1994 (received 7/27/94)

Installation of a 750 MHz Spectrometer at Harvard/MIT

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinor Court
Palo Alto, CA 94303

Dear Barry:

We recently had a pleasant experience in setting up a new Varian UnityPlus 750 spectrometer. The installation went very smoothly. The magnet arrived at our site at the Francis Bitter Magnet Lab on June 28 and was set up by Andy Sheppard from Oxford Instruments. After assembly, it was cooled on July 1 and 2. Energizing started on July 3. The magnet was brought up on a holiday schedule in three steps, and field was reached on July 5 without a quench. After installation of the console, field mapping and shimming, the first probe was tested on July 15.

We have no detectable field drift. On our first proton-only probe, we have a chloroform line shape of 5/9 and a EB sensitivity of 1100:1 (over 1 ppm noise) for our proton only probe. We see a well resolved splitting of the chloroform line due to the chlorine isotope effect (Fig. 1). We have now started routine use of the spectrometer. The first 2D protein spectrum recorded is a NOESY of the protein decorsin, an antagonist of GPIIbIIIa. The active site contains an RGD recognition sequence sitting on the apex of a hairpin loop. Fig. 2 shows a crowded region of cross peaks between amide protons of the active site residues R31, G32 and D33 and side chain protons. The increased resolution compared to 600 MHz is obvious. An NOE between R31HN and A34HB which is crucial for defining the conformation of the active site (labeled in Fig. 2) is not resolved at 600 MHz. The spectra are recorded at somewhat comparable conditions. However, the sample used at 750 MHz was only half as concentrated as the one used for the 600 MHz spectrum. In order to make the deadline for this issue of the newsletter we did not make a serious effort to record spectra at exactly identical concentrations and spectrometer settings.

With best regards

Jonathan Lee Jim Wrenn Andrzej Krezel Mark van Criekinge Gerhard Wagner

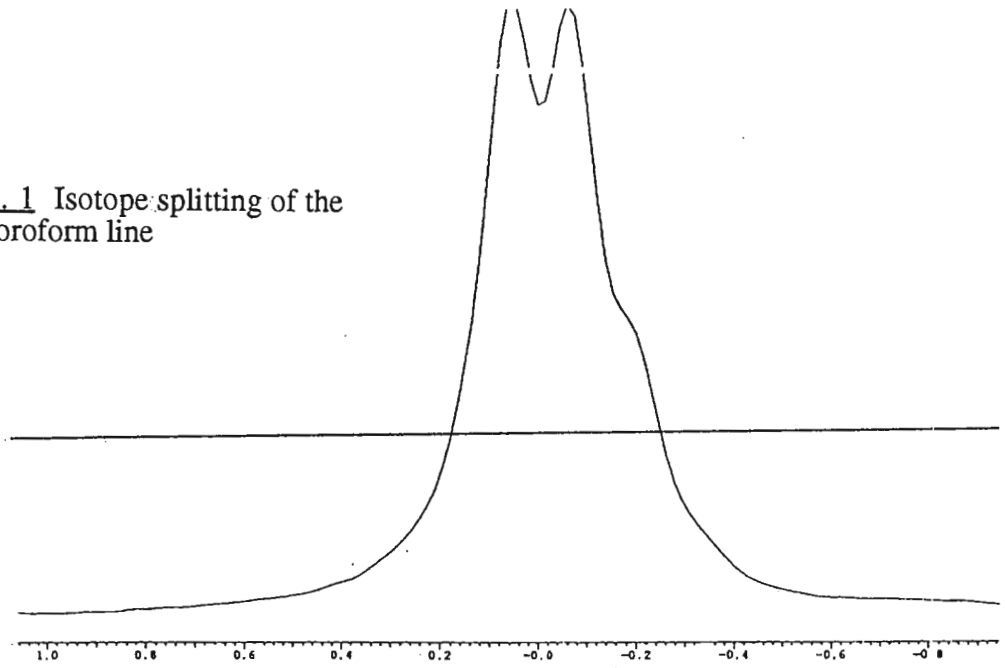

Fig. 1 Isotope splitting of the chloroform line

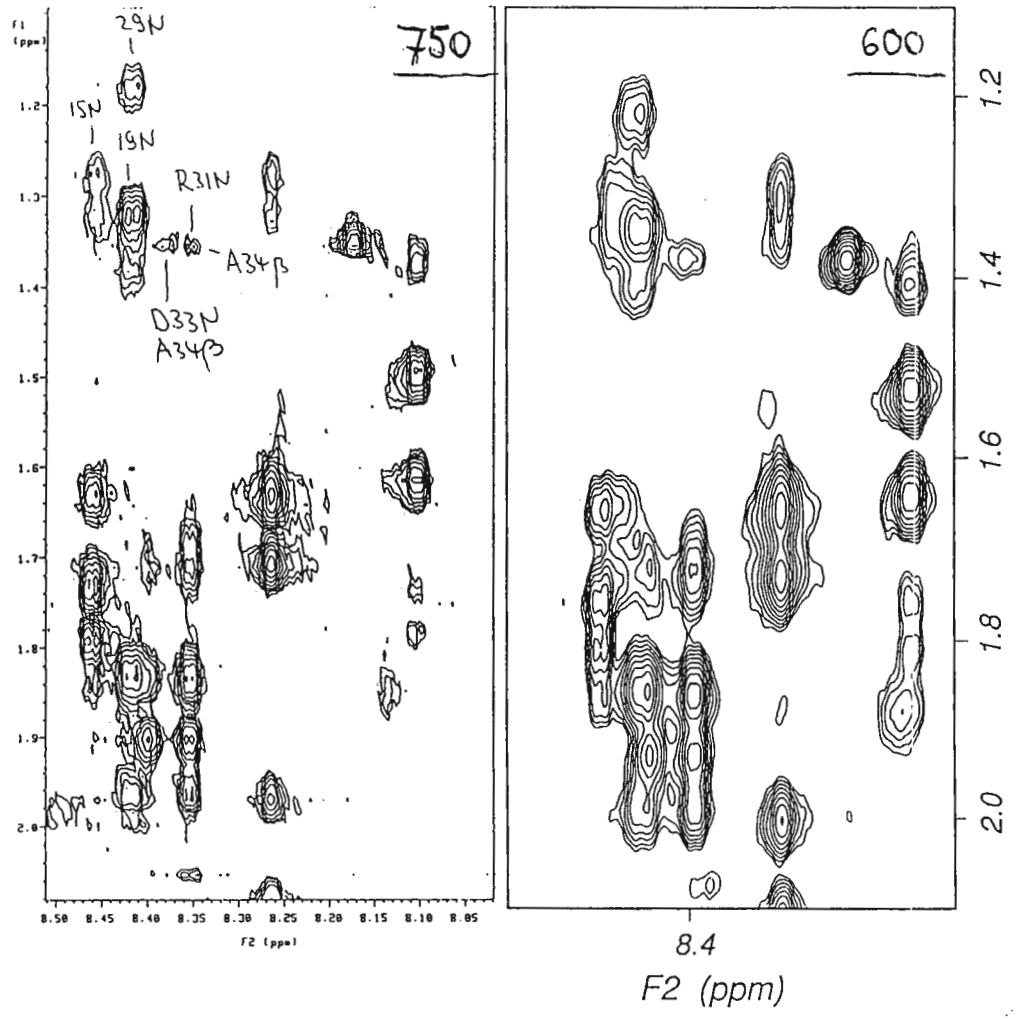

Fig. 2 Region of a NOESY spectrum of the RGD protein decorsin recorded at 750 MHz and at 600 MHz

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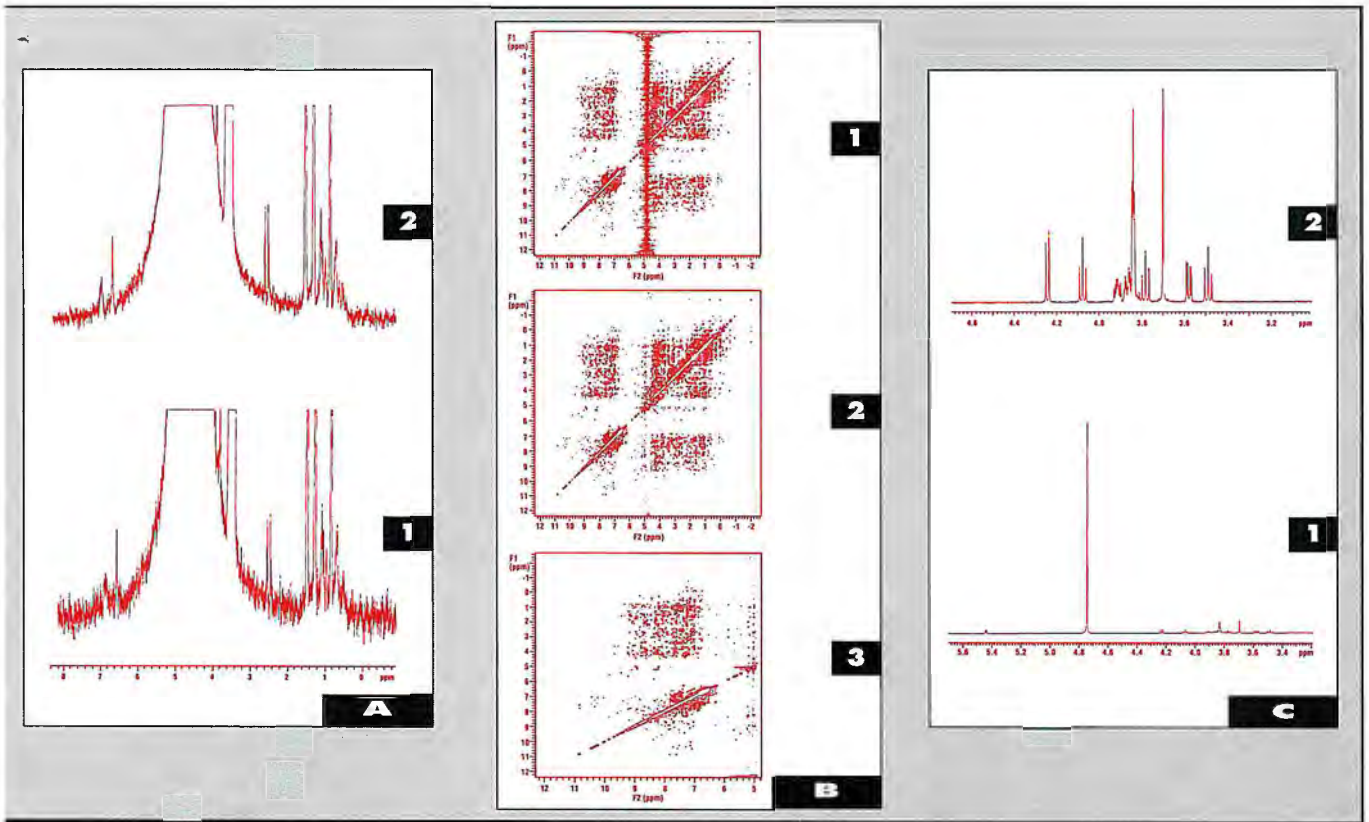

All spectra above were obtained with UNITYplus NMR spectrometers: A1) Spectrum of dilute commercial soap solution in H_2O, collected using a 5 kHz analog filter. A2) Spectrum of dilute commercial soap solution in H_2O collected using oversampling and digital filtering. B1) Water-suppressed NOESY spectrum of 1 mM lysozyme in 90% H_2O. B2) Water-suppressed NOESY spectrum of 1 mM lysozyme in 90% H_2O using digital filtering solvent subtraction to remove the residual water signal. B3) Water-suppressed NOESY spectrum of 1 mM lysozyme in 90% H_2O using digital filtering to restrict data acquisition to the fingerprint region. C1) 300 µg of sucrose in D_2O, spectral width 10 kHz. C2) 300 µg of sucrose in D_2O, using digital filtering to restrict the spectral width to 1 kHz, with elimination of the HDO signal.

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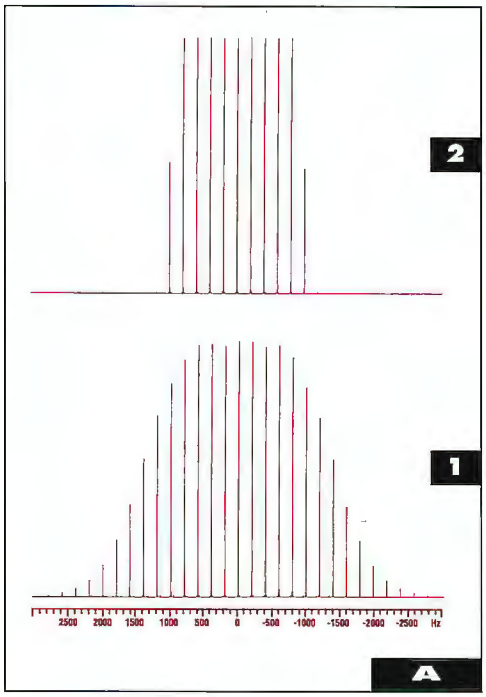
Figure A: Varian's digital filters provide both very sharp signal cutoff response at the edges of the bandwidth and extremely flat signal response within the chosen bandwidth.
A1) Profile of the signal amplitude response for a 1 kHz analog filter
A2) Profile of the signal amplitude response for a 1 kHz digital filter.



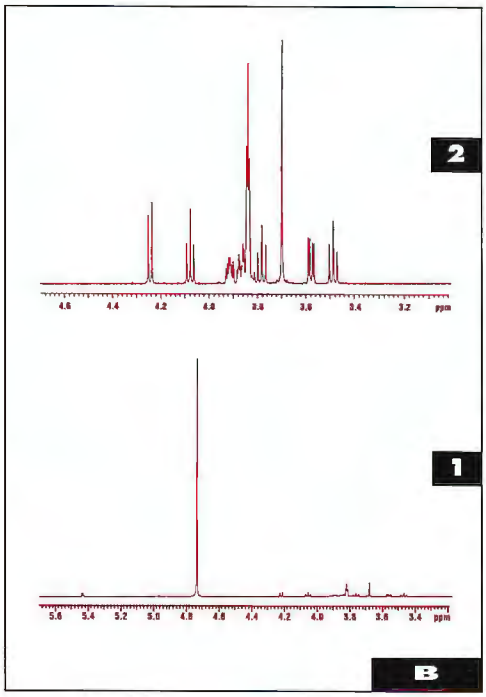
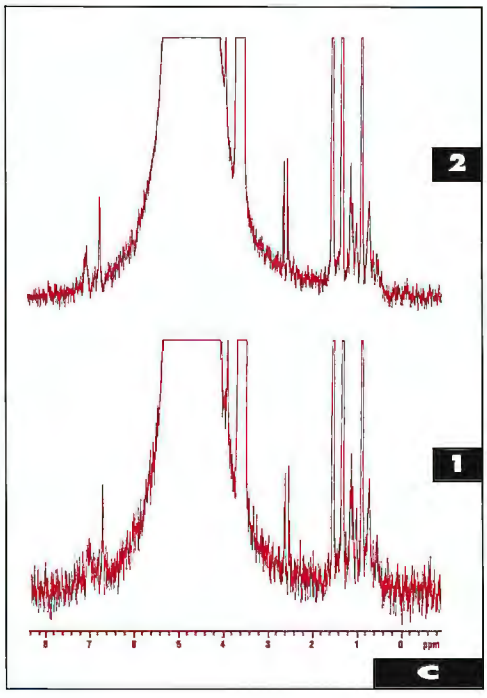


Figure B: Varian's digital filters provide the capability to limit the spectral width to a region of interest without introducing aliasing artifacts.
B1) 300 µg of sucrose in D_2O, spectral width 10 kHz
B2) 300 µg of sucrose in D_2O, using digital filtering to restrict the spectral width to 1 kHz, with elimination of the HDO peak.

Figure C: Varian's digital filters provide increased sensitivity for low level signals in high dynamic range samples.
C1) Spectrum of dilute commercial soap solution in H_2O, collected using a 5 kHz analog filter.
C2) Spectrum of dilute commercial soap solution in H_2O collected using over-sampling and digital filtering.



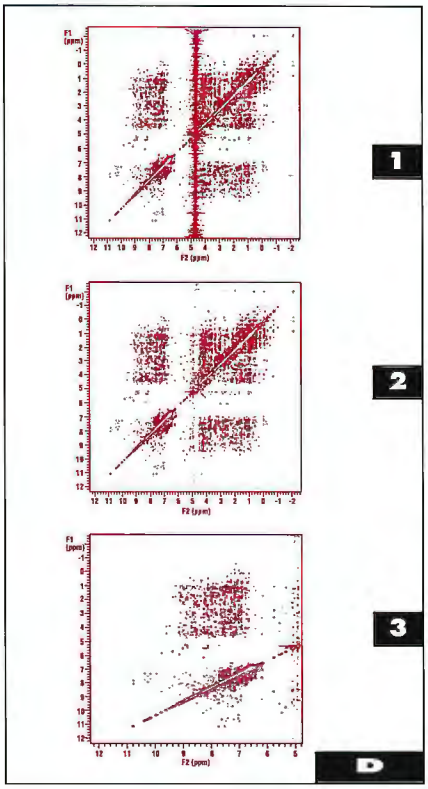


Figure D: Varian's digital filters can be applied during data processing or data acquisition.
D1) Water-suppressed NOESY spectrum of 1 mM lysozyme in 90% H_2O.
D2) Water-suppressed NOESY spectrum of 1 mM lysozyme in 90% H_2O using digital filtering solvent subtraction to remove the residual water signal.
D3) Water-suppressed NOESY spectrum of 1 mM lysozyme in 90% H_2O using digital filtering to restrict data acquisition to the fingerprint region.

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MAG-8048/434

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E-Mail JRALPH@FACSTAFF.WISC.EDU
July 13, 1994
(received 7/18/94)

Dr. B.L. Shapiro
966 Elsinore Court
Palo Alto, CA 94303

Dear Dr. Shapiro,

MANAGEMENT, A CAUTIONARY TALE

Here is a humorous contribution from an unknown source, listed as Courtesy of Alf Saunders on the copy I have. [Please excuse my not using official letterhead for this contribution]. Since I am a Kiwi, I have left the Country of Origin References intact.

John Ralph

Once upon a time, the Kiwis and the Chinese decided to have a boat race on Auckland Harbor. Both teams practiced long and hard to reach their peak performance. The Chinese won by a mile.

Afterwards, the Kiwi team became very discouraged by the loss and morale sagged. SENIOR MANAGEMENT decided that a reason for the crushing defeat had to be found, and a project team was set up to investigate the problem and recommend the appropriate action.

Their conclusion: The problem was that the Chinese had eight people rowing and one person steering. The Kiwis had one person rowing and eight people steering. SENIOR MANAGEMENT immediately hired a CONSULTANCY Company to do a study on the team's structure. Millions of dollars later they concluded that — too many people were steering and not enough were rowing.

To prevent losing to the Chinese the following year, the Team structure was changed: four were appointed STEERING MANAGERS, three were appointed SENIOR STEERING MANAGERS, one was appointed EXECUTIVE STEERING MANAGER.

In addition, a PERFORMANCE APPRAISAL SYSTEM was set up to give the person rowing the boat more incentive to work harder and become a KEY performer. "We must give the rower EMPOWERMENT and ENRICHMENT — that ought to do it."

In the following race, the Chinese won by two miles.

The Kiwis laid off the rower for poor performance, sold all the paddles, cancelled all capital investment for new equipment, and halted development of a new canoe, paid the CONSULTANTS a BONUS, and distributed the money saved to SENIOR MANAGEMENT.

DEPARTMENT OF HEALTH & HUMAN SERVICES

Public Health Service
National Institutes of Health

Dr. Bernhard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

National Institute of Diabetes and
Digestive and Kidney Diseases
Bethesda, Maryland 20892

13. July, 94
(received 7/18/94)

LOCKHOLD

Dear Barry

For some experiments (2H decoupling, gradient pulse etc.) it is necessary or helpful to interrupt and hold the 2H lock on a spectrometer under program control. Our older Bruker AM and AMX consoles are not so equipped. We have built accessories to enable us to do that.

The basic idea is shown in a block diagram below. The application of a gate pulse from a control line (RCP or CTRL) will stop the RF pulses from the lock transmitter and gate the lock receiver off. The NMR lock signal to the field controller is replaced by an adjustable small DC voltage to allow the zeroing of any drift. The computer shim signal is replaced by a fix + 1V, so the console does not complain with a 'lost lock' reply.

At the end of the gate pulse, the Tx and Rx pulses are restored. After an adjustable delay of typically 50 to 500 ms to allow the lock signal to build back up, both the NMR lock and the Comp.shim signals are reconnected.

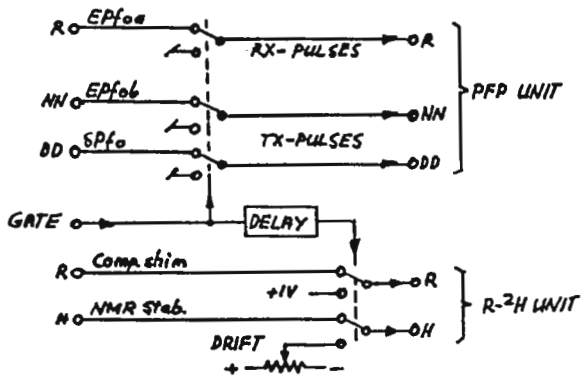
Minor surgery to the Bruker PFP and R-2H units brings the needed signals to outside connectors. Dummy plugs allow the system to run as before with the control box disconnected. With the control box connected and no gate pulse applied, the lock also works as before.

With most of our experiments the pulse repetition rate is about 1 sec. With a lock break of 100 msec and a 300 msec recovery, we have a 600 msec lock period which appears to be fully adequate with no deterioration of stability.

Anyone interested in the details can contact me for more information. Please credit this contribution to Marius Clore's account.

Rolf Tschudin
Bldg.5, Rm. B2-29
(301) 496 2692
tschudin@nih.gov

Rolf



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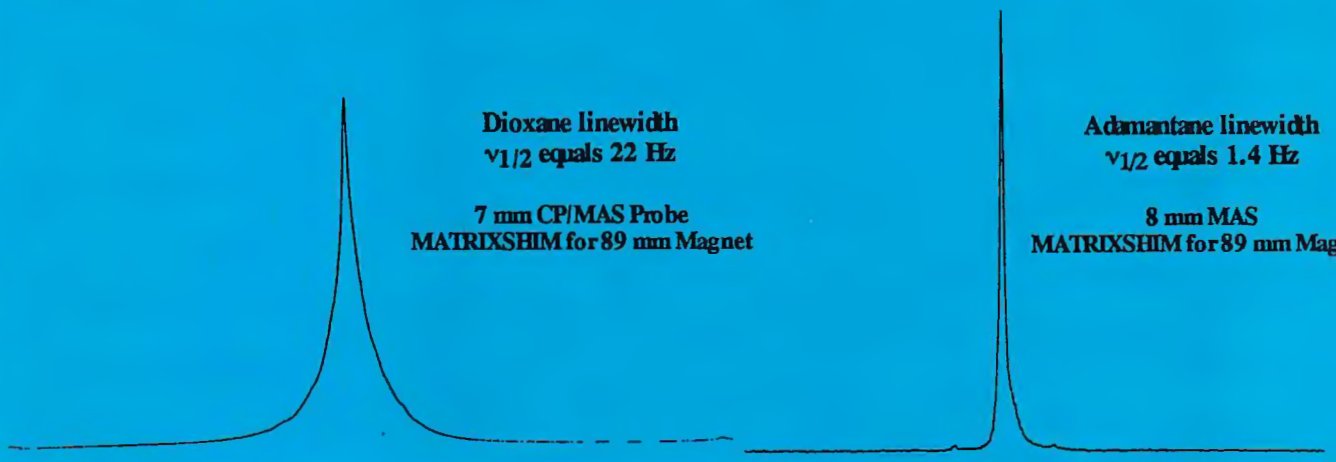

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Resonance Research, Inc. gratiously thanks Varian applications chemists for acqiuiring the spectra shown herein.

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Digital Filter Functions

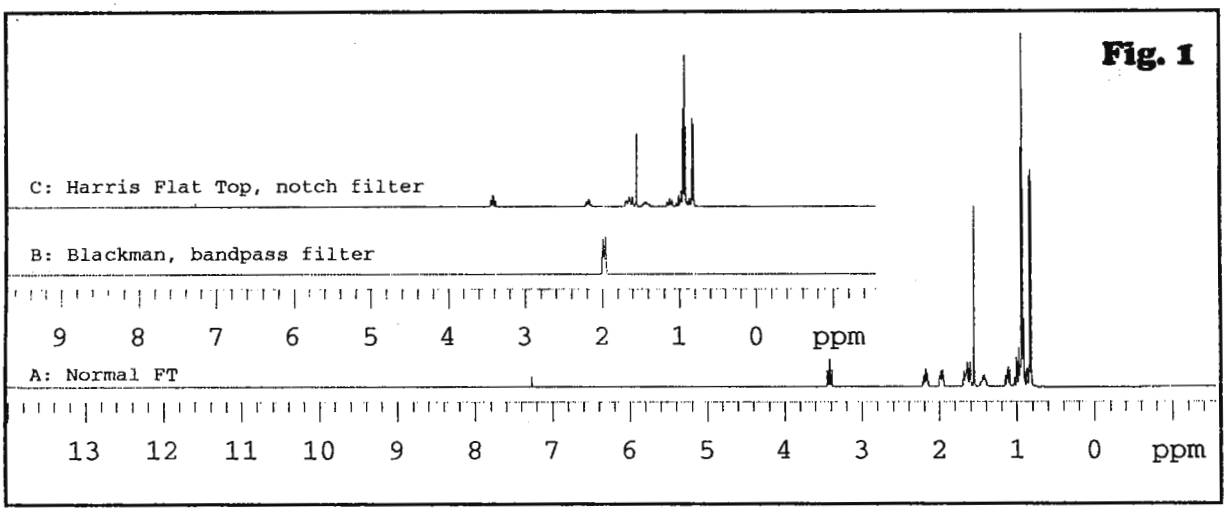
(received 7/15/94)
July 8, 1994

Dear Barry,

Digital filters are relatively new in NMR, and as a result there may be some confusion about the nature and desirability of various windowing functions. I hope I can shed some light on this subject.

A wide variety of window functions can be used for digital filtering (see, for example, *Handbook of Digital Signal Processing*, ed. Douglas F. Elliott, Academic Press, 1987). As with different analog filters (Butterworth, Bessel, quasi-elliptical), each of the various digital filter functions (Blackman, Hamming, Kaiser, etc.) was designed to optimize a different blend of filter characteristics – attenuation in the stopband, phase linearity in the passband, amplitude flatness in the passband, etc. Since there are many different types of NMR applications, it may well be desirable to choose different digital filtering functions for different experiments, *or even to apply different functions to the same data set.* No one function can serve all needs.

Figure 1 illustrates the flexibility and power of digital filtering. Figure 1A presents a simple 1D spectrum (good old "fid1d" for Varian users). In 1B we apply a bandpass filter designed using a 3001-pole Blackman window with a ±50 Hz bandwidth, detecting the multiplet near 2 ppm with the complete exclusion of all other peaks. In 1C we apply instead a notch (band reject) filter at the same frequency, using a "Harris Flat Top" window with 1457 coefficients. The peak of (dis)interest is completely removed.



While various characteristics of the filter are determined by the window function, the transition bandwidth (the region over which the filter goes from passing signal to rejecting signal) is, as it turns out, primarily influenced not by the form of the window function, but by its complexity. As with analog filters, the narrowness and steepness of the transition region is determined by the number of "poles" (a.k.a. "taps" or coefficients) in the filter. The more complex (i.e., the more poles) the filter, the sharper it can be. This is true for virtually all digital filter functions in common use.

In Figure 2 the frequency response of a Blackman filter using 51, 91, and 501 coefficients is compared. In this example we have reduced the spectral width ("downsampled") by 16 and selected (using a digital bandpass filter) the $CHCl_3$ singlet. The edge of the spectral window and the digital filter cutoff are chosen to be different so that the falloff of the peak intensities outside the passband can be seen more easily (without foldover). A series of spectra are plotted in which the filter center is shifted by 5 Hz each time; the digital filter bandwidth is 50 Hz. The point at which the $CHCl_3$ line falls on the "edge" of the filter is marked with an asterisk (*). The message is clear – the same window function can exhibit shallow or extremely sharp cutoffs, depending only on the number of coefficients.

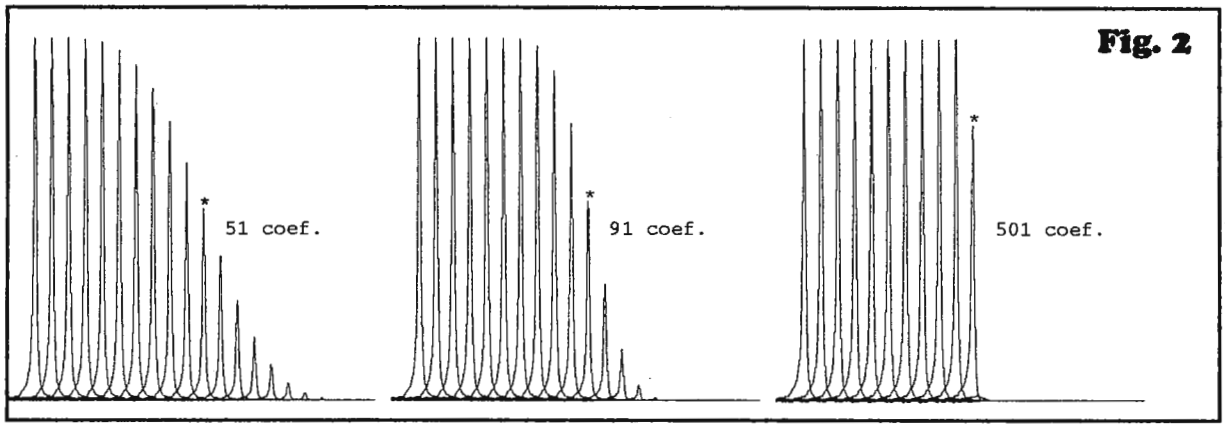


Fig. 2

Why not always use a large number of coefficients? One obvious reason is time. The more coefficients, the more time the calculation takes. Consider three possibilities for digital filtering in the usual NMR chain. The "worst" case is a digital filter operating "on the fly" (i.e., during acquisition). Here the number of coefficients chosen limits the maximum data rate (or conversely the desired data rate limits the number of coefficients). A post-acquisition filter operating interposed between the acquisition computer and the host computer presents an intermediate case. Here, the digital filter function needs only to process the FID before the next one appears; in typical situations involvings multiple transients and inter-transient relaxation delays, this increases the time available and allows more coefficients to be used. Finally, if we consider a post-acquisition filter operating on already stored data, then the only constraint on the number of coefficients is operator patience. Of course, the speed of the computer or microprocessor on which the DSP algorithm is running is also relevant.

If you do have time to apply sufficient coefficients, some amazing rejections can be achieved. Figure 3 illustrates the stopband rejection of a peak just 5 Hz outside the cutoff frequency (spectral width = 400 Hz, filter cutoff = 200 Hz, peak position = 205 Hz) as a function of the number of poles in the filter (shown above the filtered peak). When more than 1001 coefficients are used, the peak is actually completely attenuated; what appears to be a tiny residual peak in the figure is actually just a baseline shift at the edge of the filter.

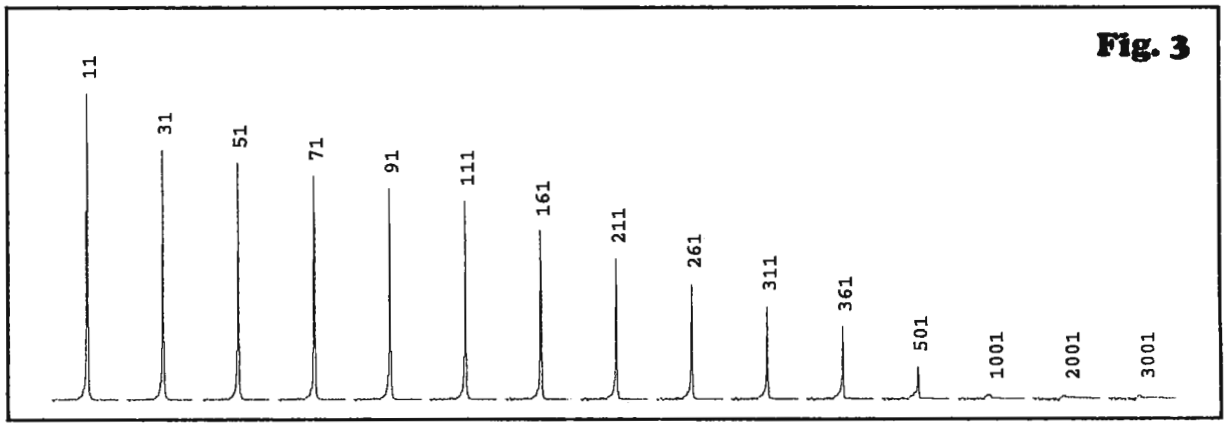


Fig. 3

All figures in this letter were prepared from a single data set using VNMR™ 5.1, which will be released this fall. MAGICAL™ macros were used to do the "hard work" – varying the number of coefficients, producing the plots, positioning the asterisks, etc. Coefficients for the notch filter were generated on a PC using *QEDesign 1000 for Windows* (Momentum Data Systems, Costa Mesa, CA), saved as an ASCII file, and transferred to a Sun for use (after minimal modification by a Unix shell script) by VNMR.

Sincerely,

Steve

Dr. Steven L. Patt
Product Manager, Software & Data Systems

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WESTERN RESEARCH INSTITUTE
The University of Wyoming Research Corporation

July 7, 1994
(received 7/11/74)

Dr. Bernard Shapiro
TAMUNMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

^{1}H NMR Determination of Water in Coals

Dear Barry:

While Fran Miknis is out fishing and thinking about new ways to apply NMR to the real world, I'll give you a run down on a very simple way of measuring total amount of water in coal or any other types of materials. The ^{1}H NMR method was developed in conjunction with our study for DOE of the role of water in coal liquefaction.

Removing the moisture prior to liquefaction reduces the reactivity of coal to liquefaction, and hence, the amount of coal converted to liquid during the liquefaction process is reduced. Chemical drying of coals is a relatively unexplored technique for removing water at low temperature. Thermal methods of drying alter the physical structure of coal as well as promote undesirable chemical reactions. Low-temperature drying of coal, on the other hand, should preserve the structural integrity, reduce retrograde reactions, reduce thermal degradation, and provide information on nonbonded, chemisorbed, and physisorbed water.

The dehydration agent 2,2-dimethoxypropane (DMP) was used to dry coal and to simultaneously determine the moisture content in coal. The reaction of 2,2-dimethoxypropane with water is shown in scheme I.

$$CH_3C(OCH_3)_2\ CH_3 + H_2O \rightarrow 2CH_3OH + CH_3C(O)\ CH_3$$

Scheme I

This reaction, in the absence of diffusion controlled reactions, is rapid and endothermic. The ^{1}H NMR of the reaction products, methanol and acetone, give single resonances for the methyl hydrogens, which are easily identified and do not overlap the hydrogen NMR resonances of 2,2-dimethoxypropane. The integration of the acetone methyl hydrogens is a direct measure of the moles of water reacted.

Hydrogen-1 NMR spectra were obtained on a JEOL GS-400 NMR spectrometer. To determine the water content in standard water samples and coal, the resonance areas for acetone (2.2 ppm) and cycloheptane (1.5 ppm) the internal standard were measured using Lab Calc™ curve-fitting routine. The curve-fitting routine for determining the area of the peaks increases the precision and accuracy of the NMR method by eliminating instrumental and other artifacts which contribute to the peak shape.

Figure 1 shows a plot of the data of the known amount of water in methanol versus the amount of water determined by the reaction with DMP and measuring the amount of acetone formed by ^{1}H NMR. Table 1 lists the precision of the ^{1}H NMR method for determining the water content in six coals of various rank. As shown in the table, the Texas subbituminous coal has the largest standard deviation of all the coals investigated. From another set of experiments, thermally drying the Texas coal gives a moisture

value of 29.17 percent with a standard deviation of ± 0.61. The poor precision or erratic results obtained by the chemical drying method for this coal may be due to interfering reactions of DMP and/or methanol with some of the coal's organic functional groups. The standard deviation for the other coals are about ± 1% or less, which is better than what one can obtain by many other moisture determination methods for coals.

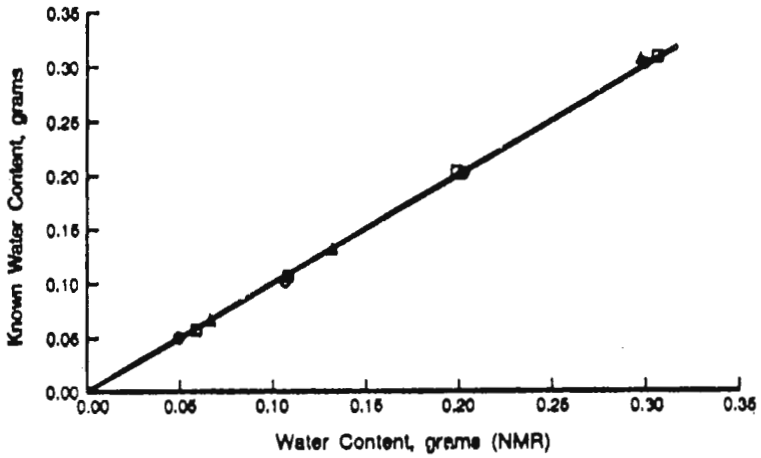

Figure 1. Known Water Content in Methanol versus the Measured Water Content using DMP and ^{1}H NMR. Solid line is the 1:1 correlation of the data

Table 1. Chemical Moisture Determination for Coals of Various Rank

Coal	Run 1	Run 2	Run 3A	Run3B	Run 4	Ave.	SD[a]
Eagle Butte	22.35	20.66	20.18			21.06	1.14
Texas	31.02	(44.16)[b]	24.96	(44.21)	29.81	28.60	3.21
Beulah Zap	(40.73)	34.71	34.34	33.26	32.09	33.60	1.18
Illinois #6	10.89	11.35	10.79			11.01	0.30
Blind Canyon	3.95	4.56	3.97			4.16	0.35
Black Thunder	24.88	22.39	23.16			23.48	1.27

[a] One Standard Deviation
[b] Samples in parenthesis were thrown out based on the fact that they lie more than 2 standard deviations from the mean of the remaining runs.

A full description of the ^{1}H NMR method will be submitted to a journal for publication in the very near future.

Sincerely,

D.A Netzel F.P. Miknis

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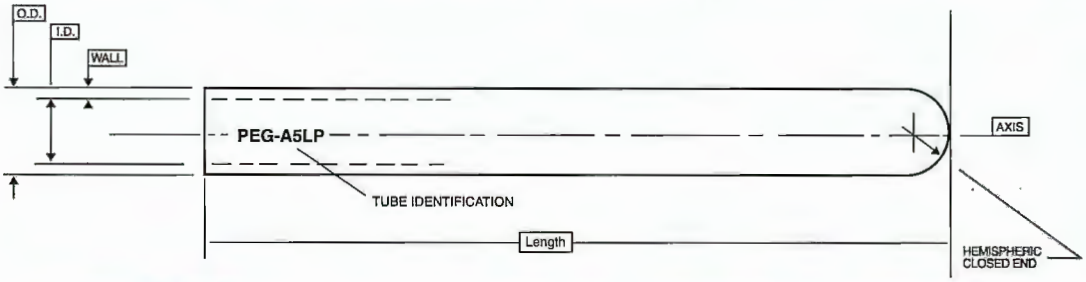

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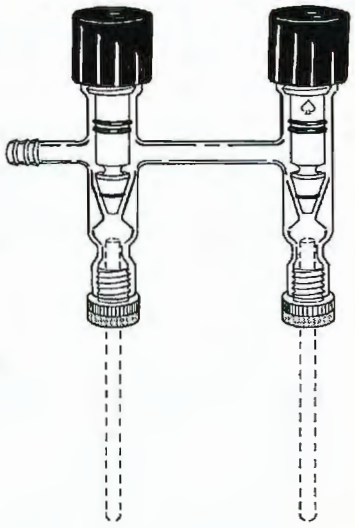

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What I never fully understood about NMR diffusion experiments.

21 July 1994

Dear Dr. Shapiro,

Our postdoc, Lee Z. Wang, has been doing some calculations on diffusion in the presence of barriers. In an attempt to understand his work, I have gained some understanding of this problem which is what I want to talk about. The hope is that some of this is new to some of the readership and will be useful.

As has been known for a long time, the problem is to figure out how the pulsed gradient spin echo (PGSE) NMR signal is affected by the diffusion of spins in the presence of barriers. This subject is even more important than in the past because of the emergence of imaging which allows the measurements of inhomogeneous diffusion coefficients with various anisotropies, leading to information on microscopic structures through which flow and diffusion take place. This all goes back to the original work of Stejskal, Cotts, and others which speaks well of those pioneers. A detailed up-to-date summary is in the excellent book: Paul Callaghan, Principles of Nuclear Magnetic Resonance Microscopy, Oxford, 1991.

In the usual PGSE experiment, magnetic field gradient pulses are applied for time δ on either side of the 180-degree pulse. The conventional notation also calls the interval between the gradient pulses Δ (so that $\delta \leq \Delta$), the diffusion coefficient D, and the dimension of the restricted space a. There are three regimes into which the problem can be (and has been) divided. The first is the so-called free diffusion limit, $\Delta D << a^2$, in which the spins hardly diffuse in the longest time of interest Δ and, thus, the diffusing spins do not, on average, encounter the barriers. The second is the so-called restricted diffusion case in which $\Delta D >> a^2$ but $\delta D << a^2$. This means that ΔD is now large enough for the spins, on average, to encounter the barriers many times during Δ but not during the gradient pulse δ. The last condition is the so-called short pulse approximation in which $\delta << \Delta$. The final case is for $\delta D >> a^2$ (which implies $\Delta D >> a^2$ because $\delta \leq \Delta$), i.e., the spins diffuse so much that, on average, they encounter the barriers many times even during δ. For this case, the signal attenuation caused by diffusion presumably has a major contribution during the gradient pulse. We call this case rapid diffusion.

There is a minor semantic difficulty here. Free diffusion is exactly the opposite of rapid diffusion, i.e., the former is the case where the diffusion is so small, the time Δ so short, or the barrier spacing so large, that the barriers are effectively nonexistent. Maybe limited diffusion is a better term. The term restricted diffusion is not exactly appropriate either because the barriers restrict the

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spins in both the restricted and rapid diffusion cases whereas the usual restricted diffusion does not include rapid diffusion.

Lee used a stochastic theory of random motion with a Gaussian phase distribution assumption to derive a general expression that is not limited to the so-called short pulse gradient approximation, $\delta D << a^2$. The resulting expression goes to sensible limits. Specifically, the attenuation exponent α, defined by the expression for the signal amplitude $S=S_0\exp(-\alpha)$, becomes, to within a multiplicative constant

$\gamma^2 g^2 \delta^2 D(\Delta-\delta/3)$, $\Delta D << a^2$, free diffusion,

$a^2\gamma^2 g^2 \delta^2$, $\Delta D >> a^2$ but $\delta D << a^2$, restricted diffusion,

and $a^4\gamma^2 g^2 \delta/D$, $\delta D >> a^2$, rapid diffusion.

The free and the restricted diffusion limits agree with the usual, well-known expressions [due to Stejskal, et al., and discussed in various parts of Callaghan, for example] while the rapid diffusion expression goes, in the limit $\delta \Rightarrow \Delta$, to Neuman's result [J. Chem. Phys. 60, 4508-4511 (1974)] for nonpulsed, i.e., cw, gradient experiments.

The physical pictures for the first two cases are well known. Without going into detail, α keeps increasing for increasing D and Δ for free diffusion because $(D\Delta)^{0.5}$ is equal to the diffusion distance and the attenuation is proportional to the width of the phase distribution. The expression for restricted diffusion, for which $\Delta D >> a^2$, is obtained by replacing $D\Delta$, the square of the diffusion distance, by a^2, the square of the barrier distance, in the free diffusion expression. α is independent of Δ and D because the numerous encounters with the walls during Δ makes the average coordinates the same for all the spins.

For the rapid diffusion case in which substantial diffusion takes place during the gradient, the dephasing of the spins depends not on the initial and final phases of the spins, as in the first two cases, but on the time integrals of their positions (which are proportional to their frequencies) during δ, as shown by Douglass and McCall [J. Phys. Chem. 62, 1102 (1958)] for the cw gradient experiment. Neuman provides a helpful insight for the δ-dependence by considering spins jumping between the positions corresponding to the two barriers. He shows that the phase distribution becomes Gaussian after a large number of wall encounters. The spins at the extremes in the distribution are those that get "stuck" at the barriers and their phase differences increase linearly with time δ.

Irv Lowe has pointed out to me that the rapid diffusion limit can be obtained by considering the dephasing of the spins in the presence of the field gradient as a T_2 process where signal should decay as $\exp(-\delta/T_2)$. Slichter (on

p.154 of the 1963 edition and pp.212-213 in the 1990 edition) shows that $1/T_2=\gamma^2H^2\tau$ for spins that jump between two fields $\pm H$ and stays at each value for time τ. In our case, $H=ag$ and $\tau=a^2/D$ so the signal exponent becomes $-\delta/T_2=-\delta\bullet\gamma^2\bullet a^2g^2\bullet a^2/D=-\delta\gamma^2g^2a^4/D$ which is the desired result.

At first sight, I had a problem thinking about the 1/D dependence for rapid diffusion. However, it is clear that as D increases with fixed δ, the phase distribution narrows because all "phase paths" become more similar as the number of wall encounters become large in the same amount of time. Furthermore, diffusion during a gradient pulse makes the spin phases more similar, immediately after the pulse. For infinitely large D, the phases will peak at the average value. Inbetween the gradients, the spins will behave as though they never saw any gradient pulses, so the mechanism that gave rise to attenuation in the free and restricted diffusion regimes goes away, too.

Callaghan points out that diffusion "imaging" has no resolution limit in the usual sense. This is true but apparently not in the fast diffusion regime because we need to overcome this "peaking" of the spin phases during the gradient pulses in order to measure the attenuation caused by diffusion and this will require stronger and stronger gradients! So, it seems that we cannot put one over on nature.

I am grateful to my colleagues in the lab who offered much (most?) of the insights here. They are Arvind Caprihan, Irv Lowe, Dean Kuethe, Allen Waggoner, and Lee Wang. I welcome further inputs. Lee's derivation, which started all this, will be submitted for publication soon.

Eiichi Fukushima

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June 22, 1994
(received 6/27/94)

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Small Angle Phase Shifts and Triple Quantum Filtered ^{23}Na NMR

Dear Dr. Shapiro:

Sodium is ubiquitous in nature. In cellular systems, a series of ionic movements across the plasma and mitochondrial membranes can be influenced by an increase in intracellular Na^+ thereby inducing changes in cellular metabolism. [1,2] In view of the possible role of sodium as a mediator of cell growth and that regulation of transmembrane sodium ion concentrations is important for cellular homeostasis, it has become of interest to develop non-invasive NMR techniques for probing transmembrane sodium concentrations and fluxes. The use of shift reagents[3] with standard pulse-observe NMR or in combination with multi-pulse multiple quantum NMR[4] of ^{23}Na is being explored in strategies for doing so.

A pulse sequence for a triple quantum filter[5] is presented for detecting biexponentially relaxing ^{23}Na. A spectrum obtained at 400 MHz of a mixture of 2M NaCl and 40% bovine serum albumin is also provided.

Yours sincerely,
Fernando Commodari

Fernando Commodari, Ph.D.
EMAIL:72704.537@COMPUSERVE.COM

[1] -E. Carafoli, *Ann. Rev. Biochem.* **56**, 395 (1987).
[2] -K. Sujita, K. Hosoi, Y. Shioda, and T. Ueha, *Biochem. Cell. Biol.* **69**, 29 (1991).
[3] -C. S. Springer, Jr.., *Ann. Rev. Biophys. Biophys. Chem.* **16**, 375 (1987).
[4] -G. S. Payne, A. M. L. Seymour, P. Styles, and G. K. Radda, *NMR In Biomedicine* **3**, 139 (1990).
[5] -Chun-Wa Chung and Stephen Wimperis *J. Magn. Reson.* **88**, 440 (1990).

```
/* VARIAN VXR-5000  PULSE SEQUENCE:  tqfb */

/* TO DETECT THE TRIPLE QUANTUM COHERENCE ARISING FROM THE */
/* BIEXPONENTIAL TRANSVERSE RELAXATION OF SODIUM */
/* Chun-Wa  Chung and Stephen Wimperis, J. Magn. Res. 88 440,1990*/
/* Personal Communication, April 30, 1990*/
/*Fernando Commodari, May 29 1990;  */

/*
- d1 - p1 (t1) - d2 - p2 (t2) - d2 - p1 (t3) - d3 - p1 (t4) - acq (t5)

        d1 = optional relaxation delay

        p1 = π/2 pulse with phase t1(echo) t3 (TQ creation) and t4 (read pulse)

        d2 = 1/2 the echo (TQ preparation) time (msec);
        not < (rof1+rof2+p2/2+p1/2)

        p2 = 180 pulse with phase t2

        d3 = TQ evolution delay (microsec); not < (rof2+rof1+p1)

        t5 = receiver phase */

            #include <standard.h>

            pulsesequence()
            {
            double d3, p2;
            d3=getval("d3");
            p2=getval("p2");

            /*PERIOD 1 */;
             status(A);
             delay(d1);
             loadtable("tqfb");
             stepsize(30.0,TODEV);

            /*PERIOD 2 */

             status(B);
             xmtrphase(t1);
             pulse(p1,zero);
             delay(d2-p1/2-p2/2-rof1-rof2);
             xmtrphase(t2);
             pulse(p2,zero);
             delay(d2-rof1-rof2-p2/2-p1/2);
             xmtrphase(t3);
             pulse(p1,zero);

              delay(d3-rof2-rof1-p1);

             /*PERIOD 3*/
              status(C);
              stepsize(90.0,TODEV);
              xmtrphase(t4);
              pulse(p1,zero);
              setreceiver(t5);

              }

/*  phase Table

t1= 11  1  3  5  7  9  11  1  3  5  7  9
     2  4  6  8  10 0  2   4  6  8  10 0
     5  7  9  11 1  3  5   7  9  11 1  3
     8  10 0  2  4  6  8   10 0  2  4  6

t2=11   1  3  5  7  9  5   7  9  11 1  3
     2  4  6  8  10 0  8   10 0  2  4  6
     5  7  9  11 1  3  11  1  3  5  7  9
     8  10 0  2  4  6  2   4  6  8  10 0

t3= 2   4  6  8  10 0  2   4  6  8  10 0
     5  7  9  11 1  3  5   7  9  11 1  3
     8  10 0  2  4  6  8   10 0  2  4  6
     11 1  3  5  7  9  11  1  3  5  7  9

t4= 0   0  0  0  0  0  0   0  0  0  0  0
     1  1  1  1  1  1  1   1  1  1  1  1
     2  2  2  2  2  2  2   2  2  2  2  2
     3  3  3  3  3  3  3   3  3  3  3  3

t5= 3  1  3  1  3  1  3  1  3  1  3  1
     0  2  0  2  0  2  0  2  0  2  0  2
     1  3  1  3  1  3  1  3  1  3  1  3
     2  0  2  0  2  0  2  0  2  0  2  0 */
```

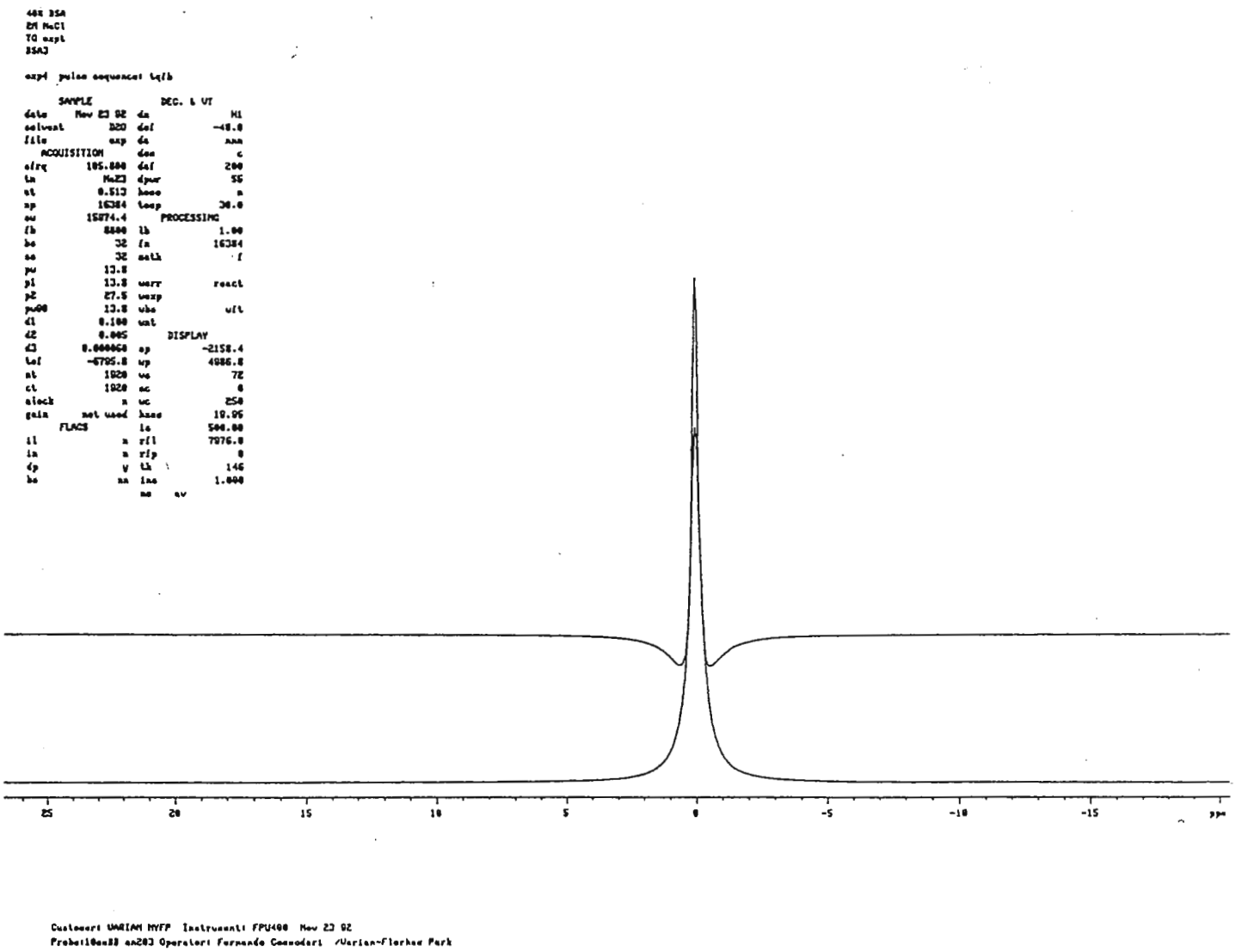

Figure 1: TQF spectrum of Na+ in a 2M mixture of NaCl in 40% Bovine Serum Albumin obtained on a UNITY 400.The bottom trace is in AV mode and the top is in phase-sensitive mode (PH). The following acquisition parameters were used : at=0.513 sec, SW=15974.4,ss=32, pw90=13.8 µsec, d1=100 msec, d2=500 msec, d3=60 µsec, and nt=1920.

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