TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 361

October 1988

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FORTHCOMING NMR MEETINGS

30th ENC (Experimental NMR Conference), April 2-6, 1989; Asilomar Conference Center, Pacific Grove, California; Conference Chair: A. N. Garroway; Contact Ms. Judith A. Watson, ENC Conference Center, 750 Audubon, East Lansing, MI 48823; (517) 332-3667.

The Society of Magnetic Resonance in Medicine - Eighth Annual Scientific Meeting and Exhibition, August 12-19, 1989; Amsterdam, The Netherlands; Contact: The S.M.R.M. Business Office, 1918 University Ave., Suite 3C, Berkeley, CA 94704; (415)841-1899, FAX (415)841-2340.

Additional listings of meetings, etc., are invited.

All Newsletter Correspondence
Should Be Addressed To:

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

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DEADLINE DATES

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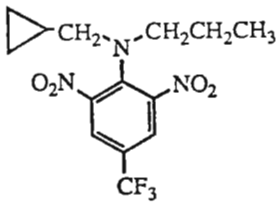
29 August 1988 (received 9/1/88)

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

In Vivo Fluorine NMR Studies of Metabolism

Dear Barry,



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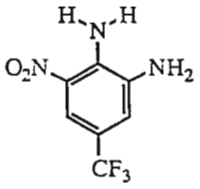
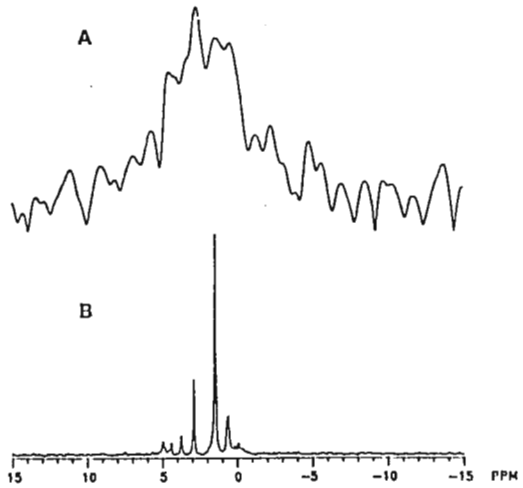


II

With the installation of our GN-300 with a 89 mm magnet we have been able to start studies of metabolism of various fluorinated compounds *in vivo* using surface coil techniques. Previous work in the lab (now in press in *Chemical Research in Toxicology*) had shown that diamine **II** is the major urinary metabolite of the herbicide Profluralin (**I**) in the rat. It was thought that **II** would be the "end product" of a series of metabolic transformations and it would appear in the liver, and ultimately in the urine, unchanged if it were ingested. A dose of diamine **II** was administered to a rat at a rate of 200 mg/kg. Urine was collected over a 24 hour period post ingestion and examined by fluorine nmr (Trace B in the Figure). Interestingly, there are at least a dozen distinct fluorinated species present in the urine, although the major compound present, identified by means of it's chemical shift, is unreacted **II**.

A surface coil examination of the liver of another rat treated in the same way was carried out; Trace A of the Figure indicates the spectrum observed 15 hour post ingestion. The resonance at *ca.* 1.2 ppm in this spectrum presumably corresponds to the diamine while the resonance at *ca.* 2.5 ppm corresponds to an acetylated form of this compound. The presence of other compounds is suggested by the spectrum but these have not been identified.

It is clear that compound **II** is *not* a stable product of the metabolism of Profluralin but, more likely, is simply the product formed most rapidly or by the largest number of pathways as **I** is detoxified.



Comparison of fluorine-19 nmr spectra at 282 MHz obtained from (A) liver in vivo at 15 hours post ingestion and (B) crude urine collected 20 hours post ingestion of diamine II.

Sincerely,

A. R. Jacobson
Postgraduate Research Chemist

J. T. Gerig
Professor of Chemistry

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CSI 2T Applications

Shielded Gradients and Localized Spectroscopy

Eddy current effects are the leading cause of errors and lack of consistent results in gradient localization methods. It is not surprising, then, that actively shielded gradients, which have dramatically reduced eddy currents, represent a significant technology advance for all forms of B_o gradient volume localization and spectroscopic imaging methods. The fast rise time and high gradient strength characteristics of the coil used in these experiments are also important.

Even without pre-emphasis, shielded gradients recover fast enough to obtain spectroscopic information at 1 msec or less after a strong gradient has been turned off (Fig. 1).

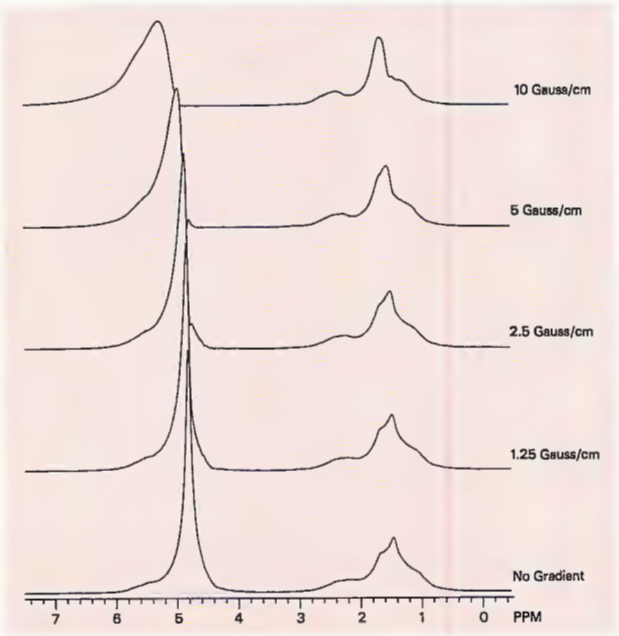

Fig. 1—Using an oil/water phantom, a 10 G/cm gradient will create a water frequency profile extending from 156 KHz to 280 KHz away from normal water resonance. Residual gradient effects of less than 0.01% (50 Hz at 10 G/cm) are observed in a spectrum acquired beginning 1 msec after a 20 msec gradient pulse.

As an example, a 4DFT spectroscopic imaging technique can resolve the four frequency domains that are associated with an NMR signal from an object: x-, y-, z-spatial coordinates and chemical shift δ. The above technique can be a practical alternative to single volume localized spectroscopy. This method allows phosphorous spectra to be obtained from well-defined regions as demonstrated in the following experiment, which was carried out on a GE CSI 2T system using high-strength, shielded gradient coils (Fig. 2). The phase-encode time is kept short (on the order of the dwell-time) to minimize phase-errors in the final spectra, as well as to avoid loss of signal due to T2 decay, which is significantly short in biological phosphates.

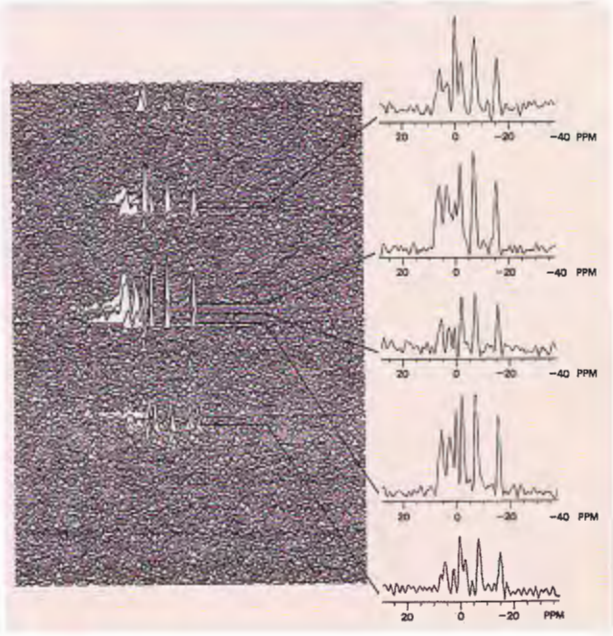

Fig. 2—Stacked plot showing 512 phosphorous spectra from 60 mm cubed region of a live rat. Each trace corresponds to 7.5 mm cubed region (voxel) from within the region of interest. The offset traces clearly show the achievable spectra and spatial resolution of the technique, as well as demonstrating localization of the liver phosphorous metabolites from that of overlying skeletal muscle. Total acquisition and processing time was two hours.

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Dalhousie University

Department of Chemistry
Halifax, Nova Scotia
Canada B3H 4J3
(902) 424-3305

August 22, 1988
(received 9/2/88)

Dr. Bernard L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303 USA

Dear Barry:

Anisotropy of Indirect $^{31}P, ^{199}Hg$ Coupling Constants

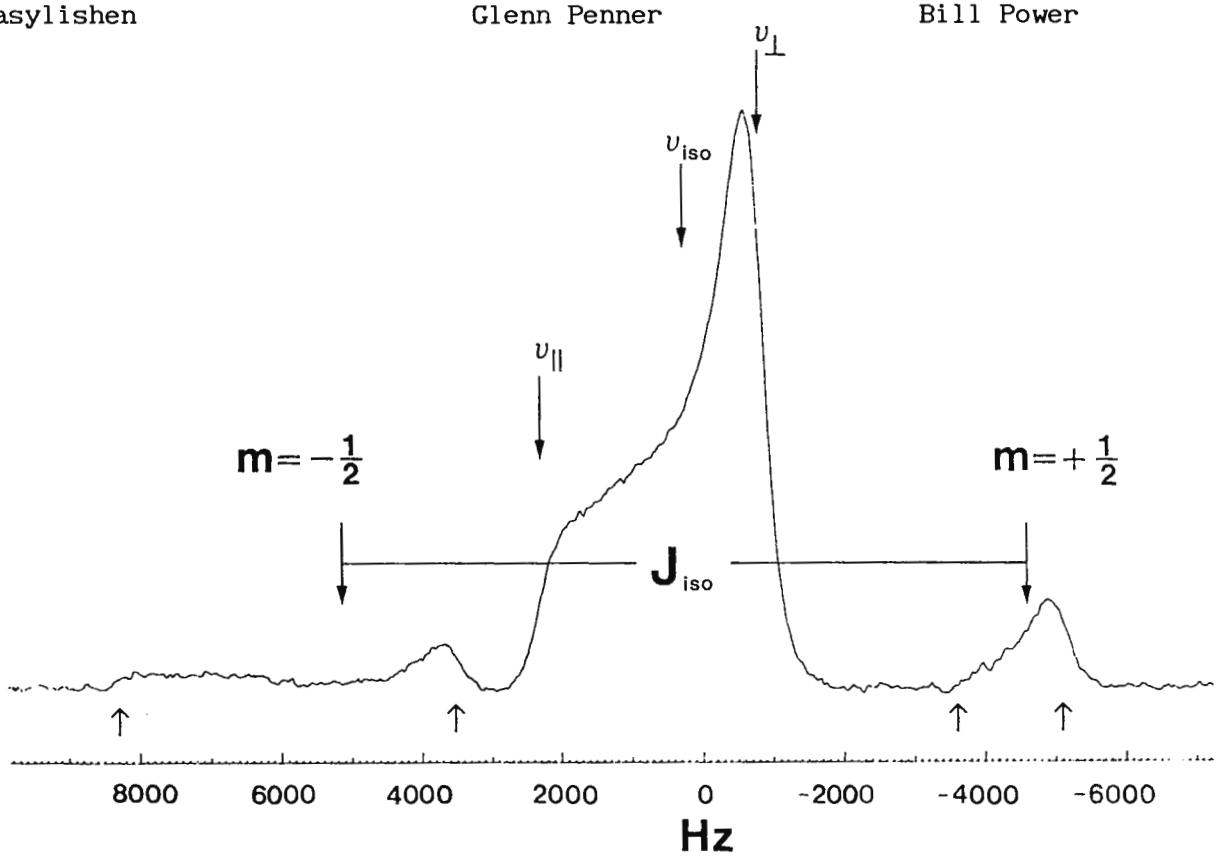
Recently we have measured a large anisotropy for $^{1}J(^{31}P^{199}Hg)$ in $[HgP(o\text{-tolyl})_3(NO_3)_2]_2$. The ^{31}P nmr spectrum of a solid powder sample is shown below. Note that the axially symmetric powder patterns resulting from the two different spin states of mercury-199 (natural abundance 16.8%) have very different breadths; 4750 and 1450 Hz respectively for the high and low frequency satellites. If one assumes that $J(^{31}P, ^{199}Hg)$ is axially symmetric, the following results are obtained: J_{iso} = 9660 Hz, J = 13,110 ± 250 Hz, J = 7940 ± 250 Hz thus ΔJ = 5170 Hz. The implication of this substantial anisotropy in J(P,Hg) is that mechanisms other than the Fermi contact mechanism must play an important role in the transfer of spin information between these two nuclei. Further details will appear in a special issue of Can. J. Chem. dedicated to Professor C. A. McDowell on the occasion of his 70th birthday.

Yours sincerely,

Rod Wasylishen

Glenn Penner

Bill Power



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DEPARTMENT OF BIOPHYSICS

August 22, 1988
(received 8/27/88)

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

Dear Dr. Shapiro:

We have recently explored the outer coordination sphere domains of a paramagnetic transition metal complex in aqueous solution with our field cycling spectrometer. Our motivation for such a study is to probe the structure and mobility of water molecules in the vicinity of such complexes as well as to measure the magnitude of the outer sphere contribution to the overall relaxation rates in the hexa-aquo metal complexes.

Three different complexes of Cr^{3+} were studied in aqueous solution at various field strengths ranging from proton Larmor frequencies of .01 MHz to 200 MHz. These complexes include hexacyanochromate(III), trioxalatochromate(III), and trimalonatochromate(III). The first two complexes have no first coordination sphere protons.

Representative results are shown in the Figure. The dominant mechanism of water proton relaxation in these solutions is modulation of the I-S dipolar interaction between the water proton nuclear spin and the central metal ion electron spin by the relative translational diffusion of the spin containing species as well as by the rapid relaxation of the unpaired electron spin. The shapes of the relaxation plot rule out an important model in which the water molecules interact with the complex anion perhaps through hydrogen bonds for a time long enough for the hydrated entity to rotate. If this were the mechanism, the relaxation profiles would be described by the Solomon, Bloembergen, and Morgan equations (1), which fail in this case.

The relaxation profiles for the three cases are included, along with their fits to the translational diffusion theory developed by Jack Freed (2). In the case of the trichelate complexes, inclusion of relaxation of the electron spin was necessary to obtain a fit to the data. However, for the cubic hexacyano complex, the electron spin relaxation time is relatively longer and modulation of the dipolar interaction is solely through the translational motion of the water and the complex.

By ruling out the rotational model, we can estimate an upper limit to the lifetime of any hydrogen bonding interactions at the surface of the anion. That is, the hydrogen bond lifetime must

be less than the rotational correlation time of the complex or about 40 ps. Finally, the diffusion coefficients obtained from the analysis, 2×10^{-5} cm^2/s at 298 K, which is the sum of the individual diffusion coefficients of the water and the complex, show that the water molecule mobility is ultimately perturbed very little by the presence of the complex ion.

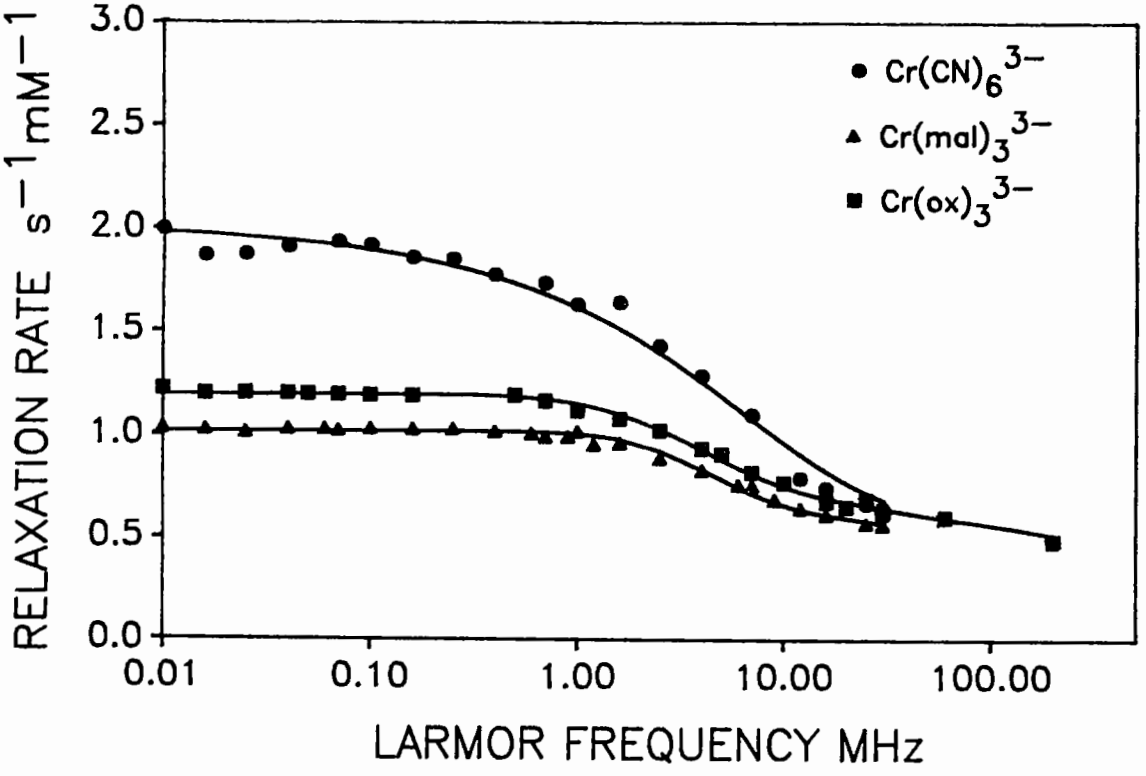
Sincerely,

Robert G. Bryant

Cathy C. Lester

(1) Solomon, I., Bloembergen, Nl J. Chem. Phys. 1956, 25, 261. Bloembergen, N., Morgan, L. O., J. chem. Phys. 1961, 34, 842.

(2) Freed, J. H., J. Chem. Phys. 1978, 68, 4034.



University of Edinburgh

Department of Chemistry

West Mains Road, Edinburgh, EH9 3JJ Scotland.

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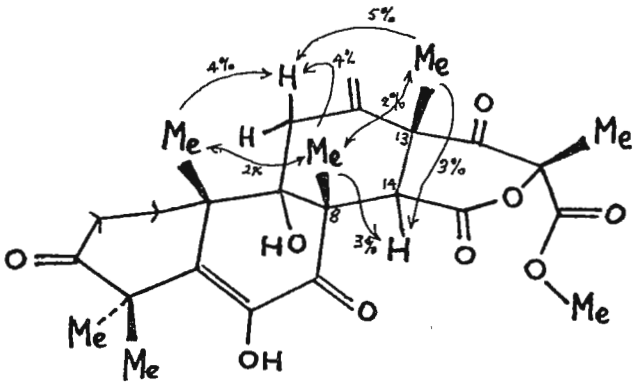
Professor B.L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto
California 94303

29th August 1988
(received 9/13/88)

Dear Barry,

Another "unexpected" proton NOE

Our previous letter (349-47) reported the observation of an NOE between diaxial protons in a monosaccharide derivative. Since then we have found another. During the complete assignment of the proton and carbon-13 nmr spectra of Terretonin we obtained some homonuclear NOE difference spectra to assist in distinguishing between the proton signals from the six methyl groups which lie in the region δ1.3 to 1.9. The structure of the molecule is known from X-ray data and the NOE's obtained are indicated on the sketch below (solvent $CDCl_3$; irradiation period 10s; 90° observation pulse). Particularly unexpected were the enhancements observed for the axial H-14 whilst irradiating each of the axial methyl groups bonded to C-8 and C-13. These are located on the opposite side of the ring system and their protons never approach closer than 3.5Å to H-14. In the absence of the knowledge of the structure, these observations would have almost certainly been taken as evidence for a cis fusion between the C and D rings. This emphasises that one must be very careful about making stereochemical deductions from NOE measurements. We think the NOE arises because the underside of the molecule (as drawn) is remarkably devoid of protons and apart from the exchanging hydroxyl proton and on occasion the mobile methoxy group, the protons of these two axial methyl groups are closer than any others to H-14.



Yours sincerely,

Dr. I.H. Sadler

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NUCLEAR MAGNETIC
RESONANCE

JUNE 1988

NMR-33

CONCURRENT MULTINUCLEAR NMR

Experiments in which two or more nuclei are monitored simultaneously are becoming of increasing importance in biological nmr applications. ^{1}H, ^{13}C, ^{31}P, ^{23}Na, and others are all important components of metabolites, and the simultaneous observation of several of these nuclei allows the spectroscopist to monitor the time course of metabolic processes. In addition, simultaneous observation is more efficient, since it uses the relaxation delay of one nucleus to pulse and observe another. With the VXR Series S line of spectrometers, all it takes is a special probe (and possibly not even that much) in order to make this experiment work. RF flexibility permits rapid switching between nuclei, and Varian's FLIPS™ pulse sequence language (Flexible, Logical, Intelligent Pulse Sequences) permits coding of both simple and complex variants of these experiments.

Varian's standard broadband switchable probe has two observation ports; one of which can be tuned to ^{1}H or ^{19}F, and the other of which can be tuned to any nucleus in a broad range (the actual range is field-dependent, but is typically ^{15}N to ^{31}P). In the favorable case of observing two X nuclei which are close in frequency, such as ^{23}Na and ^{13}C, it is actually possibly to observe signals from both nuclei from the same coil with no retuning. This allows the triple nucleus experiment ^{13}C-^{23}Na-^{1}H to be run on a standard switchable probe with no modification whatsoever; other combinations would require a special probe.

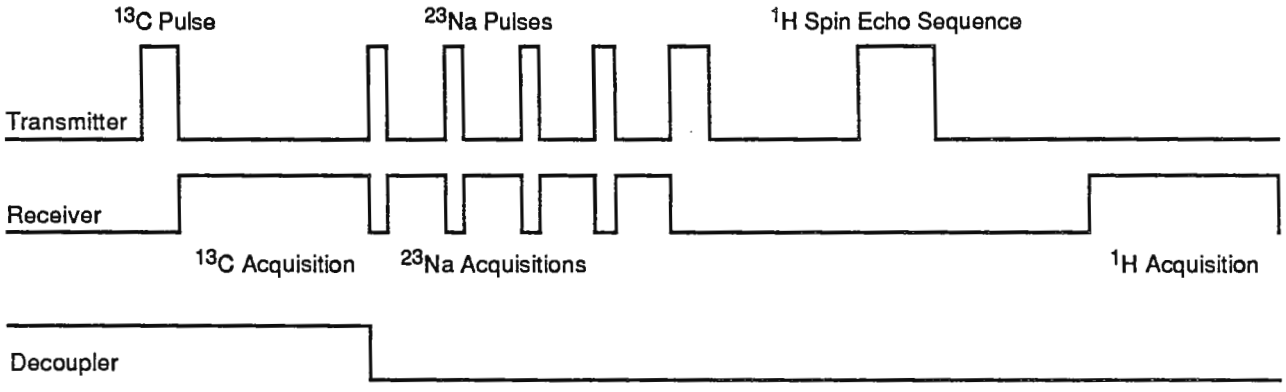

Figure 1: Pulse diagram for a typical concurrent multinuclear experiment. In the actual experiment shown in Figure 2, eight ^{23}Na FIDs were acquired, each with an acquisition time eight times shorter than that used for carbon or proton.

Changing the observation frequency during the course of a pulse sequence is accomplished with a single pulse sequence statement, with a second statement required to change configuration from high to low frequency or vice-versa. The frequency change itself takes only microseconds, while accompanying changes of relays, etc. (only necessary if ^{1}H is one of the nuclei) are accomplished in under 30 milliseconds. With the built-in flexibility of FLIPS, innumerable variants of the pulse sequence are possible. The number of nuclei can be two, three, or even more; each nucleus has its own individually controllable frequency, offset, and pulse width; a nucleus can be set to have a shorter acquisition time with multiple acquisitions taken; and essentially any pulse sequence can be used.

In the example shown in this note, a piece of raw swordfish was obtained and packed into a 10 mm nmr tube, surrounded by D_2O. The pulse sequence used consisted of a single ^{13}C acquisition, eight shorter ^{23}Na acquisitions, and a single ^{1}H acquisition obtained using a spin-echo pulse sequence. Eight acquisitions were used for the ^{23}Na since that signal has a significantly shorter T_1 and T_2, and the use of eight shorter acquisitions provides a $\sqrt{8}$ improvement in signal-to-noise for the ^{23}Na signal (after co-addition of the eight FIDs). The ^{1}H spectrum was acquired using a spin-echo sequence in an attempt to reduce the relative height of the H_2O signal present in the spectrum.

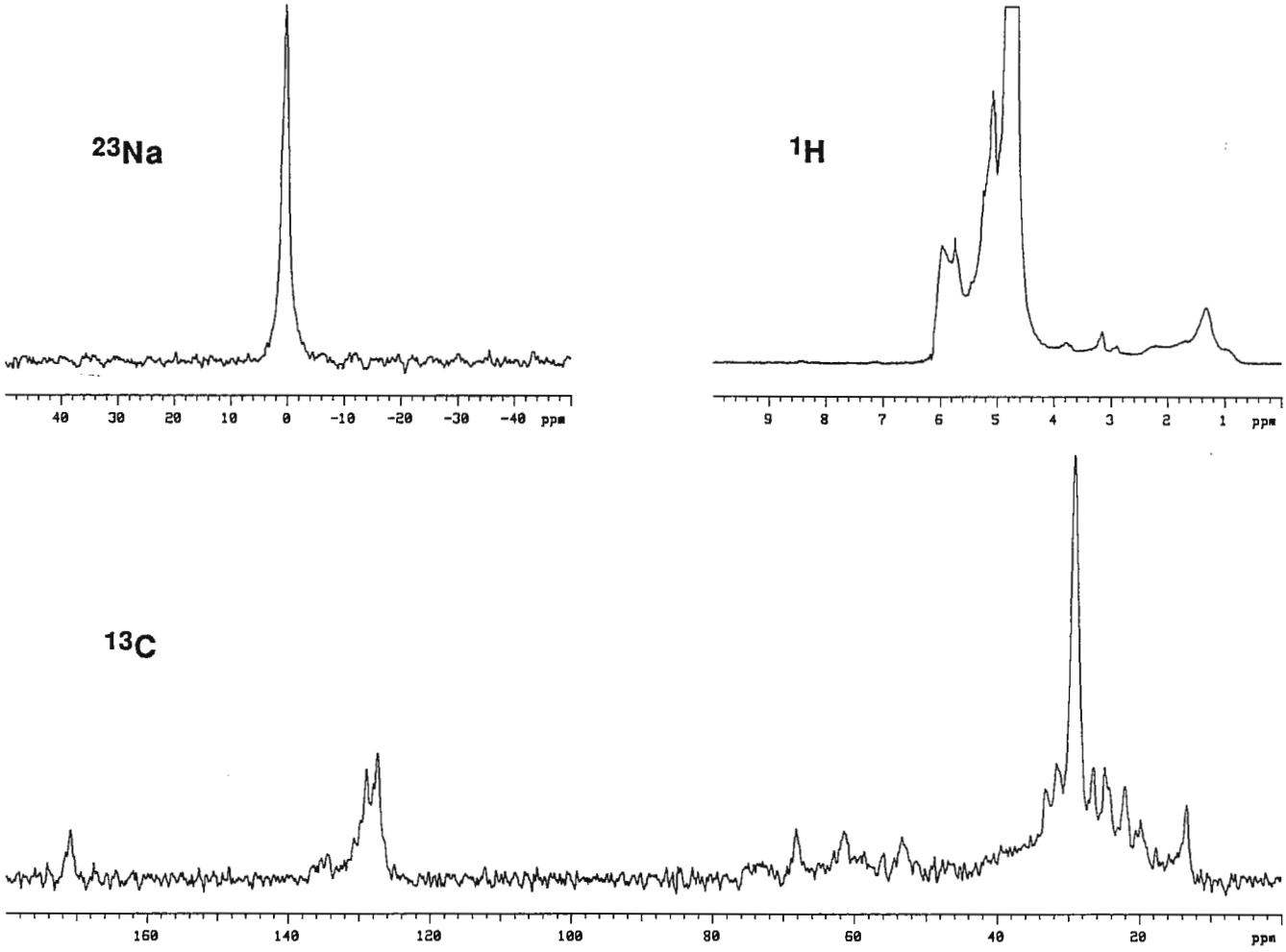

Figure 2: ^{13}C, ^{23}Na, and ^{1}H spectrum of a piece of raw swordfish, packed in a 10 mm nmr tube and surrounded by D_2O. The spectrum were acquired using the pulse sequence shown in Figure 1.

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Dr. B.L. Shapiro
966 Elsinore Court
Palo Alto, CA
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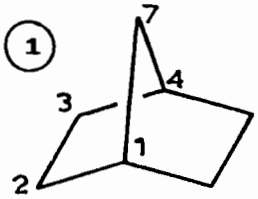
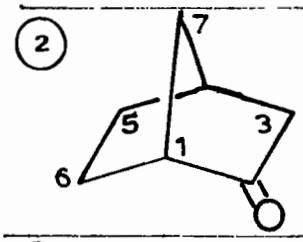
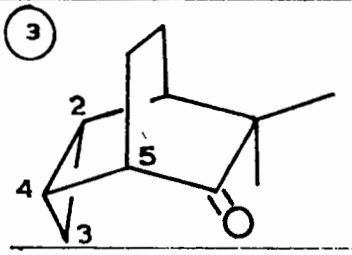
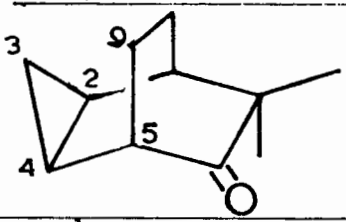
September 21, 1988
(received 9/26/88)

Dear Barry, Trends (?) in ^{2}H-induced $^{2}\Delta$ shifts for ^{13}C

As you are aware, I use ^{2}H-induced isotope shifts in ^{13}C spectra to confirm assignments in ketones after remote $^{1}H/^{2}H$ exchange. Some stereochemical differences seem fairly consistent and it was interesting that a recent paper from Harald Gunther's lab [MRC, **26**, 408 (1988)] included the comment that, in norbornane (**1**) "isotope shifts over two bonds show no special behavior and differ only slightly from" the ethane value (93.5 ppb). But, they noted that $^{2}\Delta$ for exo and endo-^{2}H-2 at C-3 parallels $^{3}J_{H,H}$(exo) > $^{3}J_{H,H}$(endo) for the C-2,-3 fragment. The same trend obtains in methylated norbornanones examined here. More recently examination of **3** revealed the opposite tendency for $^{2}\Delta$ and vic J in the cyclopropyl ring. The $^{2}\Delta$ data for norcamphor derivatives **2a-e** (a = 3,3-Me_2; b = 3.3.7.7-Me_4; c = 3,3,syn-7-Me_3; d = 1.7.7-Me_3 and e = 1.3.3.7.7-Me_5) and two isomeric [3.2.2.0] ketones are listed in the Table. There are some small differences in **2** vs **1** and methyl substitution appears to attenuate the shifts in some cases.

Skeleton	^{2}H location	$^{2}\Delta$ effects (in ppb)	
(1) 	exo-^{2}H-2	87 (C-1)	120 (C-3)
	endo-^{2}H-2	101 (C-1)	89 (C-3)
	^{2}H-1	104 (C-2)	91 (C-7)
	^{2}H-7	89 (C-1,4)	
(2) 	exo-^{2}H-6	60 (C-1)[a]	110-115 (C-5)[a]
	endo-^{2}H-6	70-90 (C-1)[b]	90-95 (C-5)[a]
	^{2}H-1	105 (C-6)[c]	85-100 (C-7)[d]
(3) 	^{2}H-4		126 (C-2) 128 (C-3)
	exo-^{2}H-3		95 (C-2) 98 (C-4)
	endo-^{2}H-3		124 (C-2) 120 (C-4)
	^{2}H-4	100 (C-5)	120 (C-2,C-3)
	^{2}H-9	75 (C-5)	112 (C-8)
	exo-^{2}H-3		90 (C-2,-4)

[a] **2a-3**; [b] **2a-c**, 85-90; **2d,e**, 70-75 ppb; [c] **2a,b**; [d] **2a**, 100; **2b,c**, 85 ppb.

I hope these data may interest one or two readers.*

*FIRST COME, FIRST SERVED. THE THIRD READER IS OUT OF LUCK. ED.

Sincerely,

J.B. Stothers (Univ. of Western Ontario)

UNIVERSITÀ DI MILANO

DIPARTIMENTO DI SCIENZE MOLECOLARI AGROALIMENTARI

VIA CELORIA, 2
20133 MILANO
TEL.(02) 2663662

Prof. B.L. SHAPIRO
Editor TAMU NMR Newsletter
966 Elsinore Court, Palo Alto
CA 94303 U.S.A.

(received 9/24/88)

"Assignment of ^{31}P phosphates in d(CGTACG) and in the complex with daunomycin"

Dear Barry,

we had recently to face the problem of assigning ^{31}P signals in oligonucleotides for a study of intercalation with antitumor agents of the daunomycin class. As phosphorus atoms are strategically located in the backbone of nucleotides, ^{31}P resonance provides a unique information on the deoxyribose-phosphates chain, but a problem in using this information is the difficulty of signal assignment. For oligonucleotides longer than a tetramer, the conventional 2D ^{31}P-H heteronuclear correlation (HETCOR) NMR spectroscopy was often unsuccessful, because the small values of H-P scalar couplings involved require relatively long D_1 and D_2 delays, which lead to a considerable loss of sensitivity (particularly at 7 T field, at which we work). ^{31}P-H reverse detection (^1H detection) experiments has been used to assign ^{31}P signals in a dodecamer (1) and hexamer duplex (2). Very recently Gorenstein (3) modified the conventional COLOC pulse sequence with direct detection to assign the phosphates in a 14 base pair oligomers.

We have slightly modified the HETCOR pulse sequence and we succeeded in assigning the ^{31}P signals in a hexamer and an octamer. We report here on the results obtained with the self-complementary hexamer d(CGTACG).

In our case we found that some increase in sensitivity is gained starting acquisition just after the last ^{31}P 90° pulse, i.e. setting D_2 to zero, and acquiring therefore without BB decoupling. The 2D spectrum (Fig.1) was then transformed in the absolute value mode. The identification of the cross-peaks was done through the three-bond and four-bond coupling of ^{31}P with H-3' and H-4' respectively because H-5' interactions could not be utilized, being their signals indifferentiated.

In the complex with daunomycin, the attribution of phosphates was done by following each ^{31}P signals on addition of increasing amounts of drug at 45°C. At this temperature the signals are in the fast exchange regime, and are enough narrow to be followed individually through the titration.

At 45° the free hexanucleotide is 66% double helix (the equilibrium constant for the melting process was derived from variable temperature measurements), but it exists entirely as double helix even at 45°C when bound to daunomycin, the intercalation acting as a stabilizing factor.

When the solution with a molar ratio R = drug/duplex = 1 is cooled below 30°C the resonance of C_5pG_6 phosphates splits in two signals, which belong to the free (-1.1 ppm) and to the bound (+ 0.4 ppm) species connected by slow chemical exchange (Fig.2).

C_5pG_6 phosphates are the only ones which show remarkable temperature effect and lowfield shift (1.5 ppm) with drug intercalation, while minor local deformations are experienced by C_1pG_6 and G_2pT_3. We have thus concluded that the hexanucleotide binds in solution two molecules of daunomycin, which intercalate in the d(CG) sequence at both ends of the helix.

(1) V. Sklenar, H. Miyashiro, G. Zon, H.T. Miles, A. Bax, FEBS Lett. 208, 94 (1986)
(2) M.H. Frey, W. Leupin, O.W. Sorensen, W.A. Denney, R.R. Ernst, K. Wüthrich, Biopolymers 24, 2371 (1985).
(3) J.M. Fu, S.A. Schroeder, C.L. Jones, R. Santini, D.G. Gorenstein, J. Magn. Resonance, 77, 577 (1988).

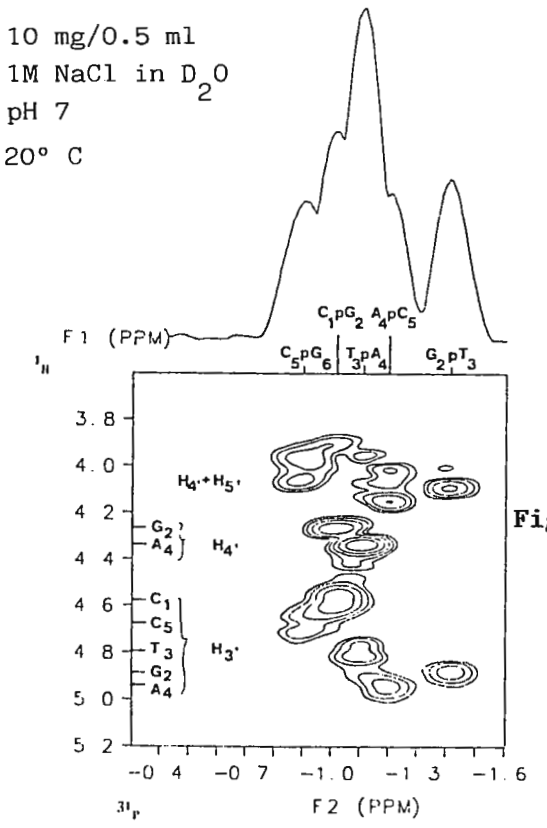


Fig.1

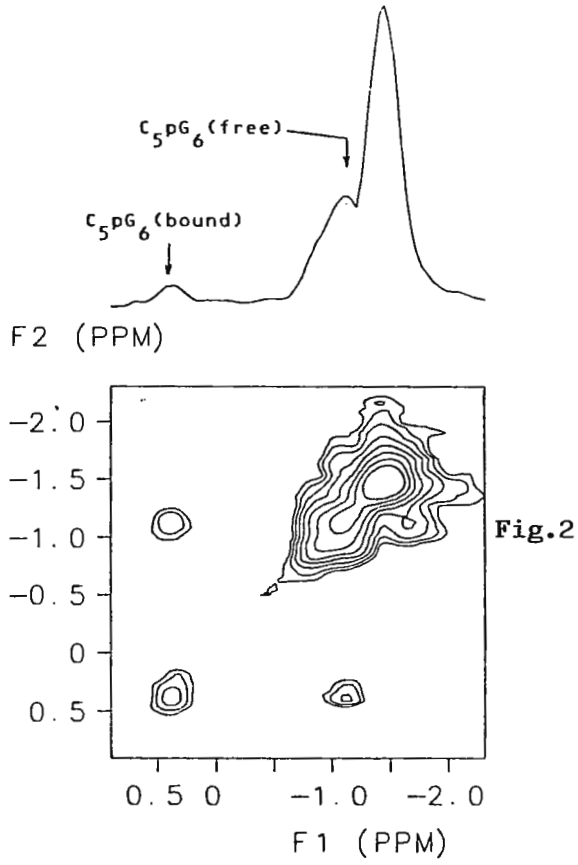


Fig.2

Sincerely yours

E. Ragg

R. Mondelli

THE UNIVERSITY OF ADELAIDE

BOX 498, G.P.O., ADELAIDE, SOUTH AUSTRALIA 5001

ORGANIC CHEMISTRY DEPARTMENT
G.M. BADGER LABORATORIES

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

31 August, 1988
(received 9/7/88)

TITLE : Temperature Calibration for ^{13}C Measurements

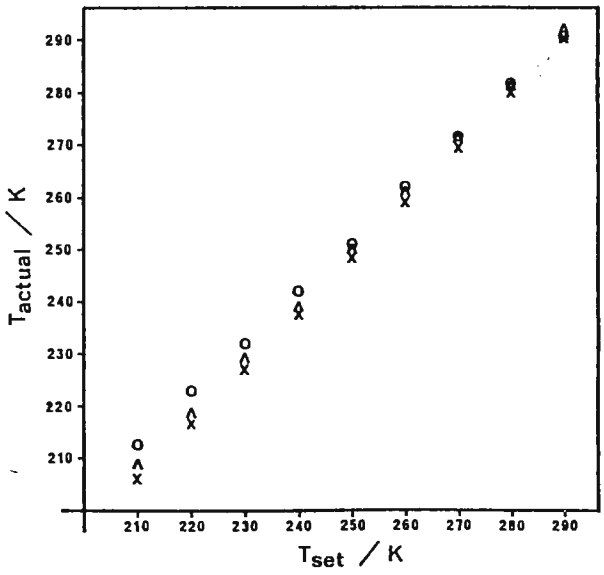
Dear Dr. Shapiro,

Our Bruker 10mm VSP (300MHz) probe was recently calibrated for temperature in the range 210-290K using ^{1}H observation of a standard MeOH solution[1]. The temperature was controlled by a Bruker B-VT 1000 unit. The correlation shows a discrepancy, from the set temperature, of about -5K at the lowest temperature, linearly varying to approximately zero at 290K (x).

To investigate the effect of ^{1}H broadband decoupling during ^{13}C measurements, the chemical shifts of a d6-acetone/CCl_4 (50/50) mixture[2] were correlated with T_{actual} under conditions of no decoupling, then repeated with a ^{1}H BB decoupler setting of 11H (power 2W), continuously applied. The heating effect was greatest at the low temperature (+6K) and least (+1K) at 290K (o).

The effect of the presence of ionic species on the heating caused by ^{1}H decoupling was investigated by adding 0.05M $Zn(ClO_4)_2$ to the above mixture and repeating the chemical shift calibration, followed by actual temperature measurement under BB decoupling conditions. The effect of the ions was to reduce the heating effect of the decoupler by about 4K at the lowest temperature, linearly upto 290K, where no significant difference was observed (^).

These results are critically dependent on experimental conditions, including N_2 gas flow (cooling gas), sample spinning rate, equilibration time and, obviously, sample composition. This emphasises the need for consistency and care in the temperature calibration and subsequent use of probes for dynamic NMR experiments.



Regards,

A Hounslow

A. M. Hounslow

P. Clarke

1. A.L. van Geet, Anal. Chem., 42, 679, 1970
2. J.J. Led & S.B. Petersen, J. Mag. Res., 32, 1, 1978

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Spectrometer Performance — AC Series

Summary of Specifications for Basic System Configurations AC Series 100, 200, 250, 300 MHz

Probehead (5 mm)	Nucleus	Test	90°pulse (μs)	S/N 100	200	250	300
^{1}H	^{1}H	0.1% EB	<10	35	85	120	175
$^{1}H/^{13}C$	^{1}H	0.1% EB	<15	20	45	70	90
	^{13}C	ASTM	<15	20	50	70	100
		10% EB		15	40	50	70
QNP	^{1}H	0.1% EB	<15	20	45	70	90
	^{19}F	0.05% TFT	<20	20	45	70	100
	^{31}P	48.5 mM TPP	<20	25	50	60	70
	^{13}C	ASTM	<15	20	50	70	100
		10% EB		15	40	50	70
VSP multinuc. ^{31}P–^{15}N	^{1}H	0.1% EB	<15	20	40	60	80
	^{31}P	48.5 mM TPP	<15	15	30	35	40
	^{13}C	ASTM	<15	20	50	70	100
		10% EB		15	40	50	70
	^{15}N	90% Form.	<25		5	8	10
			SSB %	**Lineshape (Hz)**			
All Probes (5 mm)	^{1}H	$CHCl_3$	<1	7/15	7/15	7/15	7/15
	^{13}C	C_6H_6	<0.5	3/7	3/7	3/7	3/7
				Resolution (Hz)			
All Probes (5 mm)	^{1}H	ODCB		0.2	0.2	0.2	0.2
	^{13}C	C_6H_6		0.2	0.2	0.2	0.2

Magnet:	Helium refill interval (days)			
Standard	120	120	120	120
Long hold time	200	200	190	180
Ultra-long hold time	365	365	350	340

EB = ethylbenzene (for ^{13}C with ^{1}H-dec.); ASTM=60% C_6D_6 in dioxane;
TFT=trifluorotoluene; TPP=triphenylphosphate; Form.=formamide (^{1}H-dec. without NOE);
SSB=spinning sidebands;
Lineshape: ^{1}H=$CHCl_3$ linewidth at ht. of ^{13}C-satellites/at 20% this level
^{13}C=C_6H_6 linewidth at 0.55%/0.11% level (^{1}H-dec.).
Dimensions and weights are approximate; voltage+10/–5% max. variation, otherwise power stabilizer required; other line freq. or voltage upon request.

	Standard	Options
Transmitter Freq. range	$^{1}H/^{13}C \pm 100$ kHz	full multinuc.[2]
Offset steps	100 Hz	0.01 Hz[1,2]
Phase shift steps	90°	<0.5°[1,2]
^{1}H-decoupler Freq. range	150 kHz	
Offset steps	0.01 Hz	
Phase shift steps	90°	<0.5°[1,2]
Max. power	5 W	40W[2]
Attenuator range	60 dB	80 dB[2]
Quad. receiver Spectral width	100 Hz – 100 kHz (cont.)	125 kHz[2], 50 kHz
Filter width (100 Hz Steps)	100 Hz – 100 kHz	100 Hz – 100 kHz; 150 kHz[2]
ADC	12-bit	16-bit
Computer Memory	256 K / 24-bit	up to 1280 K / 24-bit
Max. FT size	128 K words	512 K words
Multi-pulse timing resol.	0.1 μsec	0.025 μsec[2]
FT time (software)	1 K/1.5 sec	
Co-processor		8 K/1.5 sec[2]
Array processor		64 K/1.2 sec
Graphic display: colors	8	8
Pixel matrix	256 x 512	256 x 512
Plotter	A3 flat bed 8 colors	drum[2], HP with auto-feed
Printer	dot-matrix	
Storage	160 MByte disk, floppy	tape
Communication	RS 232	KERMET/ETHERNET® Fiber optic LAN

1. Standard with the AC 300E 2. Standard for AC-P version

Nitrogen refill interval (days)	Minimal room height (cm)	Weight approx. (kg)
9	276	250
10	263	220
14	297	250
Console	w 126 x d 85 x h 91 cm	
Height with display	123 cm	
Weight approx.	300 kg	
Power consumption	220 V/50 Hz/3 kW	

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Bâtiment 721
43, boulevard du 11 Novembre 1918
69622 VILLEURBANNE Cedex
Tél. 78 89 81 24 (secrétariat poste 33.70)

Villeurbanne, September 6, 1988
(received 9/13/88)

Dr B.L. SHAPIRO
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303 (U.S.A.)

T_2 MEASUREMENT WITH PROCESS CONTROLLER ON BRUKER AM 300

Dear Dr SHAPIRO,

The usual CPMG measurements of T_2 involve the following process :
- N F.I.D. are aquired for P echos (P number of points for the relaxation curve)
- a file is created giving the intensities of echos for T_2 calculation.

The number of points remains, generaly, small because a long time is necessary for each point ($5xT_1$).

In the physiological liquids the only important peak results from water and it is interesting to collect all the echos during a single CPMG sequence. This method, used in low resolution spectrometer like BRUKER PC 20, can be worked out in high resolution with the Process Controller help. It is possible to control the ADC by a micro-programme. The sampling rate and the gating are fixed by software. The points of measure are aquired at the maximum of each echo between two π pulses.
We obtain a pseudo F.I.D. and the Fourier Transform gives a lorentzian curve at zero frequency with $\frac{1}{\pi T_2}$ as width at half-height.

ADVANTAGES
- Short time for acquisition (Elimination of slow fluctuations)
  All the points are aquired during $5xT_1$
- Simple calculation of T_2 by a single Fourier Transform operation
- Elimination of any noise for frequencies higher than $4/\pi T_2$.

For $T_2 \simeq 2s$ a frequency > 0.5 Hz don't intervene in the calculation.

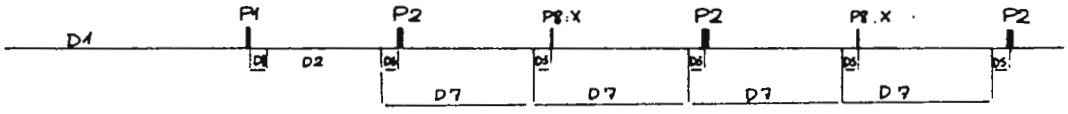
DISAVANTAGES
- The detection has to be at the exact frequency resonance
- Only one peak can be taken into account. If many peaks arise in the spectrum the first $\pi/2$ pulse will be selective.

Sincerely

J. DELMAU J.C. DUPLAN B. FENET

```
*********************************************************************
*                                                                   *
*                        CPMG-FLASH                                 *
*                                                                   *
*   MESURE RAPIDE DE T2 POUR ECHANTILLONS A RESONANCE UNIQUE        *
*                                                                   *
*********************************************************************

1  ZE
   D0                      ;Delai de stabilisation en temperature
                           ;de l'echantillon ( D0 > 10mn )
2  D1                      ;Delai de relaxation.
3  P1 PH1                  ;P1 pulse 90.
   D8 ADC                  ;ouverture du recepteur.
   D2 PH0                  ;initialisation  phase de detection
;************************  elimination des premiers echos pour
                           ;eviter la saturation du recepteur.
10 (D7) (D5 P2 PH2):T:E
   (D7)
   LO TO 10 TIMES UPR
;************************
20 (D7) (D5 P2 PH2):T:E    ;P2 pulse 180 et fermeture du recepteur
                           ;pendant P2. D7 determine la frequence
                           ;d'echantillonnage.
   (D7) (D5 P8):X          ;P8  impulsion de  declenchement  du
                           ;convertisseur.
   L1 TO 20 TIMES UPR      ;L1=TD ,nombre de points du FID c'est
                           ;a dire d'echos pris en compte.
                           ;Bouclage a la ligne 20.
   RCYC=2 PH4              ;fin de la sequence d'acquisition
                           ;avec definition de la phase du recepteur.
EXIT
;************************
                           ; cyclage de phase eliminant la composante
                           ;continue
PH0=0
PH1=0 2
PH2=1 1
PH4=R0 R2
```



D7 = D8 + D2 + D5

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5mm ^{1}H Probe

90^{o} Pulse 10 us @ 50 Watts		Sensitivity (0.1% EB)
Resolution 0.2 Hz	(ODCB)	200 MHz 80:1
Lineshape 10/20	(CDCl3)	300 MHz 160:1
		360 MHz 220:1
		400 MHz 300:1
		500 MHz 400:1

Reverse Polarization Transfer Probe
^{1}H {^{31}P-^{15}N} 5mm Probe

	5mm	10mm
90^{o} Pulse @ 50 Watts	15us	25us
Resolution (ODCB)	0.25	0.4
Lineshape (CDCl3)	10/25	18/40
Gamma H_2 (10W)		
^{15}N	2KHz	1KHz
^{13}C	3KHz	2KHz
Sensitivity (0.1%EB)		
200 MHz	60	100
300 MHz	120	200
360 MHz	170	280
400 MHz	200	330
500 MHz	300	500

Broadband Probes
High Band broadband probes cover the range from ^{31}P to ^{15}N for solutions up to 0.2 M salt. *^{31}P performance is 15% less for narrow bore magnets.*

5mm		200	300	360	400	500
^{31}P		30	60	85	100	150
^{13}C		30	60	85	100	150
^{2}H	NA=4	5	10	14	16	25
^{17}O	NA=100	20	40	55	65	80
^{15}N		4	8	10	12	16
10mm						
^{31}P		130	260	340	375	450
^{13}C		150	300	360	400	500
^{2}H	NA=4	15	30	40	50	60
^{17}O	NA=100	110	220	270	300	400
^{15}N		15	30	35	40	50
12mm						
^{31}P		150	300	400	500	550
^{13}C		180	360	500	600	700
^{2}H	NA=4	20	40	50	60	75
^{17}O	NA=100	125	250	300	350	500
^{15}N		15	30	40	50	60
20mm						
^{31}P		250	500	600	750	
^{13}C		300	600	700	800	
^{2}H	NA=4	30	60	70	90	
^{17}O	NA=100	180	350	450	550	
^{15}N		25	50	70	80	

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Instrumentation Note 3

Fun with your old shims

Last month we showed the Z_1 gradient spectrum a perfect H_0 field would give, and then looked at some results from real probes. These differed from theory in that they contained spikes; this month we'll show why two spikes are okay but more than two mean that the probe cannot be shimmed for good lineshape.

We find this useful, and you will to, in the following scenario: You're shimming a probe which is proving difficult, and you're <u>almost</u> able to make the lineshape specification. Each new setting of the high order shims looks promising, but never quite works. We have found that people who are persistant shimmers can spend days on a marginal probe, and still want to continue. With this test, which takes all of 10 minutes, you can convince anyone that a given probe cannot be shimmed.

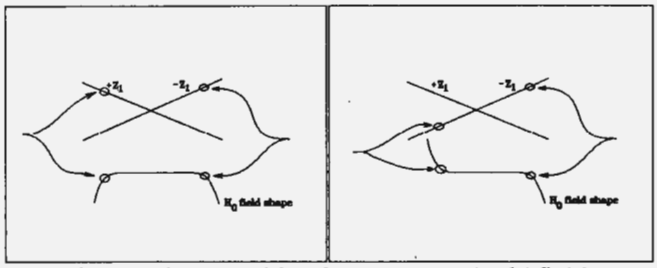
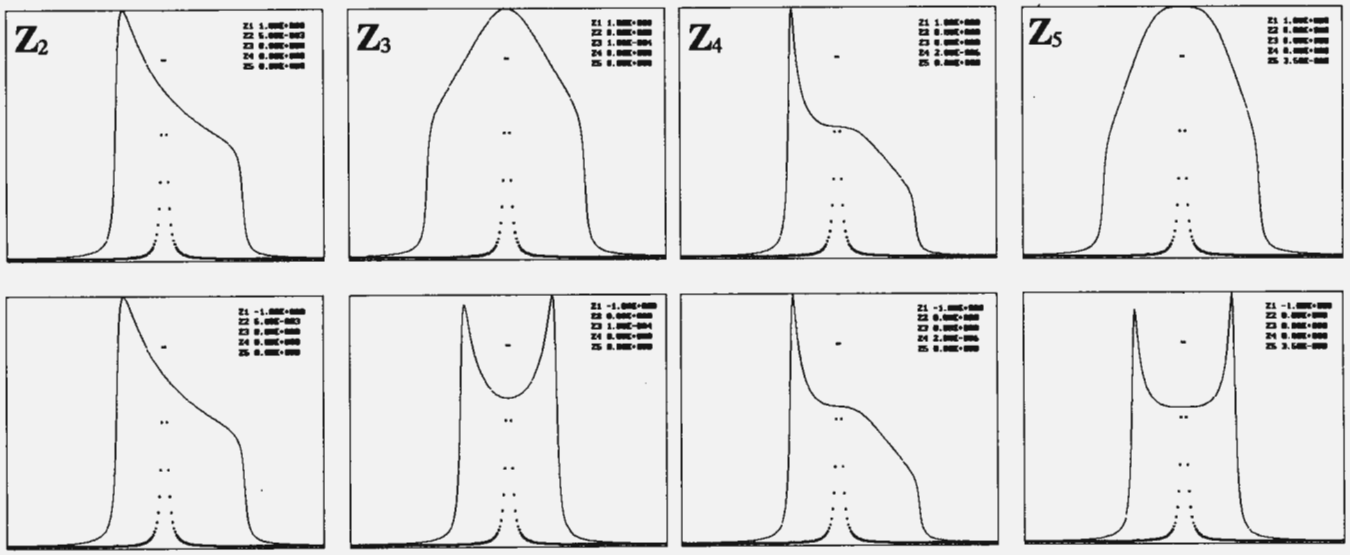


Fig. 5. Spikes resulting from even and odd fields

that one gradient cancels the shape at both ends and the other never cancels. It's easy to see that whenever the field changes smoothly from it's (uniform) value in the sample region, there should be two spikes. If there are more, that means that the field is not changing monotonically, and consequently, a higher order expression (shim correction) is needed to fit it.



We can continue to use the simulation program to generate lineshape for different conditions of H_0. If we apply higher gradients, one at a time, we see in the Figures above the result. Z1 is still used as a readout gradient, and the top and bottom spectra result from positive and negative values of Z_1. From this we see that the <u>pair</u> of Z_n gradient spectra have exactly 2 spikes- one each for even gradients, and two and none for odd gradients.

These spikes occur when the applied Z_1 gradient exactly counteracts a gradient present in the magnet, as shown in Fig. 5. (In this case the gradient is one caused by the higher order shim coil.) In Fig. 5a the dominant residual gradient is even, and both + and - Z_1 can cancel the field curvature and produce a spike. In Fig. 5b, the odd field shape means

One could fit the deconvoluted gradient spectrum to a power series to extract the shim correction needed but that usually isn't done. It just isn't necessary to analyse Fig. 6 to know that this field is fairly homogeneous, or Fig. 7 to know that this particular probe can never be shimmed.

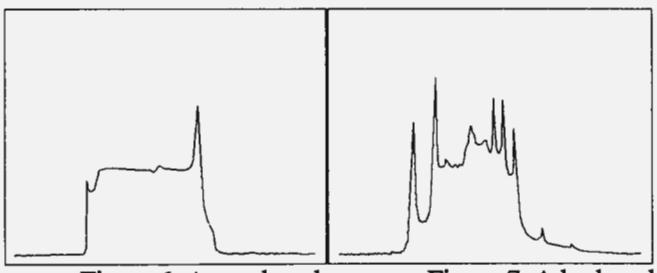
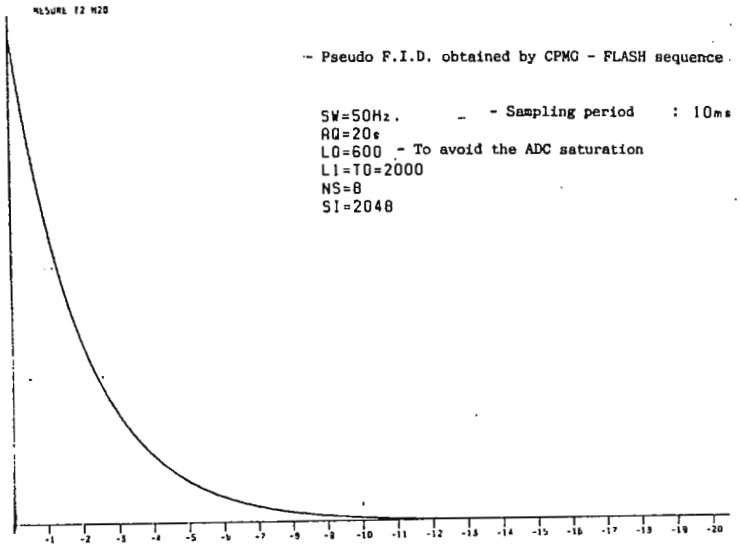
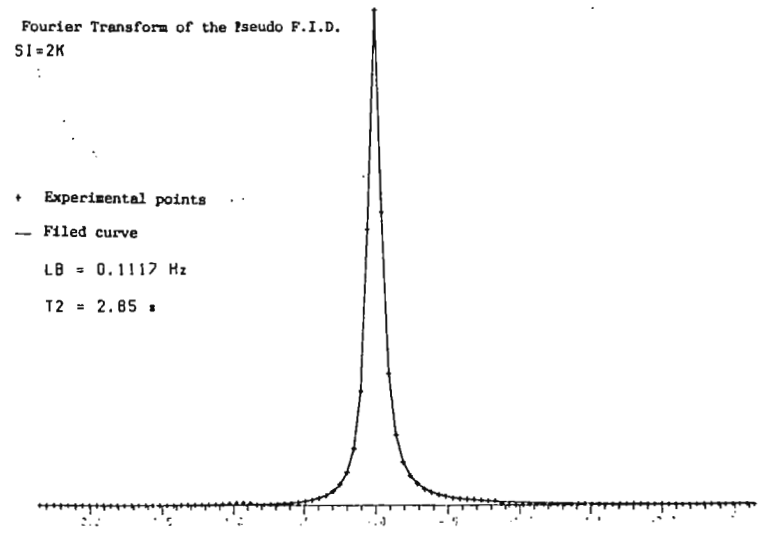


Figure 6. A good probe

Figure 7. A bad probe





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The Chemistry Division NMR laboratory is equipped with Bruker CXP-100 (solids/imaging), Bruker AM-300 (ultra-fast MAS probe), and Nicolet NTC-200 spectrometers. A GE Omega-300 NMR system is on order, and the purchase of a 500-MHz NMR is now being contemplated. Excellent resources in macromolecular modeling, computing and graphics are available.

Interested applicants should send a resume to:

Dr. Robert E. Botto
Chemistry Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Los Alamos

Los Alamos National Laboratory
Los Alamos,New Mexico 87545

(received 9/17/88)

DATE September 14, 1988

MAIL STOP MS G740

Prof. Barry Shapiro, Editor
Texas A&M University NMR Newsletter
966 Elsinore Court
Palo Alto, Calif. 94303

Dear Barry,

TITLE: **Disk Drives for Older Bruker Spectrometers**

We have a Bruker CXP-200 Spectrometer which was purchased about 8 years ago. It ended up equipped with a CDC MMD-24 Disk drive. That is a 24 Megabyte "Winchester" type drive, with no removable media. Since the disks are sealed, we have suffered no head crashes in all of the time we have had the drive. Recently the unit started to become a bit flakey giving lots of faults. We corrected the problem by cleaning the edge connectors on all of the pc boards in the drive but we decided that the drive was nearing the end of its dependable lifetime. We replaced it with a newer model CDC drive with fixed media, a FSD-160. For the computer afficionado, these are SMD interface drives They are completely compatible with the MMD's and CMD's on many Bruker (and other ?) spectrometers. They are pin for pin compatible with the CDC drives (CMD's and MMD's) provided with the earlier Bruker spectrometers. The trick is to let the Bruker controller (Board 10 in the Aspect 2000A) know what kind of drive it is talking to. We simply set the switch on Board 10 to a MMD-80. This will allow us to access only 80 Mbytes of the 160 available on the disk but that is still a lot better than the 24 Mbytes that we had before.

Bill Wageman, in INC-4, has replaced a couple of CDC CMD drives on an Aspect 2000A and a 3000 with CDC RSD-80's. These are drives similar to the FSD but with a total of 80 Mbytes of storage on removable disks. The claim is that the RSD design is more reliable than the old CMD and disk crashes should be less frequent than the 1 per year that seems to be common on most CMD drives. They have not had the drives long enough to comment on crash frequency but they are pin for pin compatible so are easy to install and get running.

Finally, both of the newer drives are about half as heavy and half as big as the older models making them easier to work on and move around. For users interested in these drives, it is probably worth buying new cables with them and be sure to get a "terminator" because the old terminator will not fit the new drive.

Sincerely,

Bill.

William L. Earl.

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13 September 1988

(received 9/26/88)

Dr. Barry Shapiro,
966 Elsinore Court,
Palo Alto, California 94303,
U. S. A.

Dear Barry:

Title: "HIGH POWER SATURATION OF NUCLEUS X "IN VIVO" VIA THE PROTON DECOUPLING CHANNEL"

In our last communication, which seems like yesterday to us but several years ago to your Ultimatum Department, we described a probe used to perform in vivo saturation experiments. We would now like to discuss the means of delivering both high and low power to this probe on a Bruker "in vivo" spectrometer which, like many others, has only a proton decoupling channel. In the first instance, we performed these experiments on a Bruker Biospec instrument which has a very wide range receiver. At the time of modification the magnet was not surrounded by a Faraday cage.

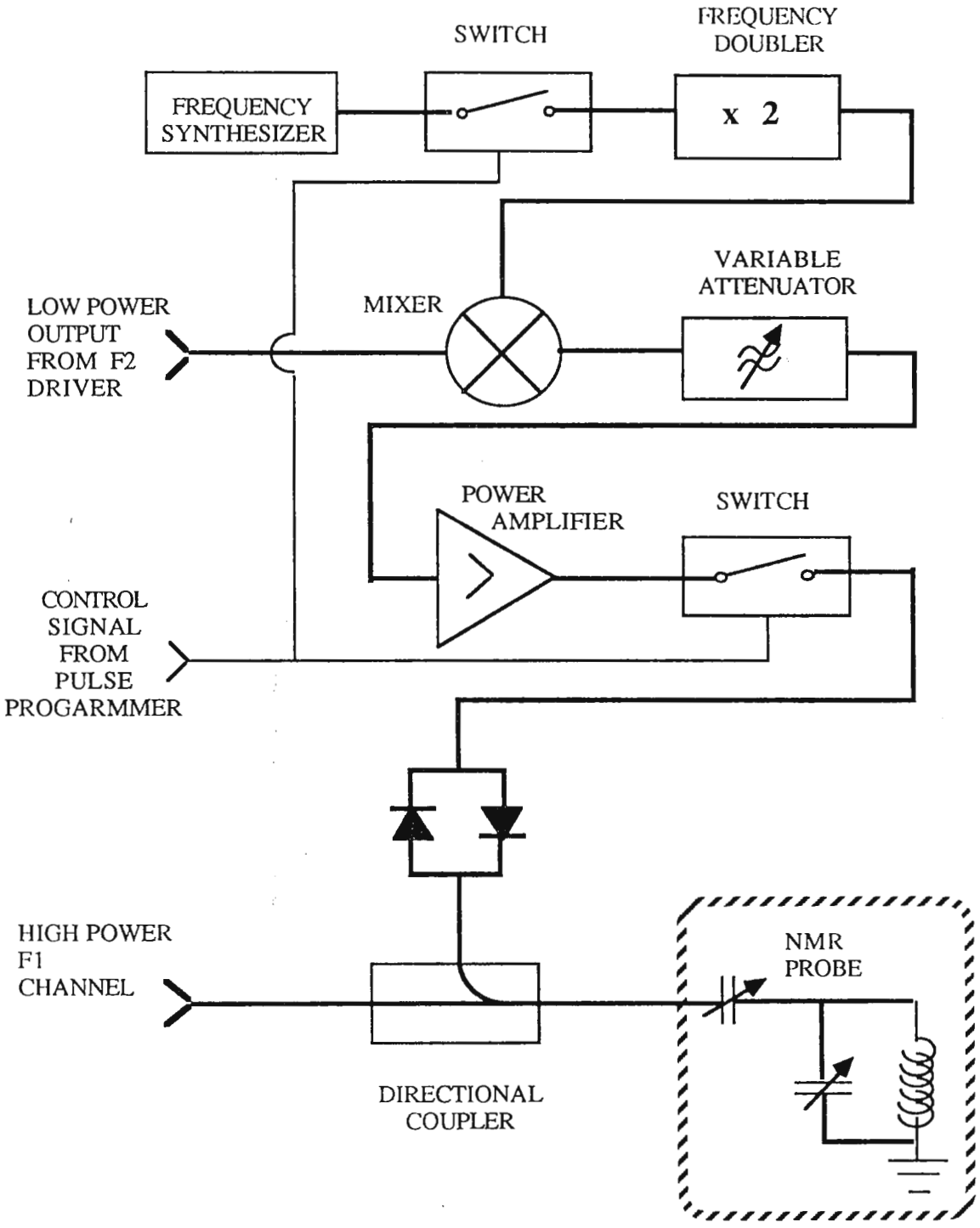
Our initial idea was to use the decoupler (200 MHz) frequency and a frequency synthesizer (119 MHz) to produce the desired 81 MHz for ^{31}P irradiation. This, even with gating, resulted in some leakage which caused saturation of the receiver. The functional solution was to obtain the 119 MHz by doubling 59.5 MHz as shown in the diagram. Provided the frequency of the synthesizer is set correctly, all other variables such as offset, power, etc. are under computer control. The shape of the pulse can be controlled using the so-called fifth channel. The double mixing with appropriate gating completely eliminates any leakage of the saturating field during acquisition.

This approach also works on an AM-360. The only difference is that two consoles from the same manufacturer have opposite polarity for the internal triggering pulses.

Kindest regards,

Paul Morris, Ian C.P. Smith, Marek Rydzy, John K. Saunders

Canada



Schematic diagram of the saturation channel

D, ^{13}C, ^{15}N, ^{17}O, ^{18}O

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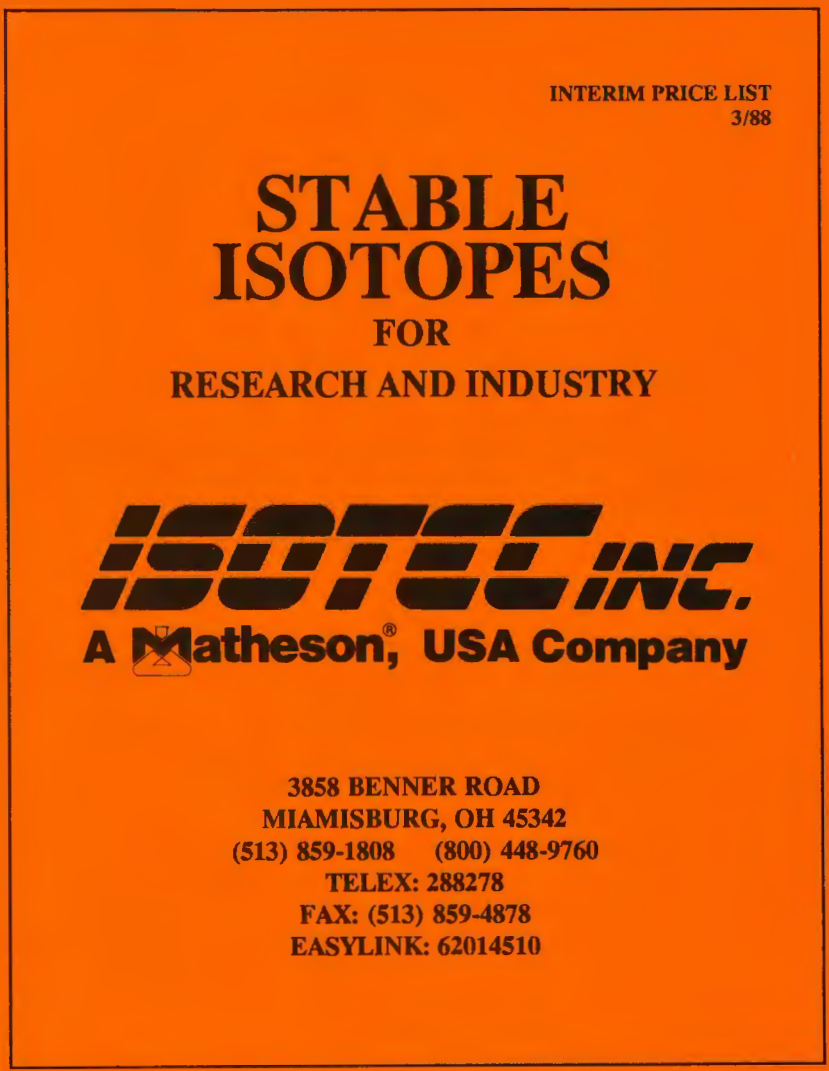


THE PROCTER & GAMBLE COMPANY
MIAMI VALLEY LABORATORIES
P.O. BOX 398707, CINCINNATI, OHIO 45239-8707

25 August 1988
(received 9/19/88)

Prof. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303

FAST F-19 MAGIC-ANGLE-SPINNING NMR

Dear Professor Shapiro:

The anti-caries benefit of fluoride-based dentifrices is due in large part to the formation of cavity-resistant fluorapatite (FAP). Pioneering work by James Yesinowski (1) demonstrated that solid-state ^{19}F MAS-NMR is particularly well-suited to the study of the mechanism by which fluoride is incorporated into the hydroxyapatite (HAP) lattice forming fluorohydroxy-apatite (FHAP) and the subsequent solid-state transformation to FAP. We are currently using ^{19}F NMR to study the surface chemistry associated with this fluoridation process.

To carry out this work one must come to terms with substantial ^{19}F homonuclear dipolar couplings. The static linewidth of CaF_2, for example, is greater than 33 KHz at 7 Tesla. Karen Ann Smith and Doug Burum (2) have recently demonstrated the ability of ^{19}F CRAMPS to give high-resolution spectra of inorganic fluorides. Our work with a variety of fluorides and fluoridated apatitics indicate that fast-MAS alone represents a viable option to multi-pulse techniques for reducing dipolar-broadening in these materials to levels where individual species can be identified and quantitated (3). Some representative data are shown below.

Figure 1 shows the ^{19}F MAS spectrum of calcium fluoride as a function of spinning speed. At 14 KHz the half-height linewidth is reduced to 1.7 KHz and 81% of the intensity resides in the centerband. Note that the more conventional spinning speeds have little effect on linewidth owing to the homogeneous nature of the dipolar interaction in CaF_2. In marked contrast is the data shown for fluorapatite.

The fluorine atoms in FAP are positioned in linear chains along the unique crystallographic c-axis. Maricq and Waugh (4) have pointed out that the homonuclear dipolar interaction for spins in a linear arrangement behave inhomogeneously under MAS conditions. This is nicely demonstrated in Figure 2 where the slow-spinning speeds are seen to give rise to typical sideband patterns. At 14 KHz the linewidth is 317 Hz (1.1 ppm) and spinning sidebands

account for only 16% of the total intensity.

The attractive feature of this approach is the simplicity of implementing the experiment. The ^{19}F spectra were obtained on a Bruker CXP-300 spectrometer equipped with a standard 5mm ultra-fast-spinning probe from Doty Scientific (5 μs 90° pulses were generated with less than 30 watts). Each spectrum represents the co-addition of 32 Bloch decays.

Please credit this contribution to S. C. Lee's account.

Charles D. Sazavsky Anthony T. Kreinbrink Robert S. Honkonen

1. Yesinowski, J. P.; Wolfgang ,R. A.; Mobley, M. J. In "Adsorption on and Surface Chemistry of Hydroxyapatite"; Misra, D.N., Ed.; Plenum; New York, 1984; p 151.
2. Smith, K. A. and Burum, D. P. Experimental NMR Conference, Rochester, N.Y.,1988.
3. Manuscript in preparation.
4. Maricq, M. M.; Waugh, J. S. J. Chem. Phys. 1979, 70, 3300.

Figure 1.

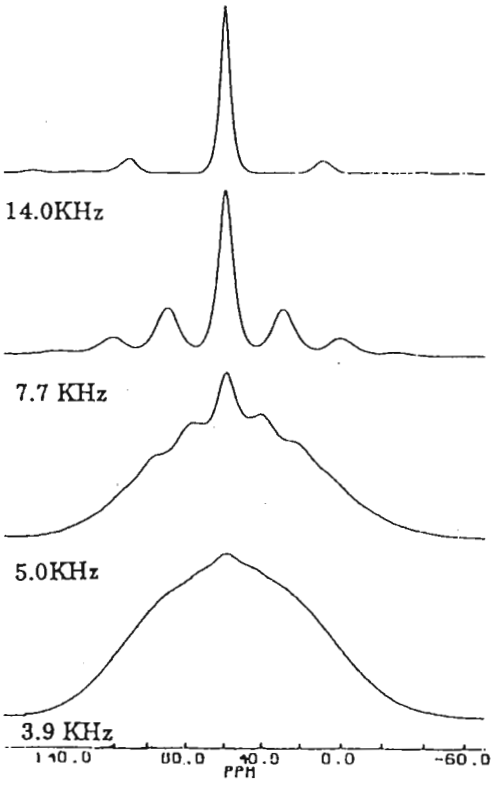
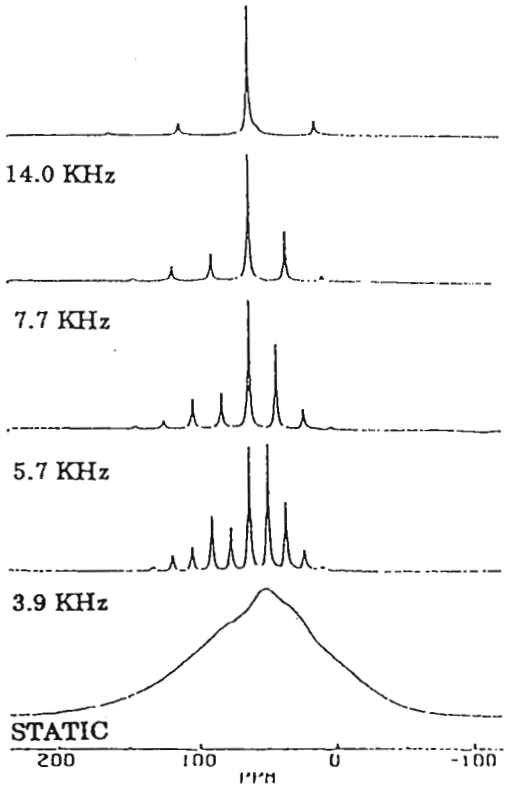


Figure 2.



F-19 MAS NMR of calcium fluoride (Figure 1) and fluorapatite (Figure 2) as a function of spinning speed.

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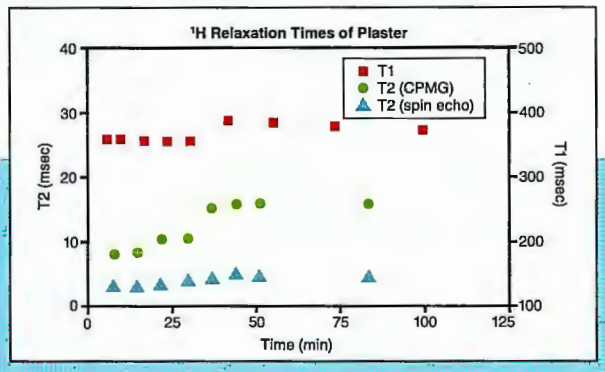

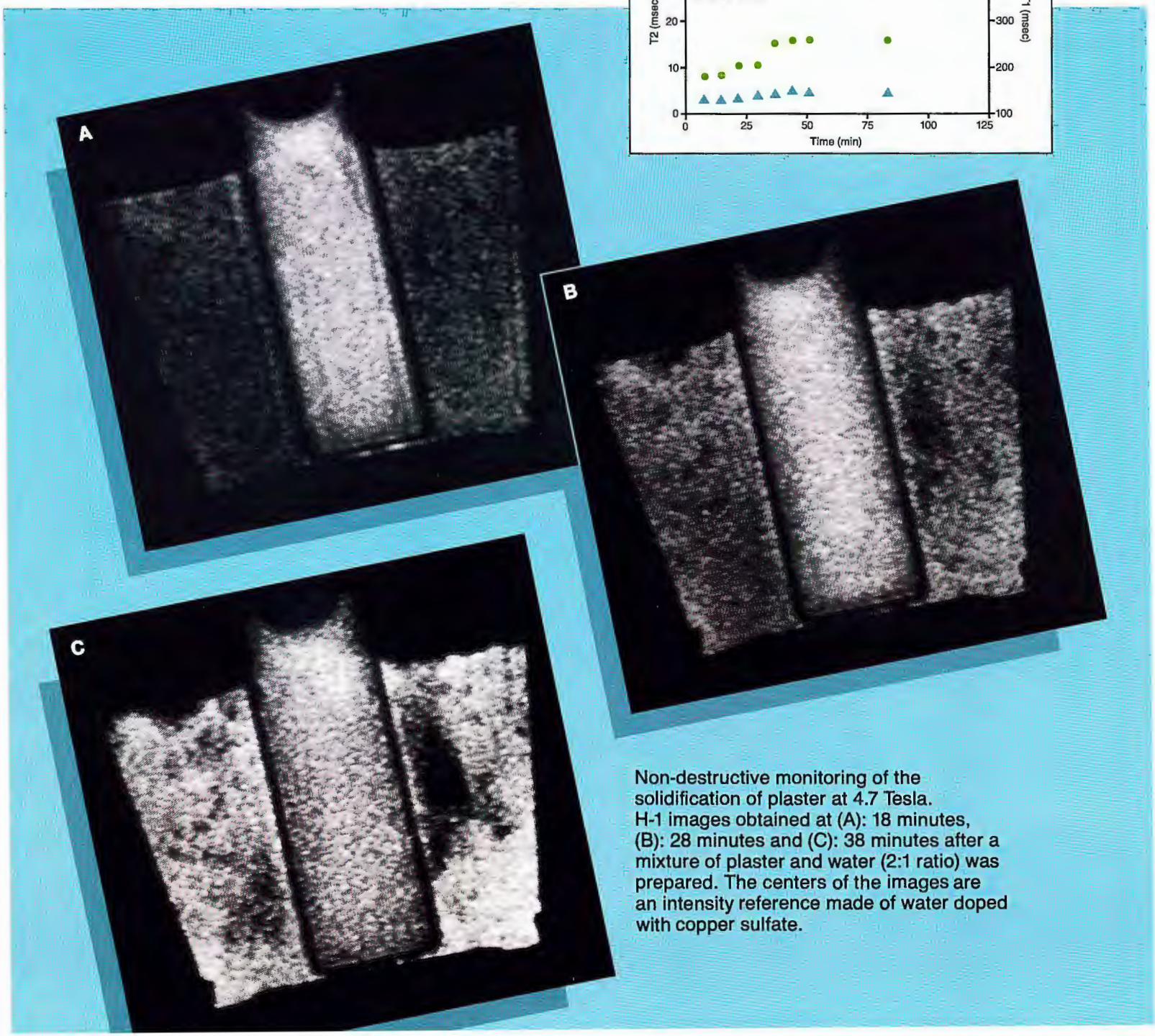

Non-destructive monitoring of the solidification of plaster at 4.7 Tesla. H-1 images obtained at (A): 18 minutes, (B): 28 minutes and (C): 38 minutes after a mixture of plaster and water (2:1 ratio) was prepared. The centers of the images are an intensity reference made of water doped with copper sulfate.

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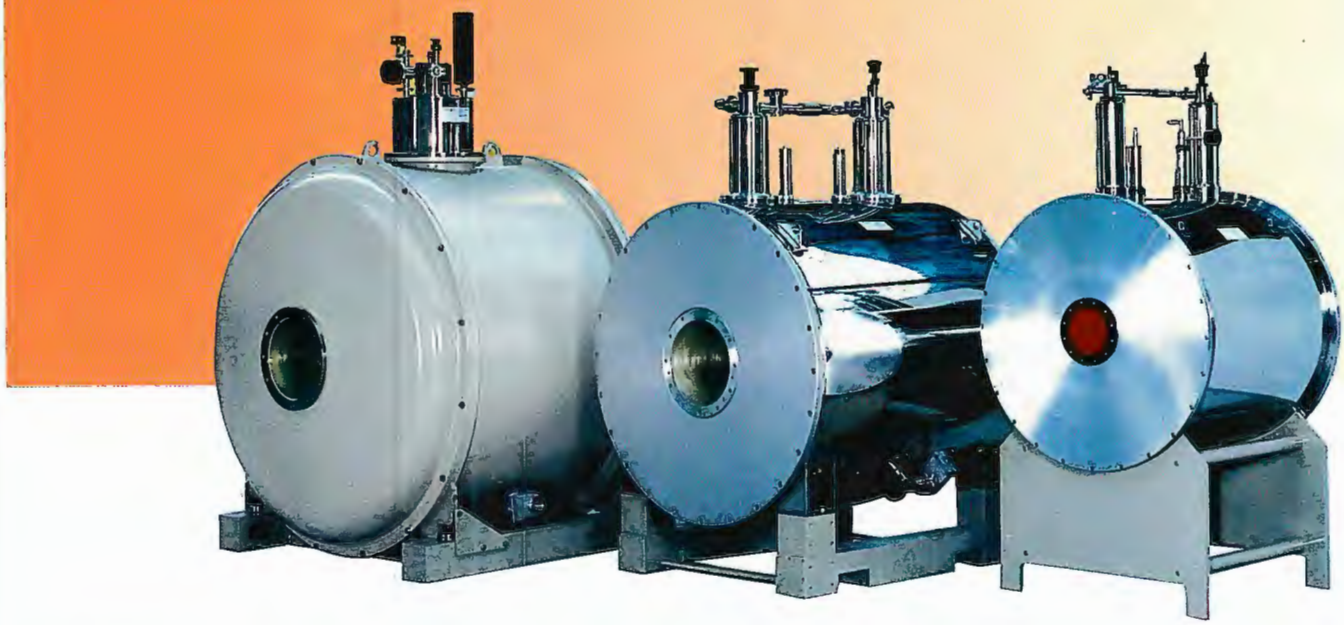
300/180	7.05T	183 mm	125 mm	4.0 G/cm	80 mm DSV ±6 ppm	35 mm DSV 0.1 ppm	5.60 m	4.45 m
200/330	4.7T	330 mm	254 mm	2.3 G/cm	140 mm DSV ±5 ppm	70 mm DSV 0.1 ppm	6.95 m	5.60 m
200/400	4.7T	400 mm	324 mm	1.8 G/cm	140 mm DSV ±4 ppm	80 mm DSV 0.1 ppm	8.50 m	6.75 m
85/310	2.0T	310 mm	225 mm	3.0 G/cm	100 mm DSV ±5 ppm	70 mm DSV 0.1 ppm	4.50 m	3.63 m

DSV = Diameter Spherical Volume
HHLW = Half-Height Line Width
PPM = Parts Per Million



200/400, 200/330, and 300/180 magnets for the NMR Imaging Spectrometer System.
(Photos courtesy Oxford Instruments.)

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Washington
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Department of Chemistry

Sept. 15, 1988

Professor Barry Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Dear Barry,

Quantification of tissue blood flow and perfusion is of importance for proper evaluation of tissue metabolism and for improvement of the effectiveness of therapeutic treatment. Muscle blood flow and perfusion is slow compared to that of many other normal tissues (*i.e.*, brain, kidney, liver, etc.). Since it will take a longer time to wash out a freely diffusible tracer from muscle, one requires a long time course of washout data to properly quantitate muscle blood flow. Thus, the use of a stable NMR active tracer such as D_2O[1–4] may offer advantages over short-lived radioisotopes for monitoring muscle blood flow rates.

A bolus of D_2O or C_4D_9OH (n-butanol) was introduced into resting rat leg muscle by either intraaortic (i.a.) injection at the iliac bifurcation or direct intramuscular (i.m.) injection. After injection, blood flow and diffusion at the capillary level distributes tracer rapidly throughout the aqueous space of the muscle. Further ongoing blood flow then removes the tracer from the muscle. The tracer residue washout decay was detected by surface-coil deuterium NMR over time. The deuterium residue washout time course was analyzed by multicompartment models[5].

Biexponential washout curves were obtained with either i.a. injection or i.m. injection of D_2O. Application of a three-compartment model[5] to i.a. injection tracer washout data yields a mean (volume-averaged) muscle blood flow of 5.2 ml/(100 g·min), a fast flow component of 112 ml/(100 g·min) with 2% volume fraction, and a slow flow component of 4 ml/(100 g·min) with 98% volume fraction. Similarly, application of the three-compartment model to i.m. injection tracer washout data yields a mean muscle blood flow of 13 ml/(100 g·min), a fast flow component of 44 ml/(100 g·min) with 25% volume fraction, and a slow flow component of 6 ml/(100 g·min) with 75% volume fraction.

In order to determine the origin of fast and slow flow components, deuterated butanol is employed as a NMR flow tracer. Butanol is lipid-soluble and *ca.* 100% extracted into tissue in a single passage. In a preliminary experiment employing direct i.m. injection of D_2O and deuterated butanol (Fig. 1), the fast flow component detected with washout of D_2O was not observed in the washout of deuterated butanol. The muscle blood flow of 5 ml/(100 g·min) employing deuterated butanol injection is comparable to the (dominant) slow flow component of 6 ml/(100 g·min) employing D_2O injection. This suggests that the fast component may result from flow-limited diffusion shunting and/or nonextracted portion of tracer. Further studies are in progress to examine this issue.

Washington University
Campus Box 1134
One Brookings Drive
St. Louis, Missouri 63130

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1. Kim, S.-G. and Ackerman, J.J.H. *Soc. Magn. Reson. Med. 7th Ann. Meet.* (San Francisco, CA), Book of Abstracts, 2:901, 1988.

2. Ackerman, J.J.H., Ewy, C.S., Becker, N.N. and Shalwitz, R.A. *Proc. Natl. Acad. Sci. USA*, 84:4099-4102, 1987.

3. Ackerman, J.J.H., Ewy, C.S., Kim, S.-G. and Shalwitz, R.A. *Ann. N.Y. Acad. Sci.*, 508:89-98, 1988.

4. Kim, S.-G. and Ackerman, J.J.H. *Cancer Res.*, 48:3449-3453, 1988.

5. Kim, S.-G. and Ackerman, J.J.H. *Magn. Reson. Med.*, in press, 1988.

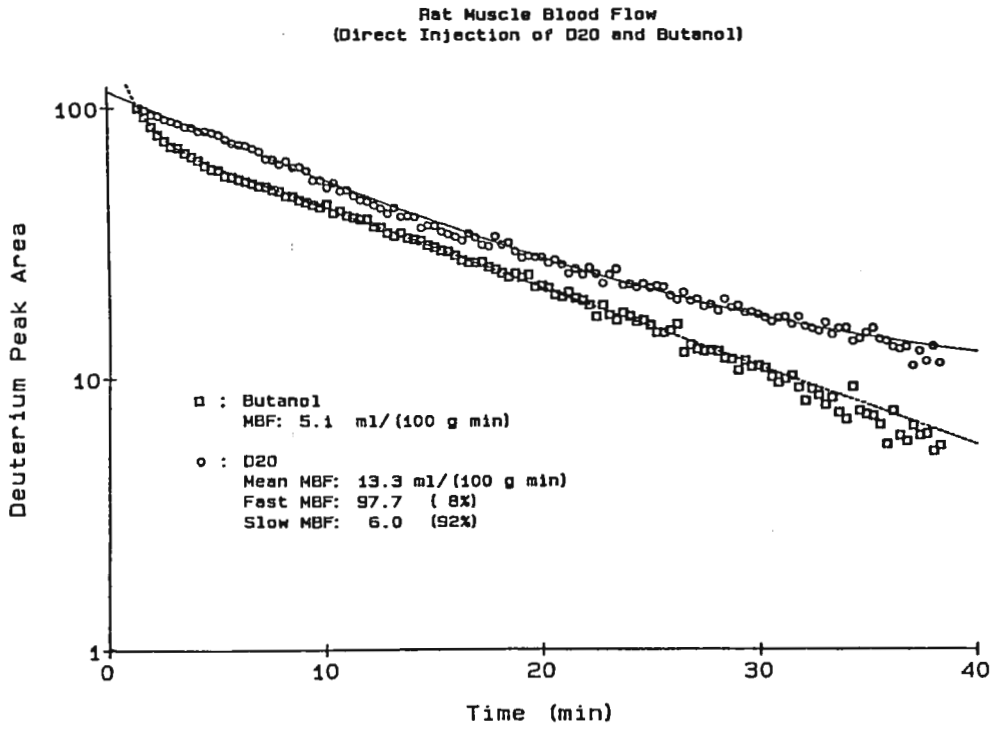

Figure 1. The tracer washout time courses (*semilog scale*) following direct i.m. injection of D_2O and C_4D_9OH. Biexponential washout curve (squares) is obtained with D_2O i.m. injection. Application of the three-compartment model yields a fast flow component of 98 ml/(100 g·min) with 8% volume fraction, and a slow flow component of 6 ml/(100 g·min) with 92% volume fraction. However, a monoexponential washout curve (circles) is obtained with butanol i.m. injection. Application of the two-compartment in-series model in this butanol washout data yields a muscle blood flow of 5 ml/(100 g·min).

Respectively

Seong-Gi Kim

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Spurious Outputs: −75dB

Phase Noise: −63dBc, (0-15KHz)
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Spurious Outputs: −70dB

Phase Noise: −63dBc, (0-15KHz)
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Interface: BCD par. or GPIB
Size: 19″W, 5¼″H, 18″D
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Switching: 5-20μs
Output: +3 to +13dBm: 50 ohm
Spurious Outputs: −70dB

Phase Noise: −63dBc, (0-15KHz)
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SAN FRANCISCO, CALIFORNIA 94143

September 13, 1988
(received 9/16/88)

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

"$^1H\{^{31}P\}$ 2D NMR Assignment of Phosphorus and H5',5" DNA Oligomer Signals"

Dear Professor Shapiro,

The purpose of this letter is to discuss some of the "nuts and bolts" of assigning the phosphate (^{31}P) signals and the H5',5" proton signals on small synthetic DNAs, and demonstrate the power of a known heteronuclear shift correlation (HSC) technique to achieve these assignments (1a,b). The main scheme of a HSC experiment is to use the unobserved nuclei's spin frequencies to modulate the signal amplitude of the observed nucleus as a function of t_1. This modulation brings about polarization transfer as a function of t_1. But the extent to which this transfer is carried out also depends on the offsets of the unobserved nuclear spins. The basic $^1H\{^{31}P\}$ HSC experiment shown in figure 1 is similar to the ^1H-^1H COSY experiment where the coherence transfer process of the second COSY pulse is to the same type of nucleus instead of two simultaneous pulses to both nuclei. Short ^{31}P T_2 values (<100ms) at 500MHz (1b) do not allow for a reasonable application of 180° decoupling pulses due to added delays (=1/2J) that are significantly greater than the T_2 value.

A good phase cycling routine is essential in removing a large number of both experimental and instrumental artefacts. However, sample spinning is not advised. Phase cycling was applied to specifically remove the axial peaks and separate out the N- and P- type peaks, and for quadrature detection. The phase cycling used (see scheme 1) is analogous to the COSY experiment in that it is selective for the N-type peaks. The first ^{31}P pulse (P1) changes the phosphorus coherence level to a negative value (-1). Unlike the COSY experiment, the second ^{31}P pulse (P3) brings the phosphorus coherence back to zero, while the ^1H pulse (P4) leaves the proton coherence level at +1. Quadrature detection was imposed on this sequence by the TPPI method, ie. phase shifting P1 by 90° after each t_1 increment.

Presaturation (P0) of the entire ^1H frequency bandwidth prior to P1 results in the enhancement of the ^{31}P spin magnetization by an internuclear Overhauser effect (1a). However, this saturation pulse was not effective in eliminating our relatively large HOD signal at 4.89 ppm. Since the ribose H3' proton signals appear around 4.89 ppm we chose to give up on this enhancement in order to more fully resolve these ~4.8 ppm ribose peaks. On our instrument (GN500) we found that the application of a long (4 second) low power pulse at the 4.89 ppm frequency was sufficient for elimination of the solvent peak. The repetition time is determined by the T_1 of the phosphorus nuclei and should be about 1.3 times the T_1 value. The 4 second delay during the presaturating pulse is sufficient to meet this criteria.

The overall assignment scheme for an oligodeoxyribonucleotide would involve, first, running a double quantum filtered COSY to assign the ribose H3' and H4' protons followed by the $^1H\{^{31}P\}$ HSC experiment. If necessary, a phase sensitive NOESY or a Hartmann-Hahn spin locking (HOHAHA) experiment may also be needed for complete assignments. A complete battery of these three homonuclear experiments are usually more than enough to assign the 1', 2', 2", 3' and 4' deoxyribose protons. Based on the H3' assignments alone, most if not all of the ^{31}P signals can be assigned. In turn these phosphorus assignments can be used to assign the H4', H5' and H5" protons. Problems arise when ^{31}P resonances overlap and when these complex deoxyribose multiplet components are out of phase and cancel each other. The latter problem is most significant in the case of the H5',5" protons. In the case of the H3' protons an overall additive effect of overlapping in phase components can be predicted based on known coupling constants and most probably explains the ease with which the H3'/^{31}P cross peaks are observed.

We applied this scheme to a synthetic hexamer, d($^{5methyl}C$ G)$_3$. The results of the HSC experiment are given in figure 1. At 25°C this hexamer (6mM-duplex in D_2O), forms a self -complementary duplex which contains five phosphate groups per strand, ie. the 5' terminal ^{5me}C does not have a 5' phosphate group. The phosphate groups are labelled 2 through 5 (as shown in figure 1). All five of the H3' protons, assigned previously by Orbons et al. (2), show coupling ($^3J_{3'-P}$) with their neighboring ^{31}P nuclei. Three of the five guanine phosphates are easily assigned

(Gp4, Gp6 and Gp2). The isochromicities of the proton resonances G2H3' and G4H3' prevented initial assignment of their neighboring cytosine phosphorus nuclei C3 and C5. However, the C3H4' and C5H4' coupling to their phosphorus nuclei resolved this ambiguity. Assignments of the unphosphorylated C1H5' and H5" protons can usually be made in the one dimensional ^1H spectra where the partially frayed terminal base pairs cause an upfield shift in these protons into the less crowded 3.6 ppm region.

As a final note, under less ideal sample conditions , ie. lower concentrations (~2mM duplex) and temperature conditions causing broader lines, it was still possible to resolve out the H3' couplings to their neighboring phosphates and subsequently allow for the assignment of these ^{31}P signals.

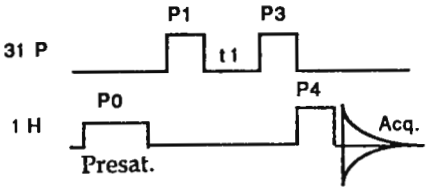
Sincerely,

Debra L. Banville

References: (1) a. Maudsley, A.A.; Ernst, R.R. *Chem. Phys. Let.* 50, 366-372, 1977;
b. Williamson, D.; Bax, A. *J. Mag. Res.* 76,174-177, 1988.
(2) Orbons, L.P.M.;van der Marel, G.A.; van Boom, J.H.; Altona, C. *Eur. J. Biochem.* 160, 131-139,1986.

SCHEME 1

Pulse Sequence



Phase Cycling for HSC

Phase of: P1*	P3=P4=P0	Rcvr
0	0	0
180	0	180
90	90	90
270	90	270
180	180	180
0	180	0
270	270	270
90	270	90

FIGURE 1

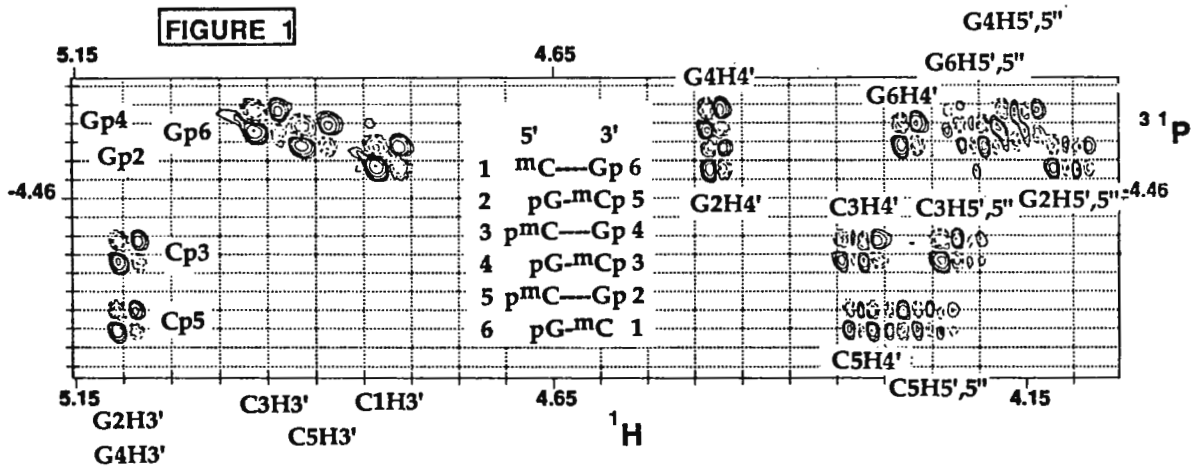


Figure Caption: $^1H\{^{31}P\}$ HSC contour plot of $d(^{me}C\ G)_3$ in D_2O at 500 MHz proton and 202 MHz phosphorus (25°C); negative peaks are plotted as dashed lines. A total of 128 t_1 increments were collected with 2048 data points and 64 scans per FID in about 10 hours. However, 64 t_1 increments would be sufficient for good resolution. The ^1H ppm scale is relative to HOD at 4.89 ppm, and the ^{31}P scale is arbitrarily set.

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Avdelningen för organisk kemi

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UNIVERSITY OF UMEÅ
Department of Organic Chemistry

Telephone
46 - 90 - 16 50 00

September 7, 1988 (received 9/13/88)

Prof Bernhard L Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303

Multivariate analysis of pulp based on ^{13}C CP/MAS NMR data.

Dear Prof Shapiro,

During the course of our continous studies of wood pulping we find some very useful results when employing the multivariate calibration technique (by partial least squares, PLS) based on ^{13}C CP/MAS NMR data.

We show some results for a cook where samples were taken at time intervals between 60 and 260 minutes (during bulk and final delignification). The samples were run on our MSL-100 system and for the data analysis 20 Hz line-broadening was introduced as was magnitude calculation of spectra. The motive is to extract quantitative chemical information from these CP/MAS spectra by PLS modelling of latent variables.

Incidentally, PLS is an extension of principal components analysis (PCA) that uses PC-like algorithms to analyze two data matrices simultaneously. One independent set of NMR measurements and one dependent set of variables from the chemical analysis are used. A regression relationship is established between matrix components, which is later used for predictive purposes.

Results for the glucose and lignin determinations are shown in the figures. The obtained model uses three PLS components (significant by cross-validation) to account for the variation in data and to obtain the predictions. The results are based on spectral variation in the 60 - 115 ppm region through 73 evenly distributed data points (every 4th data point from the original spectrum) giving suitable data matrices for analysis on any personal computer. A discussion about the conversion of raw data profiles into analyzable data suitable for PCA or PLS is soon appearing in the literature (1).

If we analyze samples taken from the final delignification period (<5% lignin) the predictions can be further improved. We speculate that the suggested existence of associated lignin-carbohydrate polymers is supported by the fact that we are able to model the lignin concentration even at these low concentrations. Thus, multivariate analysis efficiently detects the loss of such a complex by the induced changes in the cellulose resonances. We emphasize that this also put a high stress on the method considering that we use only the 60 - 115 pmm region for the modelling. Hemicelluloses can also be readily predicted by the above methods. The results reported here are part of a communication that is in print in Journal of Applied Polymer Science Symposium.

Presently we are investigating the possibility to relate NMR spectra to physical properties of the cellulose itself. Besides

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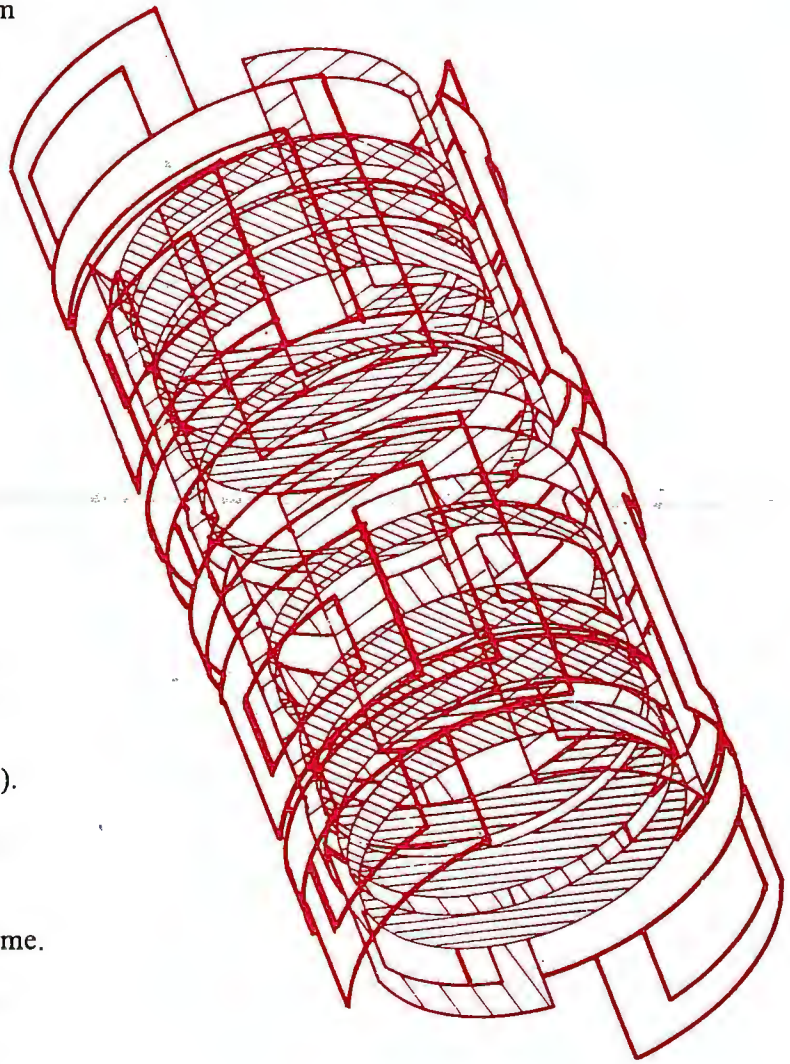

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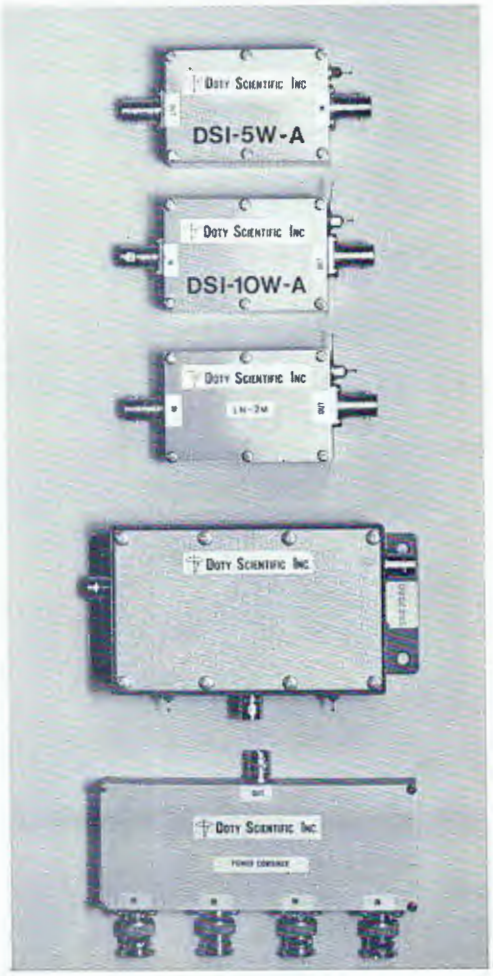

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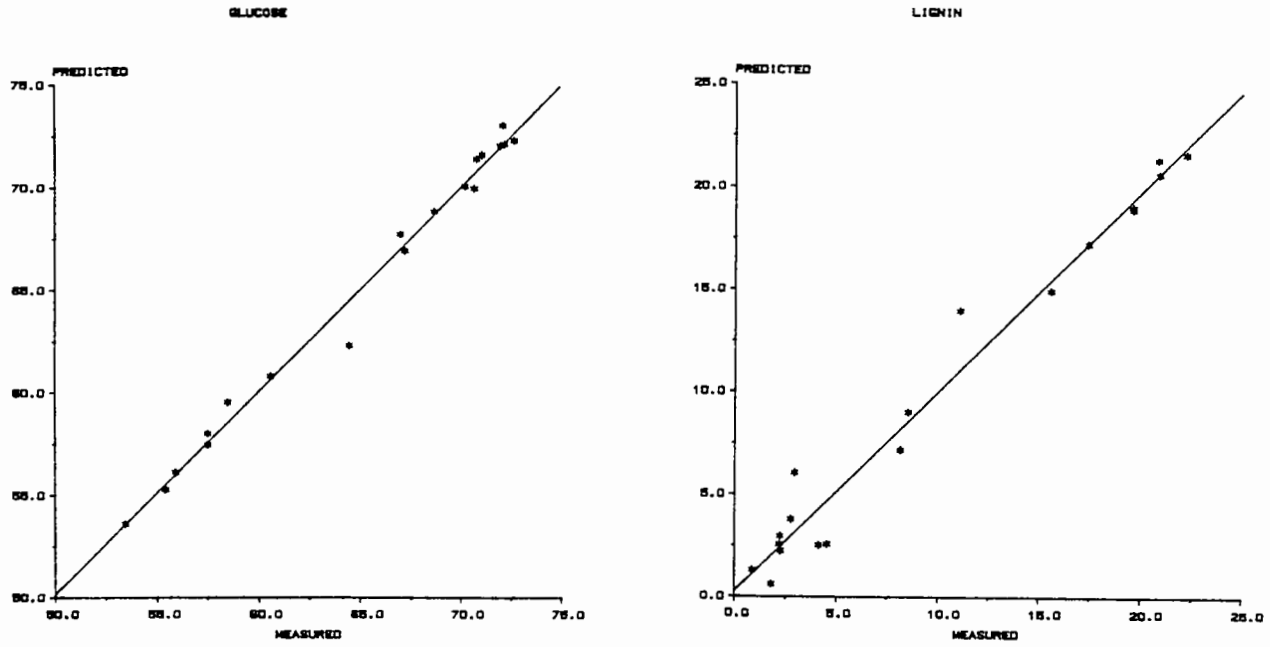
the monographs that have appeared on multivariate analysis you will find comprehensive reviews on PCA and PLS in references (2) and (3).

(1) B Nordēn and C Albano, Fuel 1988, in press.
(2) S Wold, K Esbensen and P Geladi, Chemometrics and Intelligent Lab. Systems 2, 37 (1987).
(3) P Geladi and B R Kowalski, Anal. Chim. Acta 185, 1 (1986).



Plots of NMR predicted glucose and Klason lignin concentrations (%) vs. measured glucose (GC determined) and Klason lignin values.

Yours sincerely,

Bo Nordēn

Ulf Edlund

TU Delft
Delft University of Technology

Faculty of Applied Physics
P.O. Box 5046
2600 GA Delft, The Netherlands

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

September 2, 1988
(received 9/9/88)

"Coping with hum in ISIS experiments"

Dear Dr. Shapiro,

In our group we are concentrating on spatially resolved spectroscopy. Within that framework we are busy in building a second small bore system with a 4.7 tesla superconducting magnet.
To keep also in touch with the real experimental world, and to gain some experience in this field, we thought it might be useful to compare different volume selection methods on our home built imaging system (1 tesla iron magnet, 10 cm air gap).
So we set ourselves to investigate the ISIS experiment to start with, and, as usual, the first results were rather disappointing. As is well-known, the ISIS method relies on the cancellation of signals from the non-selected regions of the sample by adding and subtracting the signals of successive cycles of the experiment. In fact the imperfection of this cancellation sets a limit to the attainable ratio of selected volume to total sample volume.
A prerequisite to good cancellation is the ability of the system to produce identical results in identical experiments. So we measured the transverse magnetization in a simple [90-t-180-echo-T-]$_n$ experiment repeatedly (with t=10 ms and T=2 s), and especially the phase of the transverse magnetization at the echo center showed a rather periodic variation of about 70 degrees peak-to-peak. See Fig. 1. It goes without saying that in this situation ISIS wouldn't work.

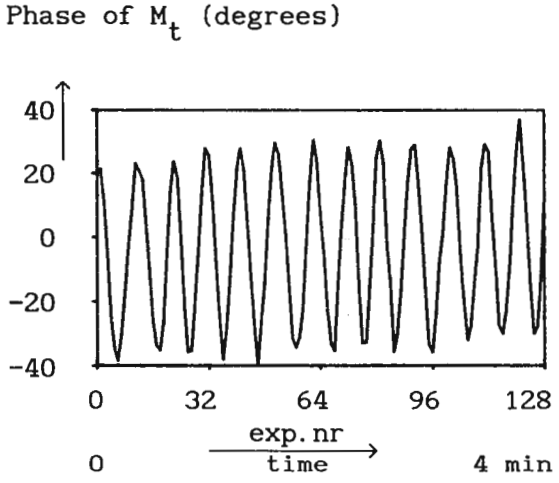


Fig. 1

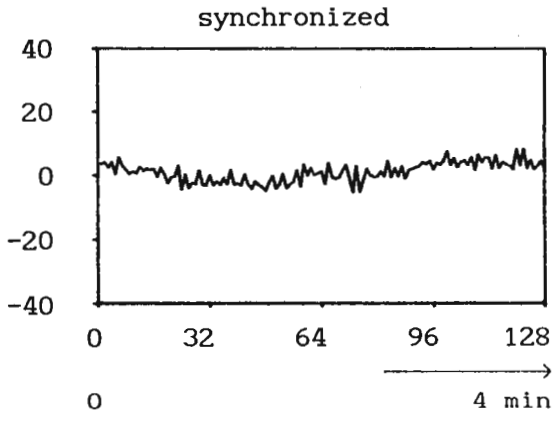


Fig. 2

(see text)

The phase variation of the magnetization suggests a periodic fluctuation on the magnetic field which, of course, originates from its power supply. We estimate this field ripple to be of the order of 1 ppm. In fact Fig. 1 shows a severe undersampled measurement of the mains frequency.

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Since it doesn't pay to try to reduce the ripple on the magnet current another order of magnitude the remedy to its effect is to synchronize the experiment with the mains frequency. It turned out not to be sufficient to set the repetition time of the experiment to an exact multiple of the inverse mains frequency since the latter suffers from random fluctuations of the order of 0.1%. Therefore, with a simple circuit, we derived a pulse from the mains frequency which we used to synchronize our pulse programmer (Nicolet 293B).
The same repetitive simple echo experiment now produced a satisfying behaviour of the phase of the transverse magnetization : noisy, less than 10 degrees peak-to-peak. See Fig.2.
Also the ISIS experiment now behaved properly as you can judge from Fig.3.
Here we demonstrate the 3D selection of a cube with a volume of about 1.5% of the volume of the sample, a bottle of water (20 cm^3). In the figure we have read out the magnetization of the selected volume in one direction. The bottle extends from about -16 kHz to +16 kHz as just can be recognized from the background signal. We used Macovski's (1) selective inversion pulses. Projections of the selected volume on the other two axes look comparable and we are happy with this result.

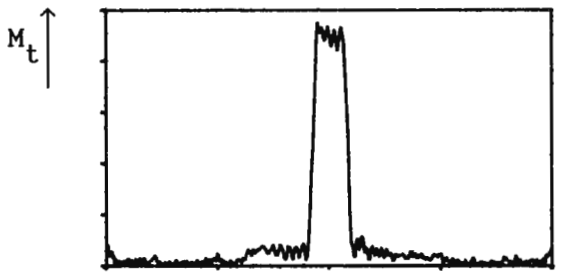

Fig.3 (see text)

Although we know that supercon's don't hum, we think that synchronizing this kind of experiments with the mains frequency might also be useful for supercon users, since their gradient amplifiers surely will produce some hum.

Sincerely yours,

P. van Gelderen, D.Korbee, J.H.N. Creyghton.

(1) Conolly,S.,Nishimura,D. and Macovski,A., IEEE Trans.MI-5,1988,106.

Please credit this contribution to the account of W.M.M.J. Bovee.

THE PENNSYLVANIA STATE UNIVERSITY
152 DAVEY LABORATORY
UNIVERSITY PARK, PENNSYLVANIA 16802

College of Science
Department of Chemistry

September 9, 1988
(received 9/16/88)

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

Subject: Remedies for spectral degradation and temperature instability in high-field spectrometers

Dear Barry,

Since the installation of our Bruker AM-500 a year ago, we have struggled with two fundamental problems, lineshape degradation and extreme sensitivity to the temperature of the environment.

The temperature sensitivity was best observed on a 5% sugar/D_2O sample by measuring the relative chemical shift of any sugar line with respect to the residual HDO line. With a simple water bath on the VT air line right before the VT air entry to the probe and without using the Bruker VT control, the sugar chemical shift reflected strongly the 25-minute heating/cooling cycle of the room air-conditioner. With the VT controller set at 30°C, the 25-minute oscillation was suppressed but the temperature excursions due to the controller were large enough to mar difference spectra and cause strong t_1 noise in two-dimensional experiments.

In consultation with Bruker personnel, we found that the remedy for the temperature fluctuation is a Haake two-bath temperature controller (Model F4-Q). The main, active bath holds the temperature to ± 0.01°C. Since it contains magnetic parts, it is placed at a safe distance from the magnet. A non-magnetic secondary bath, to which the fluid is pumped through insulated lines, is placed closer to the probe. Within the temperature range of the active bath, one circumvents the use of the BVT-100. This seems to work well for our environment.

The degradation of the lineshape and resolution constituted a more puzzling problem. It was severe in at least 1 out of 3 overnight runs. For example, we have had the proton resonance of $CHCl_3$ evolve from a single line well within specifications to a four-line spectrum with a grotesque hump at the base in fewer than 12 hours. The degradation occurred also while using the "autoshim" control on the z-gradient and maintaining the temperature at 30°C with the Bruker VT controller. After extensive monitoring of the room-temperature shim voltages, we came to the conclusion that these remained as set and that the z voltage value varied as expected under the control of the "autoshim" routine. The cause was to be found elsewhere.

As always, once you know the answer, it is obvious. In this case, the "obvious" answer was provided by a brilliant unnamed Bruker engineer. On the 11.7 T Oxford magnet, there are three N_2 boiloff ports. One was fitted with a pressure relief valve while the other two

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—Texas A&M University NMR Newsletter

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Nuclear Magnetic Resonance Imaging in Medicine and Biology

PETER G. MORRIS

This book gives the reader a sound physical understanding of the theoretical and practical aspects of NMR imaging. Morris explains the basic theory and describes the imaging systems most frequently encountered, including the two- and three-dimensional methods used in commercial systems. Instrumentation, magnet choice and design are fully discussed, and there is an extensive chapter on applications. "Recommended reading for students in physics, physical chemistry and NMR spectroscopists as well as the increasing numbers of medical specialists that are involved with generating or using information obtained from NMR techniques."

—American Scientist

1986 320 pp.; 191 illus. $75.00

Quantum Description of High-Resolution NMR in Liquids

MAURICE GOLDMAN

This book describes the main method of one- and two-dimensional high resolution nuclear magnetic resonance spectroscopy in liquids within the quantum mechanical formalism of the density matrix. In view of the increasing importance of NMR in chemistry and biochemistry, the work is particularly addressed to those scientists who do not have a working knowledge of quantum calculations. The emphasis throughout is on the actual use of NMR, so the text is neither oversimplified nor overly theoretical. The aim is to describe the basic theoretical tools needed to understand and fully exploit the valuable potential of high-resolution NMR.

(International Series of Monographs on Chemistry 15)
October 1988 288 pp.; 42 illus. $75.00

Principles of Nuclear Magnetic Resonance in One and Two Dimensions

RICHARD R. ERNST,
GEOFFREY BODENHAUSEN and
ALEXANDER WOKAUN

Written by one of the world's leading NMR research teams, this monograph presents the most comprehensive and up-to-date treatment of nuclear magnetic resonance spectroscopy available. The authors provide a unified review of the entire field, covering basic principles and techniques for the study of solutions and solids, with emphasis placed on methods of one- and two-dimensional spectroscopy. "This book is a must for every library dealing with chemistry, chemical physics, biochemistry, or biophysics and for every self-respecting NMR spectroscopist."

—Journal of Magnetic Resonance

(International Series of Monographs on Chemistry 14)
1987 640 pp.; 253 illus. $110.00

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were open to the atmosphere via an N_2 fill-tube and a finned vent. As the atmospheric pressure changed, the N_2 boiloff rate out of the two open ports varied accordingly, leading to changes of temperature at these ports. The closed port, however, was not subject to the same variation. The asymmetric temperature change caused an asymmetric contraction/expansion of the magnet supports. This, in turn, led to changes in the position of the magnet with respect to the sample, and consequently to degradation of the resolution. Clearly, the solution was to make the N_2 boiloff symmetrical and we are now using a finned vent on each of the three ports. One must note, however, that this arrangement could conceivably cause simultaneous icing of all three ports.

The sensitivity of the resolution to external pressure can be readily illustrated by plugging (or unplugging) ports with a rubber stopper and watching the effect on a sharp line. We have observed lineshape changes within 10 minutes of altering the boiloff path. We suspect this may be happening to varying degrees in many magnets of the same design.

Best regards,

Alan

Alan Benesi
Lecturer in Chemistry
Director of the NMR Facility

Juliette

Juliette Lecomte
Assistant Professor of Chemistry

CHEMISTRY RESEARCH CENTER *National Taiwan University*
ROOSEVELT ROAD, SECTION 4
TAIPEI, TAIWAN, REPUBLIC OF CHINA
PHONE: 3935359 • 3935357

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

September 12, 1988

Dear Dr. Shapiro:

We are seeking for a postdoctoral research associate to study molecular dynamics using multinuclear magnetic relaxation techniques. The applicant must be a brand new ph.D.(within three years of receiving ph.D.). Anyone interested please contact Prof. Lian-Pin Hwang, Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC, sending a curriculum vitae and the names and addresses of two referees, or send BITNET electronic mail to AC7B0003@TWNMOE10.

Thank you a lot for your help.

Truly yours,

Lian-Pin Hwang

Lian-Pin Hwang
Professor of Chemistry

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An array of Polyflon non-magnetic capacitors, many of which are used in NMR/MRI applications.

Polyflon's rugged trimmer and variable capacitors meet rigid NMR/MRI specifications.

Polyflon's variable, trimmer and fixed capacitors meet critical non-magnetic, high voltage, high power, high Q NMR specifications.

A test report was recently submitted to Polyflon by a University deeply involved in NMR research. Polyflon trimmers were subjected to various tests in order to gather essential data (Q, DF, L, ESR, EPR) for use in the design of NMR RF equipment. Tests were conducted at 10, 100, 200, 400, 500, and 600 MHz. These trimmers were first exposed to a 4.7 Tesla magnetic field for detection of the presence of any magnetic particles in the trimmers. These tests conclusively showed there were no magnetic particles present.

Maximum dissipation displayed by the trimmers was 0.000125 with a minimum less than 0.0001, resulting in Q measurements from 8,000 to more than 10,000, at 600 MHz. (NOTE: Customers, who have tested Polyflon trimmers in their own laboratories, have measured Q's greater than 20,000 at 500 MHz.) The inductance of the trimmers was less than one nHy and maximum ESR at 160 milliohms with minimum EPR at 100 megohms.

Polyflon trimmers and variable capacitors provide linear tuning with no reversal in capacitance during capacitor adjustment. They are used in NMR pulsed applications with operating voltages up to 15 Kv peak and duty cycles ranging up to 10 %. Standard range of variable capacitor designs are available with a minimum capacitance of less than 1 pF to a maximum capacitance of 125 pF.

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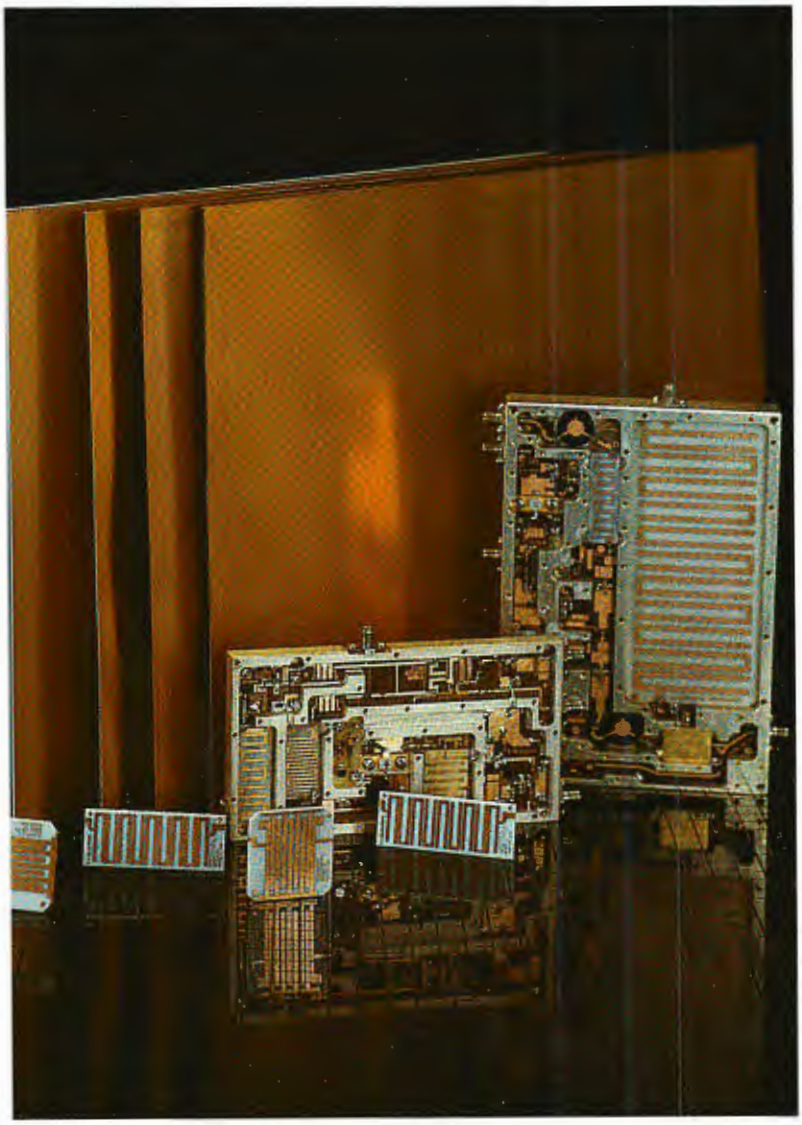
- **Low ESR**
- **High EPR**
- **Linear tuning (no capacitance reversal)**
- **High voltage capability**
- **Rugged design**
- **Long operating life**

Material Technology for NMR Product Applications



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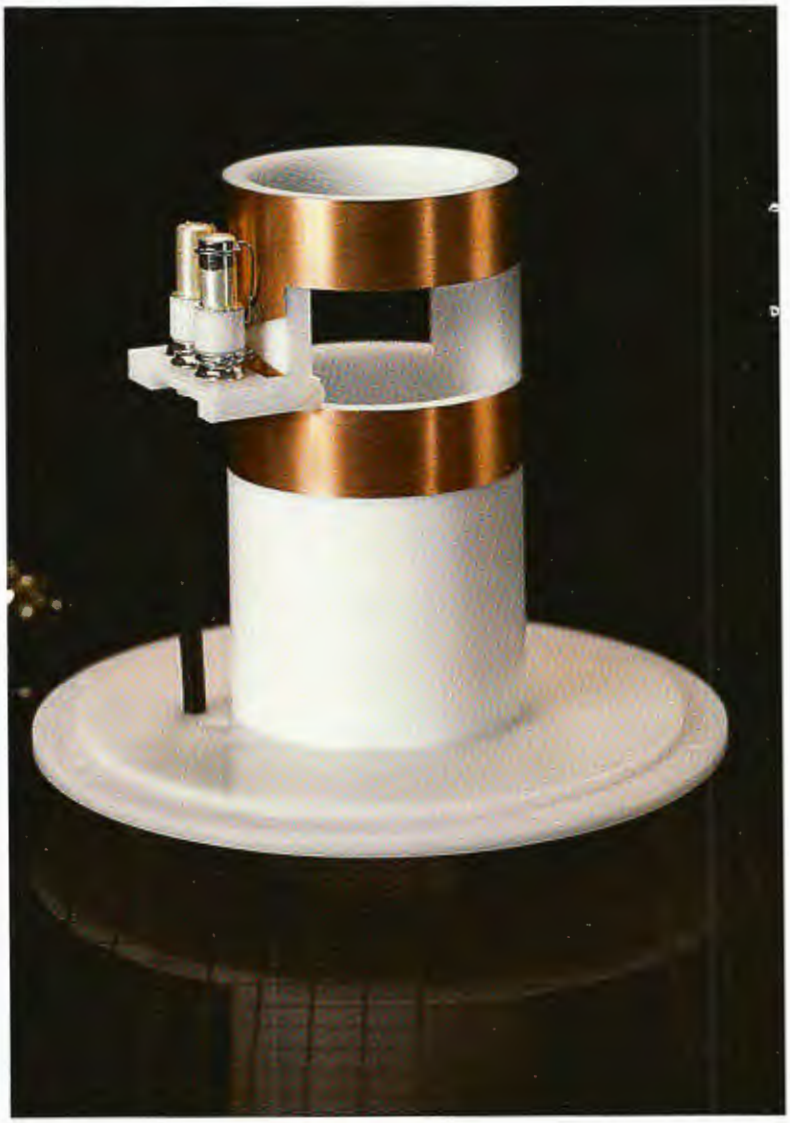

80 MHz copper plated PTFE saddle coil assembly.

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Michigan Technological University

Houghton, Michigan 49931

College of Sciences and Arts
Department of Physics
906/487-2086

September 21, 1988
(received 9/24/88)

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

An inexpensive spectrum analyzer

Dear Dr. Shapiro:

In our research group we have only occasional need for a spectrum analyzer and find that when we do need one, those on campus are inaccessible. We found, however, that our sweep generator - used for probe tuning - can be used as an inexpensive emergency substitute. The set-up is illustrated in the figure below and only requires a spare mixer and a simple RC low pass filter. By adjusting the (optional) attenuator(s) one can achieve values which are quite adequate for trouble shooting. The size(s) of various spectrum peaks are adjusted in turn to a standard size and the attenuator dial is used to read off numbers.

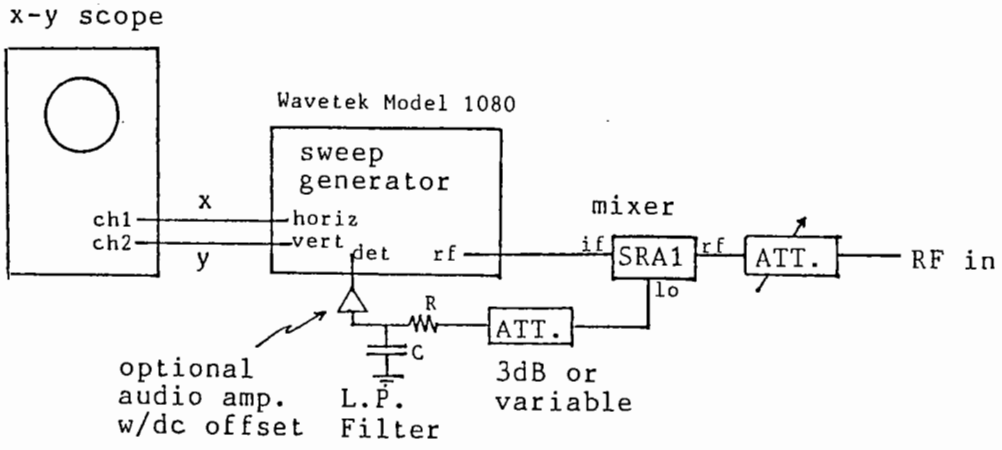
While this idea may not be entirely new, it is so simple and cost effective that it perhaps deserves repeating.

Sincerely,

BH Suits

Bryan H. Suits
Assistant Professor

BHS/lad



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Institut für Organische Chemie

A-8010 Graz, 19.8.88
Heinrichstraße 28
Tel. (0316) 380

(received 8/31/88)

Prof. B.L.Shapiro
TAMU NMR Newsletters
966 Elsinore Court
Palo Alto, California 94303
USA

Dear Dr. Shapiro :

Is it still valid to use an AMX spin type approximation for the description of relaxation if $J/\delta\sigma = 0.3$?

It's a well known fact that spectroscopic life is relatively easy as long as spins are weakly coupled. The elegance and straightforward applicability of the mathematical apparatus sometimes seduces one to treat problems in this way although it is known that they are of higher complexity. To get some imagination of how sensible the fit of proton relaxation in an AMX spin type case responds to the $J/\delta\sigma$ values we would like to show a description of the relaxation behavior of 2,3-dibromopropionic-acid (DBPA).
Dissolving DBPA in $CDCl_3$ leads to a ^1H spectrum, which is clearly not of a pure weakly coupled type ($J/\delta\sigma$=0.25) but certainly not a typical ABX type either. Anyhow calculation of the diffusion constants by applying the normal mode relaxation analysis as described by Grant, Werbelow, and Vold was performed and a fit onto the experimental defined relaxation curve obtained. Both the diffusion constants as well as the values of the random fields seemed to be quite reasonable if e.g. the diffusion constants obtained by the fit procedure were compared to values calculated using the NMR independent method proposed by Knauss. To get some insight into the reliability of the results we repeated the experiment but now dissolved DBPA in benzene. This strongly changed the spectral appearance as now a clear AMX type ($J/\delta\sigma < 0.1$) exists. The multidimensional fit procedure was again highly significant and best suited to represent the measured relaxation data. The diffusion constants are almost identical as in the prior case, and their different values reflect the fact that the in-plane-rotation certainly differs from the slow out-of-plane-rotation due to solvent solute effects.

	C_6D_6		$CDCl_3$		
	Hx	Hm	Hx	Hm	Knauss
D_{xx} 10^9 :	0.45	0.90	0.46	0.75	4.92
D_{yy} 10^9 :	5.88	7.10	6.01	8.95	5.14
D_{zz} 10^9 :	32.33	27.20	32.92	29.93	22.50
ja	0.10	0.10	0.10	0.10	
jm	0.10	0.10	0.10	0.10	
jx	0.06	0.06	0.06	0.06	

For the best in NMR . . .

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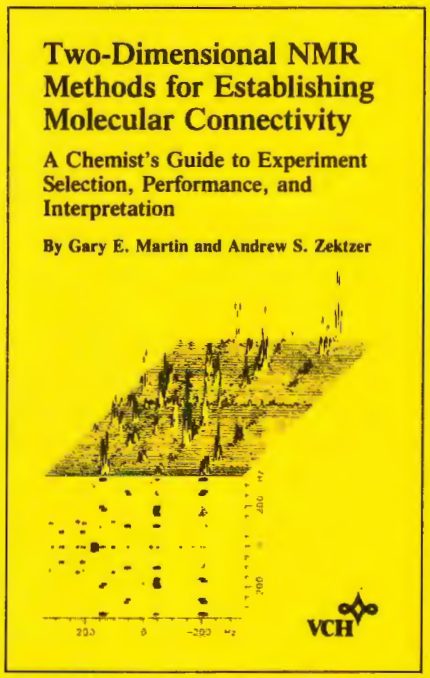
NEW!



TWO-DIMENSIONAL NMR METHODS FOR ESTABLISHING MOLECULAR CONNECTIVITY

A Chemist's Guide to Experiment Selection, Performance, and Interpretation

Gary E. Martin and Andrew S. Zektzer, **University of Houston**

An invaluable guide to two-dimensional NMR spectroscopy designed for the novice who wants to use the technique, but needs a path through the bewildering array of methods and acronyms and the mathematical rigor found in most books.

1988 508 pp. 6½ x 9 Cloth
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TWO-DIMENSIONAL NMR SPECTROSCOPY

Applications for Chemists and Biochemists

Editors: *W.R. Croasmun,* Kraft Research and Development Company
***R.M.K. Carlson,* Chevron Oil Company**

Written for chemists and biochemists who are not NMR spectroscopists, but wish to use the new techniques of two-dimensional NMR spectroscopy, this book brings together for the first time much of the practical and experimental data needed.

Methods in Stereochemical Analysis, V. 9
1987 480 pp. 6⅛ x 9¼ Cloth LC # 86-32539
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PHOSPHORUS-31 NMR SPECTROSCOPY IN STEREOCHEMICAL ANALYSIS

Organic Compounds and Metal Complexes

Editors:

John G. Verkade
Iowa State University
Louis D. Quin
University of Massachusetts

". . . this is an excellent book with well-connected chapters that are remarkably consistent in terms of their level of coverage, clarity of organization, and comprehensiveness. Unquestionably, this is a landmark volume not only for the field of ^{31}P-NMR spectroscopy but also for phosphorus chemistry in general."

— *Journal of the American Chemical Society*

". . . a book of reference and discussion that users of phosphorus NMR have been needing for some time . . ."

— *Magnetic Resonance in Chemistry*

Methods in Stereochemical Analysis, V. 8

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ELECTRON NUCLEAR DOUBLE RESONANCE SPECTROSCOPY OF RADICALS IN SOLUTION

Application to Organic and Biological Chemistry

Harry Kurreck, Burkhard Kirste, and Wolfgang Lubitz
Free University, Berlin

This book describes the principles of ENDOR spectroscopy and TRIPLE resonance with particular emphasis given to applications in organic chemistry and biochemistry.

Methods in Sterochemical Analysis

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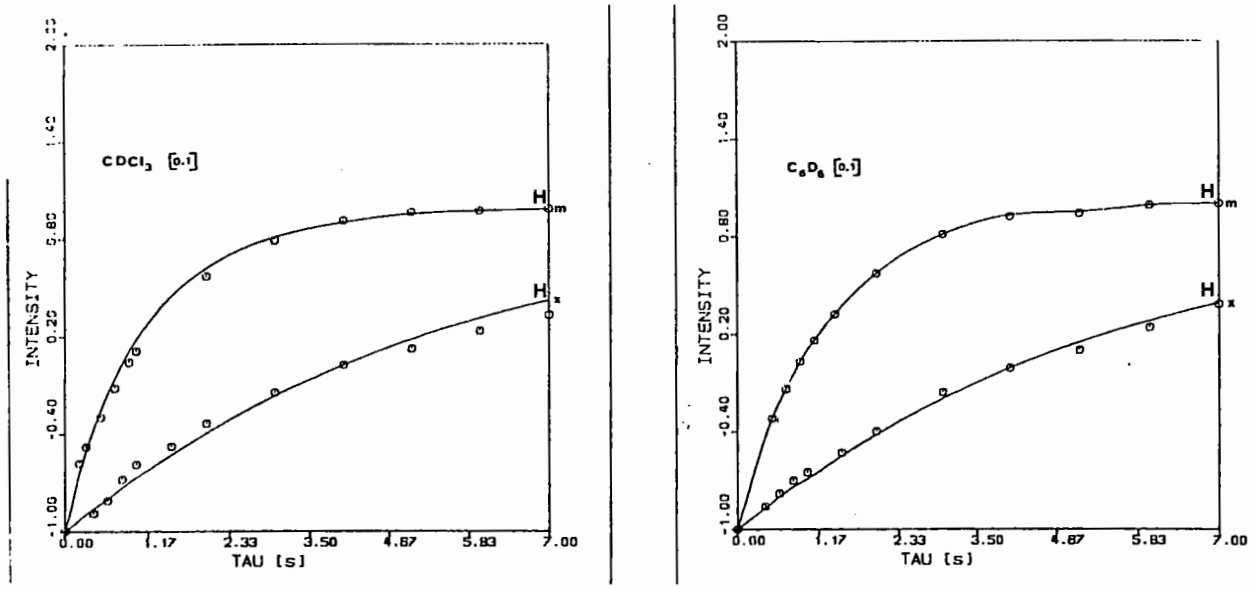
Diffusion constants and random fields obtained using a multiparameter fit procedure for the description of the relaxation behavior of the protons Hx and Hm in DBPA. The DBPA [0.1 mol/l] was taken as a dimeric unit the two bromine atoms located in trans position. The following graph shows the measured T1 values (inversion recovery) as points, the fit is represented by the curves.



To sum up, one can see that relaxation may be described well using the formalism of weakly coupled spins as long as the effects of $J/\delta\sigma$ are not that severe that a description as proposed by the group of Vold is inevitable.

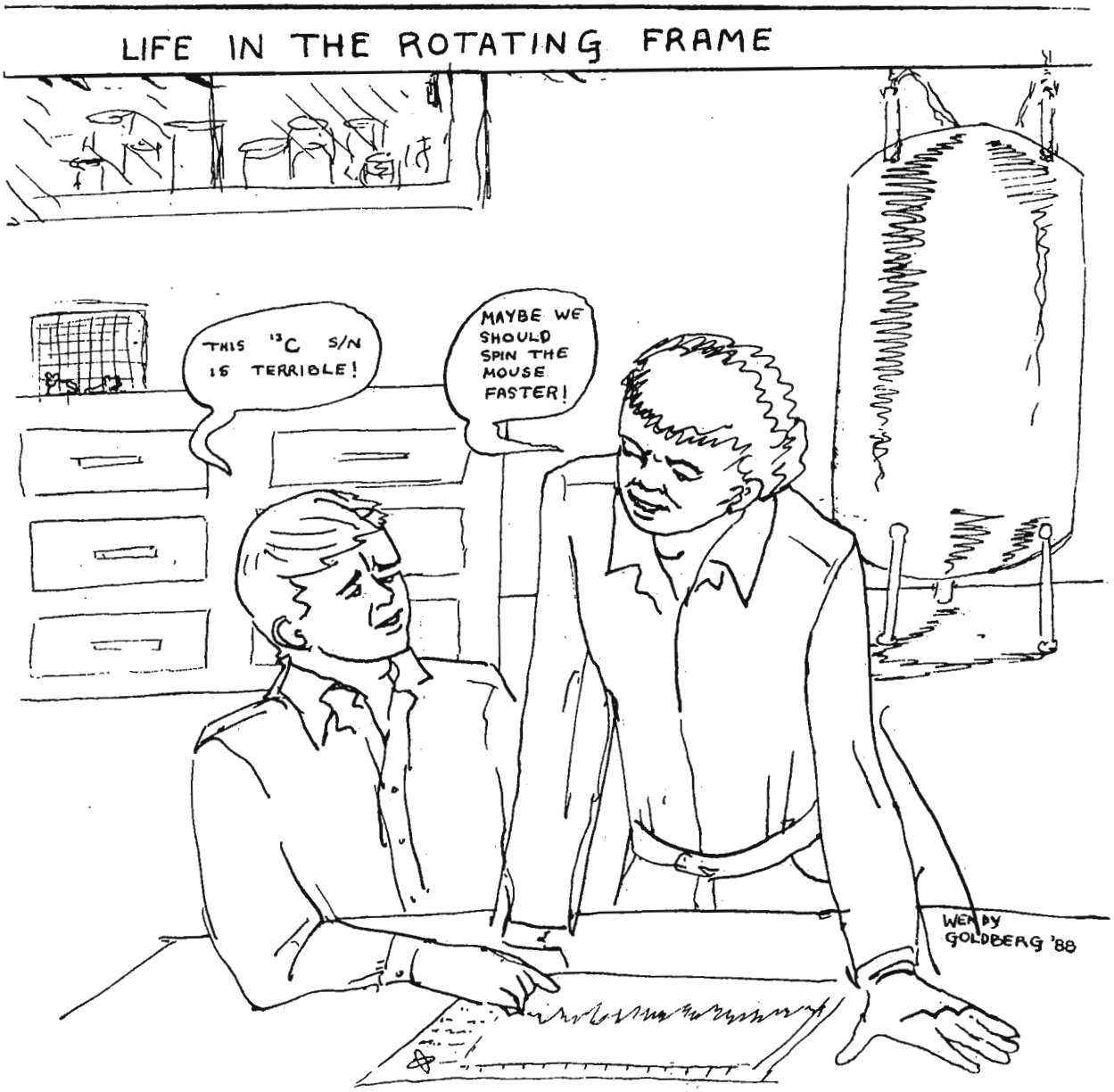
Yours sincerely,

Heinz Sterk

Robert Konrat

POSITION AVAILABLE

A position is available for an NMR spectroscopist with a Ph. D. in chemistry or extensive equivalent experience with state-of-the-art two-dimensional spectroscopy. Some experience in computing is also desirable. The position includes the operation of a high-field FT-NMR instrument, the supervision of instrument operators, and the instruction of faculty, graduate students, and postdoctoral fellows in modern NMR techniques. The successful applicant will have the opportunity to engage in NMR research independently or in collaboration with the faculty. The starting date is as soon as possible. Interested applicants should submit their qualifications to Dr. S. W. Schneller or Dr. M. D. Johnston, Jr., Department of Chemistry, University of South Florida, Tampa, Florida 33620-5250 by 11 November. USF is an EO/AA employer.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THIS ^{13}C S/N IS TERRIBLE!
MAYBE WE SHOULD SPIN THE MOUSE FASTER!
WENDY GOLDBERG '88

TEXAS A&M UNIVERSITY

DEPARTMENT OF PETROLEUM ENGINEERING
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ADVANCED IMAGE PROCESSING: TRANSFER OF IMAGING DATA FORM THE NICOLET 1280 TO A PC VIA THE PARALLEL PORT

1 SEPT 88
(received 9/15/88)

Professor Shapiro,

We have recently installed and have begun to use our new General Electric 2T/CSI. Our major field of interest is in enhanced oil recovery and focuses on the study of flow through porous media, i.e. oil and water through rock. We think this process can be better understood with the aid of magnetic resonance imaging.

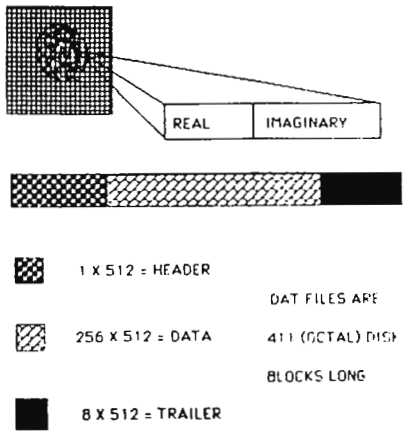
With only a few months of actual usage time, we have already concluded that we will never be able to investigate the details of the flow phenomenon without better image processing. The GE system is basically a modified medical imager with a 31cm bore and Accustar gradients (20 gauss/cm). The images generated by the GE software, GEMCSI, reveal the fine structures of rock, but information on the pixel by pixel basis is not available with this system.

We now report a rapid and very economical way of obtaining the pixel information in the form of a 2 dimensional array of numbers. These numbers, of course, correspond to the processed NMR signal.

Image data files (.DAT), generated by GEMCSI, can be transferred to a PC via the parallel port on Nicolet 1280 processor. A FORTRAN program is used to read the binary format of the .DAT files and to print the data to the 1280's parallel port.

A multiplexer box was used to convert the parallel output form the 1280 to serial input on the PC COM PORT 1. The data was captured on the PC with a terminal emulator program and stored on a hard disk. In most cases, the data was less than a megabyte and was stored on a floppy disk.

General Electric supplies a FORTRAN compiler and full screen editor for the Nicolet 1280 processor. The format of the .DAT files was obtained from GE (Figure 1). A FORTRAN program was then used to strip the desired data from the binary file (Figure 2).



The Logical Connection Box, from Fifth Generation, is normally used as a multiplexer allowing several PC's to access various connected devices. Parallel to serial conversion is performed automatically by the logical connection. In our case, parallel in to serial out was setup in the unit

The terminal emulation program on the PC can be any program that is able to capture incoming data and direct it to a file (i.e. PC-PLOT-iv from Micro Plot Systems). Transmission rates will vary depending on how the data is formatted. When transmitting at 9600 baud, downloading takes about twenty minutes. The strip and download FORTRAN program on the 1280 (Figure 2) also allows

the user to to set a window on the data. This eliminates transferring the noise that appears outside of the data and reduces the downloading time. The window, however, can only be set as a square area.

```
      PROGRAM MAIN
      CHARACTER FNAME*10,LF*2,IANS*2
      INTEGER IBUF(512)
     ,,REAL(256),IMAG(257)
      EQUIVALENCE(REAL(1),IBUF(1))
      EQUIVALENCE(IMAG(1),IBUF(256))
      LF=CHAR(10)
C---- OPEN FILES
      PRINT*,'D A T A  R E D U C T I O N  PRGM'
      PRINT*,' '
      PRINT*,'This is for .DAT files ONLY '
      PRINT*,'ENTER File Name with EXTension  '
      READ(*,3) FNAME
3     FORMAT(A10)
      OPEN(UNIT=5,FILE=FNAME,STATUS='OLD')

C---- THE HEADER CONTAINS IMAGE INFORMATION
      READ(5) IBUF
      PRINT*,'Information from file HEADER '
      PRINT*,' '
      PRINT*,'Number of acquisitions = ',IBUF(4)
C     PRINT*,'GCSISW = ',IBUF(26)
      IMRES = IBUF(26)**2*2*2
      PRINT*,'IMAGE resolution  ',IMRES
      PRINT*,' '
      PRINT*,'      enter return to continue '
      READ(*,33) IANS
 33   FORMAT(A)
      PRINT*,' NOTE: '
      PRINT*,' This is a diagram of an image hardcopy,'
      PRINT*,' TURN hardcopy UPSIDE DOWN and then enter'
      PRINT*,' the limits shown in the following diagram.'
      PRINT*,' '
      PRINT*,'                                X = (256,256) '
      PRINT*,'-------------------------------------------- X'
      PRINT*,'|       |.................................    '
      PRINT*,'|       |.................................|'
      PRINT*,'|       |.................................|'
      PRINT*,'|       | end  row ---> **$** *,..........|'
      PRINT*,'|       |.............*****$**$**.........|'
      PRINT*,'|       |.............****$** **$ ***,.....|'
      PRINT*,'|       |.............***** **  ** ***,....|'
      PRINT*,'|       |/noise/...*** /image/ * ****,.....|'
      PRINT*,'|       |/area /....****$**** **** *,......|'
      PRINT*,'|       |...........^.***** ** *****.^.....|'
      PRINT*,'|  --   |...........|..* ***$ $ ***..|.....|'
      PRINT*,'| ----  |...........|.....********....|.....|'
      PRINT*,'|       |begin row-+-----> ***.......|.....|'
      PRINT*,'|  %%   |...........|.................|.....|'
      PRINT*,'| %&&&  |...........|.................|.....|'
      PRINT*,'| % &&  |...........|.................|.....|'
      PRINT*,'|  %%     .....start column ...end column |'
      PRINT*,'---^-- X ------------------------------    '

      PRINT*,'    | X = (0,0) '
      PRINT*,'    |  '
      PRINT*,' upside down GE logo
```

```
      PRINT*,' ENTER THE BEGINNING ROW # '
      READ(*,*) IBEG
      PRINT*,' '
      PRINT*,' ENTER THE ENDING ROW # '
      READ(*,*) IEND
      PRINT*,' '
      PRINT*,' ENTER STARTING COLUMN  '
      READ(*,*) ISC
      PRINT*,' ENTER ENDING COLUMN  '
      READ(*,*) IEC
      PRINT*,' '
      PRINT*,' '
      PRINT*,'-------   FC-PLOT INFORMATION   -------'
      PRINT*,' '
      PRINT*,' TO BEGIN DOWN LOAD: '
      PRINT*,' Run FC-PLOT on PC'
      PRINT*,' make sure parallel cable is in Logica.
      PRINT*,' Connection box, [#4 parallel in]'
      PRINT*,'  <ALT>-F to enter PC filename'
      PRINT*,'  <ALT>-I to enable download '
      PRINT*,'  <ALT>-Q to close PC file'
      PRINT*,'  <ALT>-X Exit FC-PLOT '
      PRINT*,' '
      PRINT*,' Enter retrun to continue '
      READ(*,33) IANS
C-----
      WRITE(10,*) 'FILE NAME: ',FNAME
      WRITE(10,*) 'IMAGE RESOLUTION: ',IMRES
C-----
      WRITE(10,*) 'BEGIN ROW = ', IBEG
      WRITE(10,*) 'END ROW   = ', IEND
      WRITE(10,*) 'BEGIN COL = ', ISC
      WRITE(10,*) 'END COL   = ', IEC
C---- MOVE DOWN THE FILE
      DO 21 J=1,IBEG-1
      READ(5) IBUF
21    CONTINUE
C---- START READING ACTUAL DATA
C
      DO 22 K=IBEG,IEND
      READ(5) IBUF
C
C---- ONLY THE REALS ARE PRINTED AT THIS TIME
C---- another program will be available to print
C---- reals and imaginares.  an IF stmt in the loop
C---- will slow things down.
C
C---- LOOP FROM START COL TO END COL FOR EACH ROW
      PRINT*,'SENDING ROW ',K,' COLUMNS ',ISC,' TO ',IEC
      DO 23 I=ISC,IEC
C---- TO PRINT IMAGINARIES
C---- WRITE(10,100) REAL(I),IMAG(I)
       WRITE(10,100) REAL(I)
100    FORMAT(' ',I6)

 23    CONTINUE
        WRITE(10,*) ' E-O-C '
 22    CONTINUE
       WRITE(10,*) ' END OF DATA FILE'
        CLOSE (5)
        END
```

Figure 2

The packed form of the .DAT file, the .IMG file, can also be tranferred. The information contained in these files have been modified to accommodate the 4-bit plane black/white monitor. Also, the data is packed two pixels to one 2-bit word. A shift operation is implemented in FORTRAN to separate these out.

We are continuing to develop a program on the Macintosh II (color) to process the information from the .DAT files to give color representations of the image. If you are using an IBM/PC like for terminal emulation, like we are, transfer to the MAC is easily accomplished using the TOPS network by Sun Micro Systems.

We look forward to communicating with anybody concerning this aspect of image processing and hopefully we will be able to exchange ideas.

Sincerely,

James W. Jennings
Director
Engr. Img. Center

Carl M. Edwards
Tech. Director
Engr. Img. Center

K. Stefan Capps
Computer Sys. Manager
Dept. Petroleum Engr.

John W. Robinson
Research Associate
Engr. Img. Center

CSI 2T Applications

Nondestructive petrophysical applications[1]

Nuclear magnetic resonance (NMR) can nondestructively image a wide range of physical and chemical properties of porous rocks and multiple fluid phases contained within their pores. The images can be taken at reservoir temperatures and pressures, with spatial resolution on the millimeter and submillimeter level.

NMR images the concentration, M_o, of a variety of nuclei, their longitudinal and transverse relaxation time curves (T_1 and T_2), and their chemical shift spectra. In rocks, NMR images the mobile fluids and the interactions of these fluids with the confining surfaces of the pores. Some of the oil core parameters that can be studied by NMR imaging are: porosity, oil and water saturation, pore size and permeability, diffusion coefficients, oil viscosity, and wetting state. In addition, cores are scanned to determine disturbed zones, open and closed fractures, drilling-mud invasion, and correlation with well logs.

NMR imaging is being used in an increasing number of petrophysical and reservoir engineering applications. The insights provided by this imaging technique promise to further the understanding of primary and supplementary oil recovery processes.

The examples shown here are NMR images of Bentheim sandstone, Indiana limestone and Bakers dolomite obtained on a GE CSI 2T imaging system. Sample diameters were 2″ O.D. Images were obtained with a 3″ proton imaging coil.

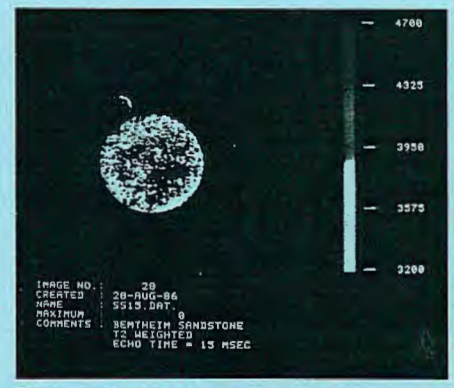


Fig. 1—Bentheim sandstone

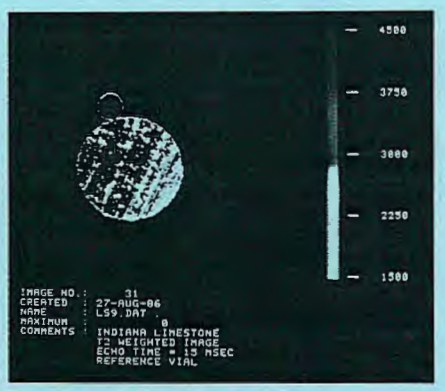


Fig. 2—Indiana limestone

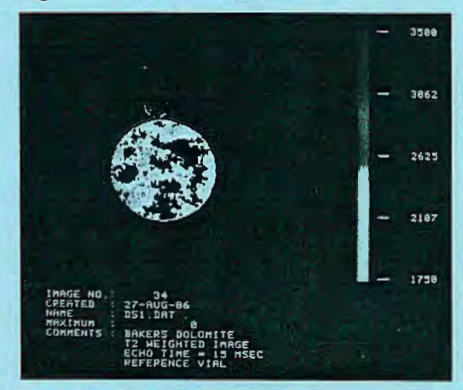


Fig. 3—Bakers dolomite

Parameters, all images: TR = 2 sec, TE = 15 msec, NA = 2, FOV = 12 cm, matrix = 512 × 512.

Color enhancement and annotation: CATPIX software developed by Shell Development Co.

Acknowledgement:
Harold J. Vinegar, Shell Development Co., Bellaire Research Center, Houston, Texas

Reference:

[1]Vinegar, H.J.: X-ray, CT and NMR Imaging of Rocks. *Journal of Petroleum Technology* (March 1986), 257-259.

GE NMR Instruments

255 FOURIER AVENUE, FREMONT, CA 94539
(415) 683-4408, FAX (415) 490-6586

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JEOL'S GSX-FT NMR Systems

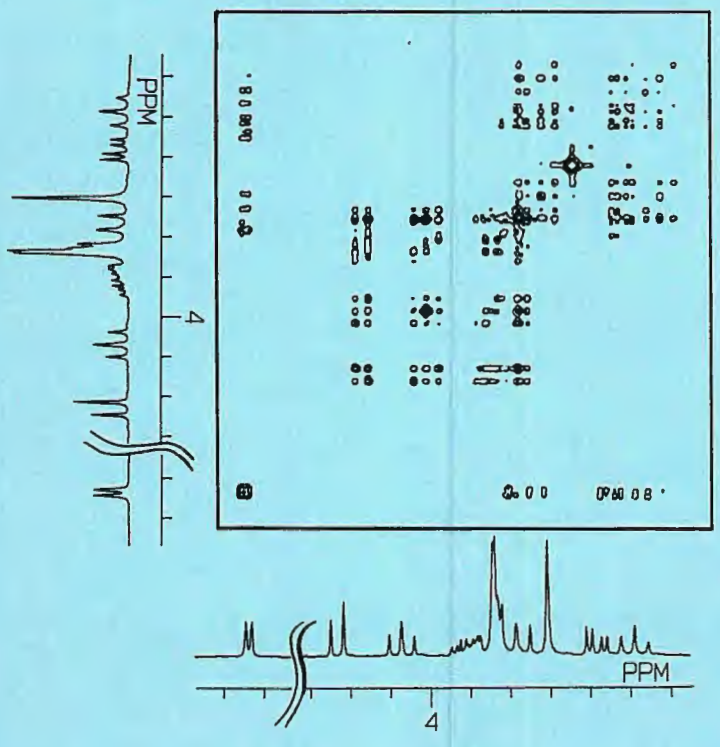
Application: Pulse Programming

The GSX pulse programmer was designed with sufficient flexibility and range to do the most sophisticated routines you see in the current literature. While these routines may be of no interest for your present NMR applications, the next issue may have just the perfect experiment. As an example of these capabilities, consider HOHAHA.*

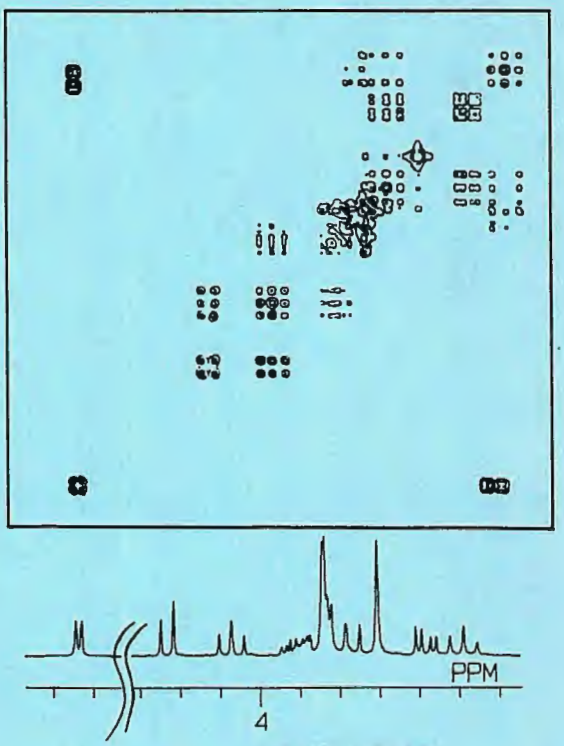
The HOHAHA experiments which use MLEV-17 for spin locking are very good for providing connectivity, especially in small molecules which produce poor RELAY experimental results. The spin locking allows coherence transfer which can be controlled by the mixing times. Directly coupled protons can be detected with short mixing times (20 ms) while longer mixing times result in relayed coherence transfers — many times with more sensitivity than RELAY experiments.

The data below are from a wide bore GSX-270 and compares the normal COSY experiment using 3 mg of sucrose in D20 with the HOHAHA experiment run on the same sample. The spin locking used for the HOHAHA produces relayed coherencies which are shown by the additional cross peaks in the contour plot.

HOHAHA DATA



COSY DATA



*Ad Bax and Donald G. Davis, *J. Mag. Res., 65, 355 (1985).*

JEOL
Serving Advanced Technology
11 Dearborn Road, Peabody, MA 01960
(617) 535-5900

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