THE NMR NEWSLETTER

No. 442

July 1995

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	Frequency Range	Resolution	Switching Time[1]	Phase-Continuous Switching[2]	Rack-Mount Cabinet Dim.[3]	Remote-Control Interface	Price Example[4]
PTS 040	.1-40 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$5,330.00 (1 Hz resol., OCXO freq. std.)
PTS 120	90-120 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$5,330.00 (1 Hz resol., OCXO freq. std.)
PTS 160	.1-160 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$6,495.00 (1 Hz resol., OCXO freq. std.)
PTS 250	1-250 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$7,440.00 (1 Hz resol., OCXO freq. std.)
Type 1 **PTS 310** Type 2	.1-310 MHz	1 Hz	1-20μs	standard	3½"H×19"W	BCD (std) or GPIB (opt)	1 Hz resol., OCXO: $6,425.00 1 Hz resol., OCXO: $5,850.00
PTS 500	1-500 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$8,720.00 (1 Hz resol., OCXO freq. std.)
PTS 620	1-620 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$9,625.00 (1 Hz resol., OCXO freq. std.)
PTS 1000	0.1-1000 MHz	optional .1 Hz to 100 KHz	5-10μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$11,830.00 (1 Hz resol., OCXO freq. std.)
PTS 3200	1-3200 MHz	1 Hz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$14,850.00 (1 Hz resol., OCXO freq. std.)
PTS x10	user specified 10 MHz decade	1 Hz	1-5μs	standard	3½"H×19"W	BCD (std) or GPIB (opt)	$3,000.00 (1 Hz resol., OCXO freq. std.)
PTS D310	two channels .1-310 MHz	.1 Hz	1-20μs	standard	5¼"H×19"W	BCD (std) or GPIB (opt)	$8,560.00 (.1 Hz resol., OCXO freq. std.)
PTS D620	two channels 1-620 MHz	.1 Hz/.2 Hz	1-20 μs	standard	5¼"H×19"W	BCD (std) or GPIB (opt)	$13,240.00 (.1 Hz/.2 Hz resol., OCXO freq. std.)

1 Switching Time is dependent on digit (decade) switched; see detailed instrument specifications.

2 For applicable digits, see detailed instrument specifications.

3 Bench cabinets are 17" wide.

4 Prices are U.S. only and include Manual and Remote (BCD) Control; PTS 3200 Digital Front Panel.

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Varian, Analytical Instrument Division

FORTHCOMING NMR MEETINGS

ISMAR 1995, Sydney, NSW, Australia, **July 16-21, 1995**; Contact: Dr. W. A. Bubb, Dept. of Biochem., Univ. of Sydney, Sydney, NSW 2006, Australia. Phone: +61-2-351-4120; Fax: +61-2-351-4726; Email: ismar95@biochem.su.oz.au. See Newsletter 437, 20.

NMR Symposium at the 37th Rocky Mountain Conference on Analytical Chemistry, Denver Colorado, **July 24-27, 1995**; Contact: Dr. Alexander J. Vega, DuPont Central Research and Development, P.O. Box 80356, Wilmington, DE 19880-0356; Tel. (302) 695-2404; Fax: (302) 695-1664; e-mail: vega@esvax.dnet.dupont.com. See Newsletter 432, 34.

3rd Scientific Meeting, Society of Magnetic Resonance, and 12th Meeting European Society for Magnetic Resonance in Medicine and Biology, Nice, France, **August 19 - 25, 1995**; Contact: Society of Magnetic Resonance, 2118 Milvia St., Suite 201, Berkeley, CA 94704; Tel. (510) 841-1899; Fax: (510) 841-2340.

Western Biotech Conference, San Diego, CA, **October 18 - 21, 1995**; Contact: Western Biotech Conf. Registr'n., c/o Tom Lobl, Tanabe Research, 4540 Towne Centre Court, San Diego, CA 92121; Tel. (619) 622-7035; Fax: (619) 622-7080; E-mail: tjlobl@cerf.net.

37th ENC (Experimental NMR Conference), Asilomar Conference Center, Pacific Grove, California, **March 17 - 22, 1996***[sic]*; Contact: ENC, 1201 Don Diego Avenue, Santa Fe, NM 87501; (505) 989-4735; Fax: (505) 989-1073.

38th ENC (Experimental NMR Conference), Orlando, FL, **March 23 - 27, 1997***[sic]*; Contact: ENC, 1201 Don Diego Avenue, Santa Fe, NM 87501; (505) 989-4735; Fax: (505) 989-1073.

Additional listings of meetings, etc., are invited.

By now, you should have received your subscription renewal invoice. If you have not, please contact us.

If you have received your invoice, please initiate payment promptly. You cooperation will be appreciated.

BLS & LWS

Dr. Barry Shapiro
The NMR Newsletter
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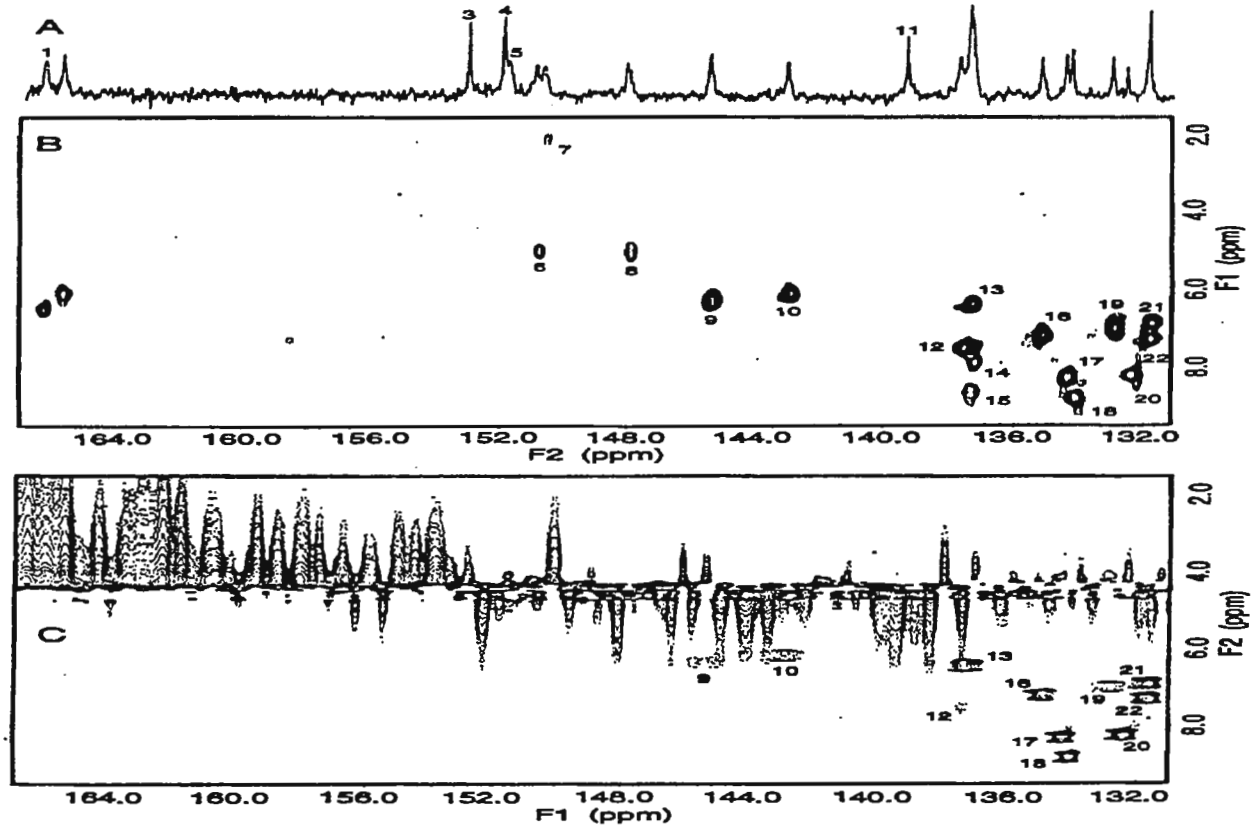
International: 61-3
E-mail: brownlee@latrobe.edu.au

Dear Barry,

(received 6/5/95)

^{15}N-Detected Experiments of ^{15}N Labeled Paramagnetic Compounds.

We have recently shown that ^{15}N-detected 2D experiments (developed many years ago) are essential for the NMR study of paramagnetic compounds such as iron containing proteins[1]. ^{15}N resonances do not suffer from paramagnetic broadening to the same extent as proton resonances thus in ^{15}N labelled paramagnetic compounds, the sensitivity[2] is comparable or better to the corresponding ^{1}H-detected experiment. For compounds studied in water there is an additional advantage in that the spectra are essentially free of artefacts associated with solvent suppression. Results of such experiments obtained for a 4 mM sample of ferredoxin from *Clostridium pasteurianum* in 50 mM phosphate buffer in a 5 mm sample tube clearly illustrate these advantages. These spectra were obtained on a Bruker AM-400 using the 10 mm broad band multinuclear probe. Our recent upgrade to DRX-400 and more suitable probes should lead to considerably better results.



A. Hyperfineshifted amide region of N-15 spectrum of *Cp*Fd.
B. Hyperfineshifted amide region of N-15 2D detected INEPT spectrum of *Cp*Fd.
C. Hyperfineshifted amide region of H-1 2D detected HMQC spectrum of *Cp*Fd.

Please credit this contribution to Professor David Kelly's subscription. With best wishes,

Maruse Sadek Bob Brownlee

1. M. Sadek, S. D. B. Scrofani, R. T. C. Brownlee, and A. G. Wedd, *J. Chem. Soc. Chem. Comm.*, 105 (1995).
2. M. Sadek, R. T. C. Brownlee, *J. Mag. Reson.*, in press (1995).

Q-SWITCHING™

Bruker has developed a series of probes with switchable quality factor, called Q-Switch™ probes. These probes enable rapid switching (<2 µs) between a high and low Q factor of the proton channel.

The Q-switch probe offers a solution to the mutual coupling between a strong NMR signal and the radio frequency coil of the probe known as radiation damping. Radiation damping adversely affects samples with intense resonance lines. Since it increases for probes with higher quality factor "Q", reducing the Q minimizes this effect.

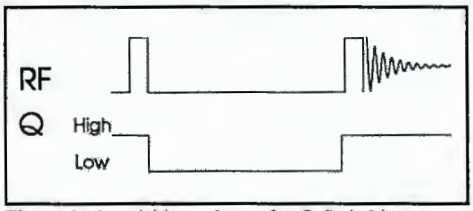


Figure 1: Acquisition scheme for Q-Switching during free-precession

A traditional approach to reduce radiation damping has been to lower the Q of the probe by detuning the probe circuit. However, this results in a loss of sensitivity since the induced voltage in the coil is also proportional to Q. Other approaches to reducing radiation damping have included the use of spin lock pulses or magnetic field gradients. *Now with the Bruker Q-Switch probe a high Q factor can be used during rf pulses and data acquisition for maximum efficiency and sensitivity, while a low Q mode can be used for suppression of radiation damping during free precession delays in the NMR sequence.*

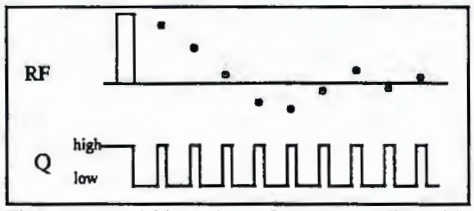


Figure 2: Acquisition scheme for data sampling with Q-Switching

With the Q-Switch probes, rapid switching of the Q (<2 µsec) allows suppression of radiation damping without sacrificing sensitivity. Typically, Q-Switching occurs *between* the excitation pulse and data acquisition (Figure 1). But its benefits can also be realized by applying Q-switching *during* the actual data acquisition (Figure 2), which is now possible due to the rapid switching ability of this accessory.

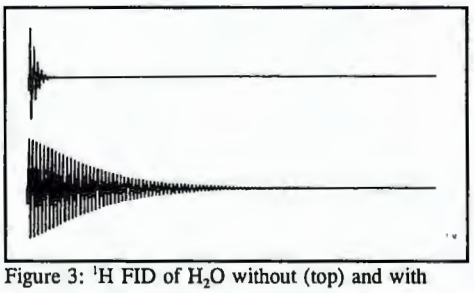


Figure 3: ^{1}H FID of H_2O without (top) and with (bottom) Q-Switching during acquisition

The benefits of Q-switching are evident in the observation of H_2O (Figure 3). The proton free induction decay for water is significantly increased by reducing the Q during the acquisition. The resultant spectra (Figure 4) clearly shows a narrower linewidth for the water resonance by the reduction of radiation damping.

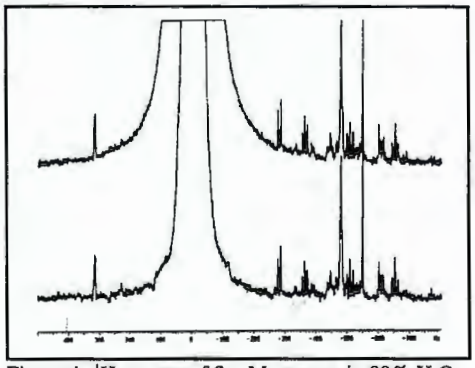
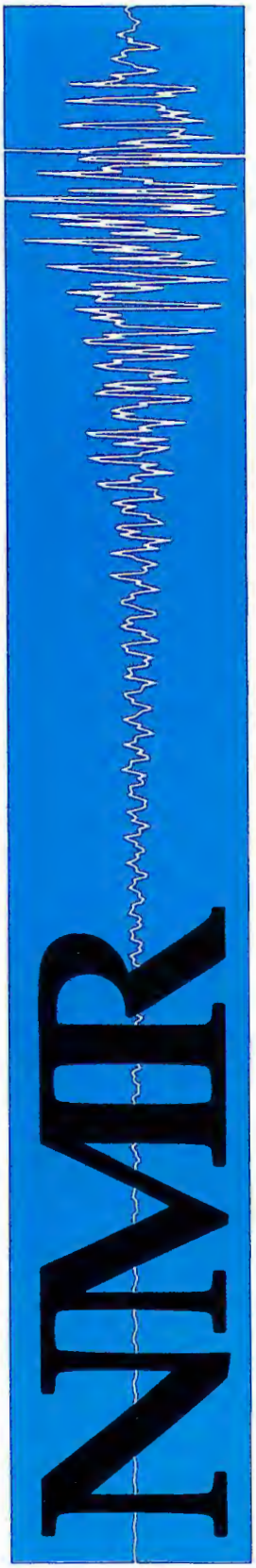


Figure 4: ^{1}H spectra of 2 mM sucrose in 90% H_2O without (top) and with (bottom) Q-Switching during acquisition



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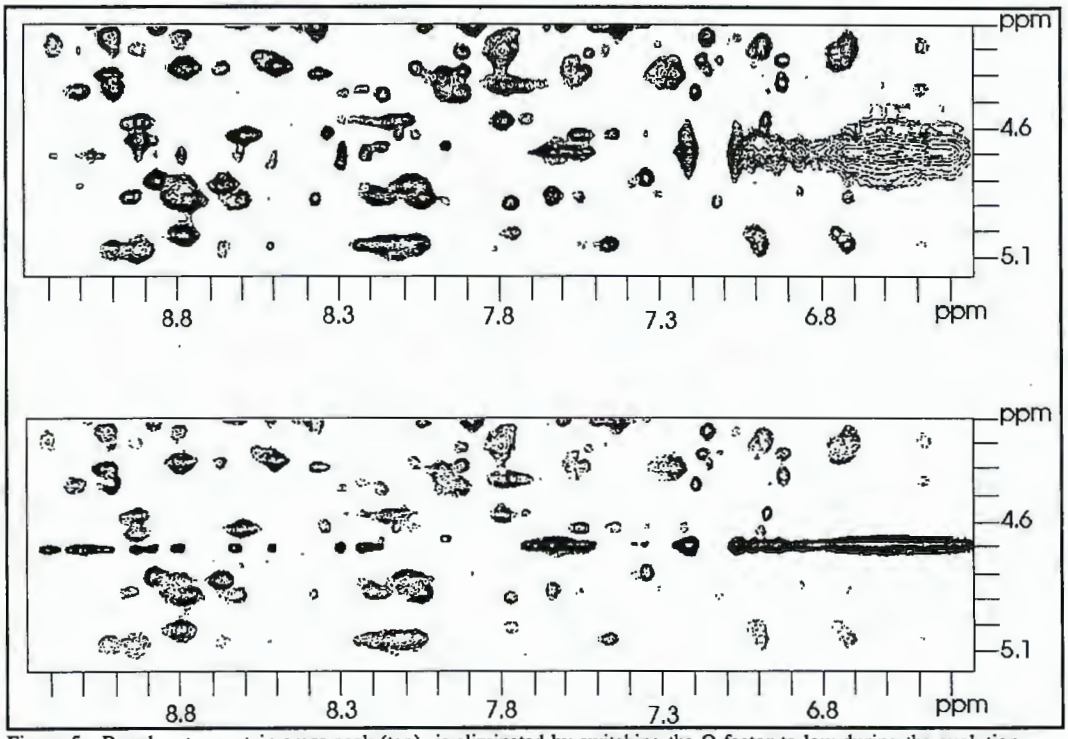

Figure 5: Broad water-protein cross peak (top), is eliminated by switching the Q factor to low during the evolution time t_1 (bottom)

The use of a Q-Switch is particularly attractive for the observation of intermolecular cross peaks between proteins and water, where experiments recorded at high Q result in substantial line-broadening of the water-protein cross peaks. The extent of line-broadening caused by radiation damping is illustrated by a NOESY experiment on an aqueous solution of lysozyme (Figure 5). Switching the Q factor low during the evolution time efficiently eliminates radiation damping. The resulting narrowed resonances in f_1 allows the observation of cross peaks between the water signal (4.7 ppm) and the lysozyme NH and aromatic CH protons.

Q-Switch™ probes (5 mm inverse with or without gradients) are available for 500, 600 and 750 MHz UNIX based Bruker spectrometers. Contact your local Bruker representative for more information.

references:
1. C.G. Anklin, M. Rindlisbacher, G. Otting, F.H. Laukien, *J.Magn.Reson. B* **106**, 199 (1995)
2. W.E. Maas, F.H. Laukien, D.G. Cory, *J.Magn.Reson. A* **113**, 274 (1995)
G. Otting, E. Liepinsh, *J.Magn.Reson. B* **107**, 192 (1995)

DEPARTMENT OF HEALTH & HUMAN SERVICES

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4940 Eastern Avenue
Baltimore, MD 21224

Dr. Barry Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

June 9, 1995
(received 6/16/95)

Dear Dr. Shapiro,

A QUIET, SELF-CONTAINED COMPRESSED AIR SUPPLY FOR NMR LABORATORIES

As part of the installation of a Bruker AMX 400 spectrometer in our laboratory, we were confronted with the lack of a suitable compressed air supply for the new console. While the site selected for the installation was excellent in terms of vibration, RF interference, and proximity to ferromagnetic objects, the compressed air supplied to this room was exceedingly wet and dirty and fluctuated in pressure between 20 and 65 psig. Moreover, we planned to use the AMX to perform lengthy MAS solids experiments, which demand a very stable source of dry, clean air (≤1 micron) at high flow rates (≥8 SCFM at 75 psig). Consequently, we decided to abandon the house air supply and set up a dedicated compressed air system for the NMR laboratory.

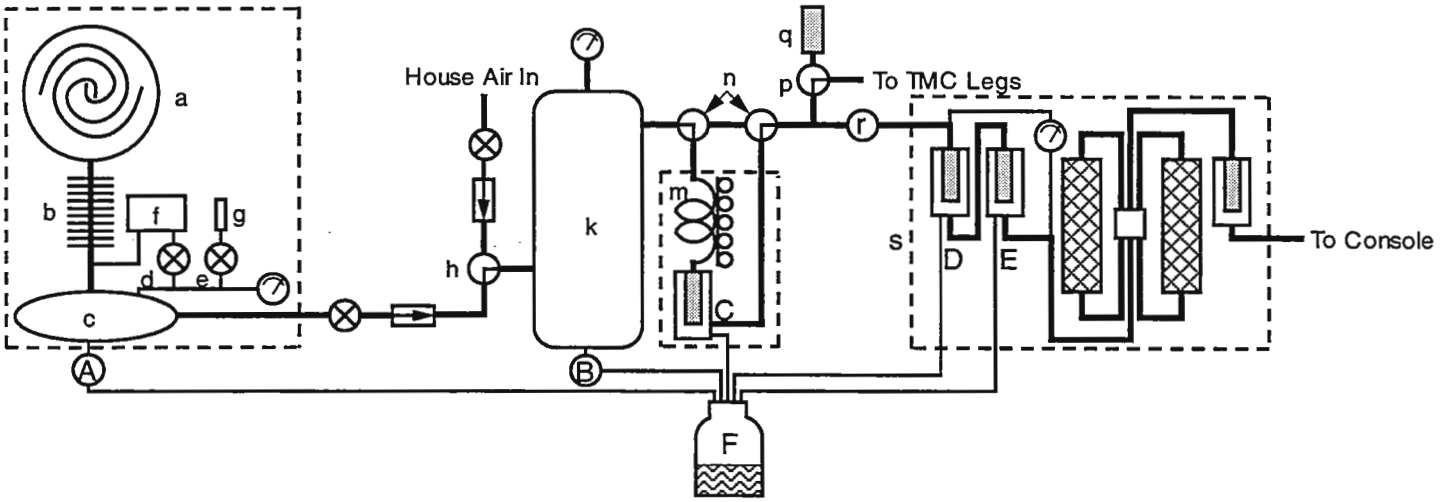
A survey of all rooms and utility closets within close proximity to the installation site revealed no space for locating a conventional air compressor of the size needed to supply the spectrometer console and accessories. Thus, we were forced to locate the new compressor inside the NMR laboratory itself. This situation created a special design challenge since conventional piston compressors, particularly oil-free models, generate deafening noise and considerable vibration while running. Clearly, an unconventional solution was required.

Through consultation with a local pneumatic equipment company, we learned about a new generation of oil-free, rotary scroll compressors which have just recently become available for general use. These units compress air between two aluminum spirals, one of which rotates while the other is fixed. An air-tight seal between the scrolls is achieved without oil by self-lubricating plastic tips on the ends of the rotating scroll and no valves are needed to control air intake or exhaust. Compared to piston models, rotary scroll compressors are extremely quiet (49 dBA) and vibration free and generate compressed air essentially free of pulsation. Further, rotary scroll compressors run at a lower temperature (ca. 52 °C discharge) than piston compressors, resulting in less heat output to the room and permitting less elaborate aftercooling and drying units to be employed after the compressor. Finally, rotary scroll compressors are ideally suited for continuous operation as they can run 5000-10000 hours before routine maintenance is required.

Figure 1 shows a diagram of our compressed air system. A Powerex 3 HP compressor (a) driven by a 208 volt 3 phase motor at 2700 RPM produces compressed air at up to 8.6 SCFM at 100 psig. The compressor exhaust flows through an air-cooled heat exchanger (b) into a 6.6 gallon receiving tank (c) within the compressor enclosure. By turning valves (d) and (e), the compressor may either be operated in conventional start-stop mode or continuously. In the latter case, the compressor will periodically exhaust air to the room through the LoadGenie™ regulator (f) when the internal tank pressure reaches the upper set point (125 psig). The exhaust flow will stop once the tank pressure falls to 100 psig. By contrast, when the compressor runs in start-stop mode, the pressure transducer (g) causes the compressor itself to start at 100 psig and stop at 125 psig. We find that start-stop mode is ideal for inserting and ejecting samples, while continuous operation permits fast, stable magic angle spinning without the need for large external buffer tanks.

The output of the compressor unit is fed into a more-or-less conventional cooling and drying system consisting of a 30 gallon vertical steel tank (k), an Arrow A-10 refrigerated air drier (m), which reduces air dew point to about 4 °C, and a Balston 75-20 desiccant air drier (s), which yields a dew point of -100 °C and dust filtration to 0.1 microns. The 30 gallon tank serves not only to buffer pressure changes as the compressor starts and stops and to collect moisture but also protects MAS and high-resolution spin turbines from sudden

depressurization. In a "crash and burn" test, we shut down the compressor while the system was spinning a 7mm MAS rotor at 5 kHz. The sample continued to spin at 5 kHz for two minutes, then slowly spun down over about 3 minutes. Bypass valves (h) and (n) are included to permit servicing of the compressor and refrigerant drier and for switching to house air in the event of a dire emergency. A valve (p), exhaust silencer (q), and regulator (r) are provided between the refrigerant and desiccant driers to provide air for TMC magnet legs and for isolating the Balston unit for service.



The compressor and external receiving tank are equipped with solenoid drain valves (A) and (B) which are opened for 5 seconds every 45 minutes on a staggered schedule to prevent excessive pressure loss. These solenoid valves were installed in place of the manufacturer-supplied pneumatic float drains since the latter showed a tendency to stick in the closed position after extended use on these two drains. The refrigerant and desiccant driers utilize pneumatic drains (C), (D), and (E), and all five drain lines feed into a 20 liter heavy-walled glass bottle (F) for condensate collection. The condensate is usually emptied once every two weeks.

All the plumbing connecting the components of this system is composed of 1/2" copper tubing to prevent rusting and water vapor permeation. For further stabilization of flow during compressor and Balston drier cycling, we plan to install an epoxy-coated aluminum receiving tank between the Balston drier and the spectrometer console. Below are the addresses of the vendors mentioned in this letter:

Powerex, Inc. (SLP03 and SLP05 rotary scroll compressors): 150 Production Drive, Harrison, OH 45030, (513) 367-3120, (800) 544-0350, FAX (513) 367-3125

Arrow Pneumatics, Inc. (refrigerant air driers), 500 N. Oakwood Rd., Lake Zurich, IL 60047, (312) 438-9100, FAX (312) 438-7110

Balston, Inc. (desiccant air driers and accessories), 260 Neck Rd. Box 8223, Haverhill, MA 01835, (800) 343-4048, (508) 374-7400, FAX (508) 374-7070

Please credit this letter to Dr. Richard Spencer's subscription.

Sincerely,

Ken Fishbein
Facility Manager, NMR Unit

Richard G.S. Spencer
Chief, NMR Unit

Phone: (410) 558-8176
FAX: (410) 558-8173
Email: fishbein@vax.grc.nia.nih.gov

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1H-19F HOESY: Utility and Limitations

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

June 14, 1995
(received 6/19/95)

Dear Barry:

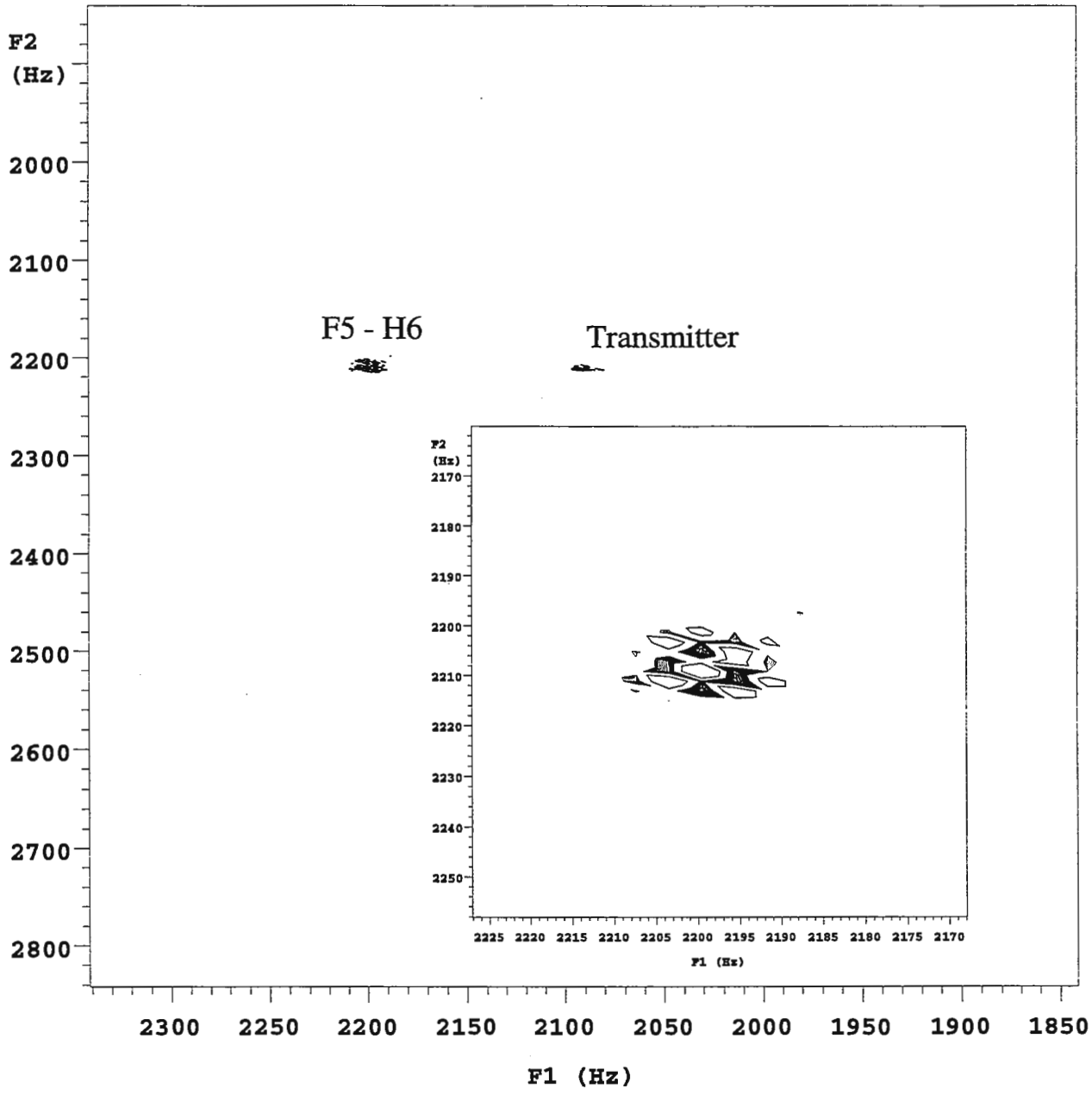
Our interest in RNA as a site of action for the anti-cancer drug 5-fluorouracil (FUra) has led us to investigate the utility of 2D ^{1}H-^{19}F experiments to explore the orientation of FUra in RNA. The HOESY experiment has been around almost as long as its NOESY cousin, but has seen considerably less use. One reason for its sparse application is due to hardware requirements. Probes routinely used for biological NMR do not have two coils that may be simultaneously tuned to high band nuclei. In reviewing the literature on the ^{1}H-^{19}F HOESY experiment we found a report from Ponzy Lu and co-workers that showed the theoretical ^{1}H-^{19}F HOE to be similar in sign and magnitude to ^{1}H-^{1}H NOEs. The HOE "null" region occurs at correlation times near 1 nanosecond making observation of ^{1}H-^{19}F HOEs in duplex DNA and RNA of typical length (e.g decamers) non-ideal. We have observed some beautiful HOE spectra on monomeric FUra and one is included in the figure. We have convinced ourselves that the poor S/N in HOESY spectra of FUra substituted RNA duplexes is not caused by low sample concentrations, but is due largely to negligible HOEs at these correlation times. The good news is ^{1}H-^{19}F HOEs should be highly useful in larger RNAs and RNA-protein complexes.

Sincerely yours,

Parag Sahasrabudhe

William H. Gmeiner

P.S. Thanks to Agustin Kintanar for letting us borrow ISU's 1H/19F Nalorac probe.


F2
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Pulse width	20 ms	20 ms
Duty cycle	Up to 10%	Up to 10%
Amplitude droop	5% to 20 ms typ.	5% to 20 ms typ.
Harmonics	Second: -25 dBc max. Third: -24 dBc max.	
Phase change/output power	10° to rated power, typ.	
Phase error overpulse	4° to 20 ms duration, typ.	
Output noise (blanked)	< 10 dB over thermal	
Blanking delay	< 1 µ s on/off, TTL signal	
Blanking duty cycle	Up to 100%	
Protection	1. Infinite VSWR at rated power 2. Input overdrive 3. Over duty cycle/pulse width 4. Over temperature	

Supplemental Characteristics:

Indicators, front panel	1. AC power on 2. CW mode	4. Overdrive 5. Over pulse width	6. Over duty cycle 7. LCD peak power meter
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Dr. Bernard Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

June 13, 1995
(received 6/16/95)

Dear Dr. Shapiro,

Title: GERIATRIC REMEDY FOR A VXR

Earlier this year, the 11 year old ENI 5100L rf power amplifier, in our VXR-500, experienced geriatric problems which we determined could not be remedied economically. Since we use the VXR-500 almost exclusively for carbon-13 analysis, we were anxious to replace the rf amplifier with minimum down-time. After a quick review of our options, we chose to order an American Microwave Technology model 3206 power amplifier as a replacement.

SEARLE

The urgency of our situation was conveyed to the understanding folks at AMT and, amazingly, we received the 3206 in four working days. We installed, tested and calibrated the unit on the fifth working day, and rested on the sixth (a saturday).

After replacing the ENI 5100L (which required 4.5 kW of AC power) with the AMT 3206 (0.35 kW of AC power) the operating temperature inside the VXR cabinet is much lower. We are very pleased with our choice, and with the flawless performance of the new amplifier.

Regards,

Bob

Robert W. Dykstra

The Wellcome Foundation Ltd

The Wellcome Research Laboratories

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(received 6/20/95)

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

Dear Barry,

Selective Inverse-Detected Long-range Heteronuclear J-Resolved NMR Spectroscopy

Measurement of long range proton-heteronuclear spin-spin couplings, particularly ^{1}H-^{13}C couplings, is of importance in many areas of chemical structural identification. We have developed a new method for measuring such coupling constants, based on a modification of the HSQC pulse sequence and which is shown in Figure 1(a). Single quantum coherence arising from a proton (I) is transferred to a directly attached carbon, or other hetero-nucleus, by an INEPT procedure and this then evolves only as long-range heteronuclear coupling because of the application of a hard 180° pulse on the carbon nuclei and a simultaneous selective 180° pulse on a given proton in the middle of the evolution period. The 180° pulse refocusses the carbon chemical shifts as well as all heteronuclear couplings except those to the proton which has been selectively inverted. At the end of the evolution time, the observable term for the detected proton is then transferred to proton magnetization at the last stage of the pulse sequence and gives rise to in-phase absorption line-shapes in both dimensions. After FT, a 2-dimensional spectrum results with the normal ^{1}H NMR spectrum in F_2 and at each ^{1}H chemical shift of the protons, coupling splittings due to $^{n}J_{CH}$ appear along F_1. **The couplings are from the selectively inverted proton to the carbon which is attached to the proton giving rise to the chemical shift in F_2 (see Fig. 2).** The experiment can be carried out in the phase-sensitive mode, and this results in higher sensitivity and better line-shape in both dimensions, very useful for measuring small coupling constants. The delay, Δ, is set to $(4^{1}J_{CH})^{-1}$ and the phase cycling program is ϕ_1 = 0, π, ϕ_2 = 0, 0, π, π, ϕ_r = 0, π, π, 0. In addition, it is possible to incorporate z-magnetic field gradients into the pulse sequence to select appropriate coherence pathways, albeit with a loss of sensitivity. There are two ways to apply the gradients as shown in Figure 1(a). It is possible to apply two gradients with a ratio of 4:1 and in this case, the time between the two gradients is fixed throughout the whole experiment. Alternatively, it is possible to apply three gradients with ratios of 2:-2:1 and, in this case, while the first two gradients may reduce the effect caused by the 180° pulses, the time between the gradients changes as the evolution time increases over the different increments in the 2-dimensional experiment. The pulse sequence may also be achieved without pulsed field gradients and, in this case, it is necessary to add a trim pulse immediately before the second ^{1}H 90° pulse and a $90°_{x}$ pulse before data acquisition. The trim pulse along the x axis may be used to saturate the $^{12}CH_n$ signals, and adding the fourth 90° pulse converts the last part of the pulse sequence into a BIRD sequence to increase the efficiency of the suppression since the intensity of the $^{12}CH_n$ signals could recover during the evolution period (as this is usually larger for the J-resolved experiment than for other correlation spectra), the BIRD sequence having no effect on the desired signals since the delay Δ is $(4^{1}J_{CH})^{-1}$. The pulse sequence may be executed with or without heteronuclear decoupling during acquisition. The experiment can also be carried out using direct heteronuclear detection in order to measure the long range ^{1}H-^{13}C coupling constants to quaternary carbons. This pulse sequence is shown in Figure 1(b). The preparation scheme could be a single 90° pulse with broad band ^{1}H decoupling to gain the NOE intensity advantage, or a DEPT sequence for sensitivity enhancement. We have used the PENDANT sequence for the preparation, which enhances the sensitivity for the protonated and quaternary carbons.

Applying the selective pulse at the ^{1}H resonance of H1' of adenosine in dmso-d_6 gives the 400 MHz ^{1}H NMR spectrum shown in Fig. 2. The usual one-dimensional ^{1}H NMR spectrum of adenosine is shown in

Fig. 2(a) with the resonance assignments. Fig. 2(b) shows the inverse-detected selective heteronuclear long-range J-resolved spectrum with ^{13}C decoupling during acquisition. In F_1, all resonances are centred on F_1 = 0 and the only splittings in F_1 arise from long range couplings to the selectively inverted proton. Thus H8 shows a doublet splitting of 4.03 Hz and this arises from the three bond coupling between the selectively inverted proton H1' and the ^{13}C at C8 to which H8 is directly bonded. Similarly, the H2' resonance shows a doublet splitting of 3.51 Hz caused by two bond coupling between H1' and the ^{13}C at C2' which is directly bonded to the proton at 2' position. This result can be confirmed by direct measurement of the ^{13}C NMR spectrum without ^{1}H broadband decoupling.

Although this approach requires a series of experiments for the selective inversion of each proton and is therefore more time consuming than a 2-dimensional correlation experiment, the J-resolved method requires little time for each acquisition to obtain good digital resolution in F_1 and in most cases the long range coupling between a few selected nuclei is sufficient for the determination of the molecular conformation. The method should be useful for measuring three bond ^{1}H-^{13}C coupling constants in nucleosides to determine the *syn-anti* conformational preferences and for studying conformations around the glycosidic linkages in carbohydrates where anomeric proton resonances are usually well resolved. It may also be useful in peptide conformational analysis for evaluation of long range couplings between Hα protons and the carbonyl carbon of the previous residue and between the Hα proton and the NH proton of the subsequent residue.

Yours sincerely,

MAILI LIU R. DUNCAN FARRANT JANET M. GILLAM JOHN C. LINDON

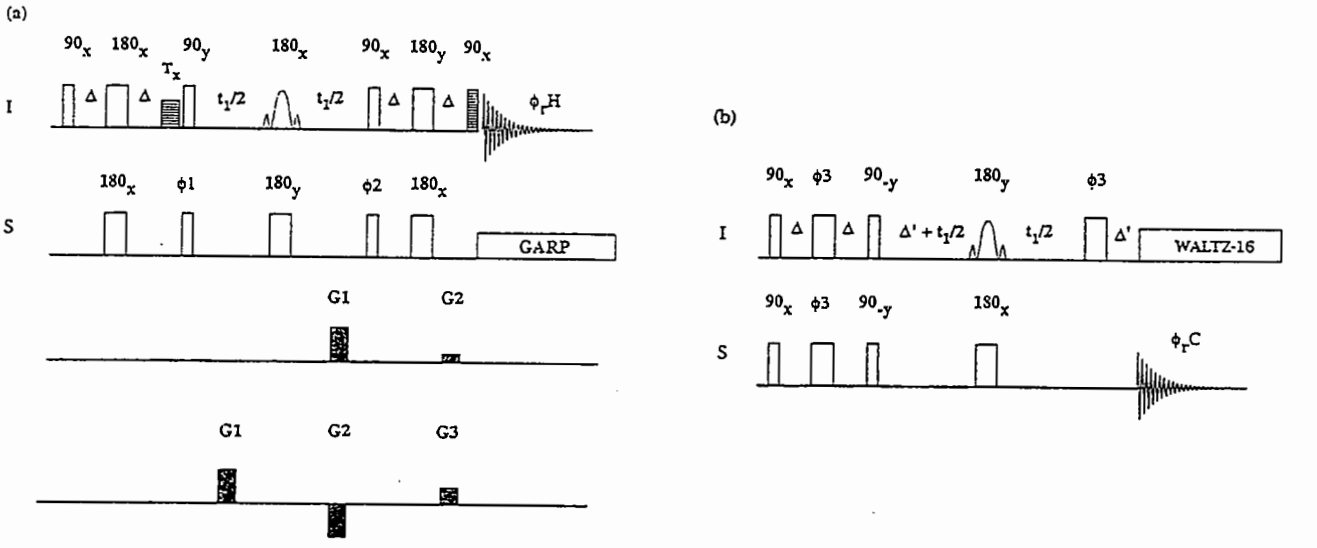

FIG. 1. NMR pulse sequence for (a) the inverse-detected selective heteronuclear long range J-resolved experiment showing two possible ways of incorporating z-magnetic field gradients for coherence selection and (b) the direct heteronucleus detected version. The narrow symbols are 90° pulses, the wide symbols are 180° pulses and the barred symbols are trim pulses with T_x having a duration of 2.5 ms. The delay Δ' is set to $5^{1}J_{CH}/8$. The phase cycling is as shown except ϕ_1 = 0°, 180°; ϕ_2 = 0°, 0°, 180°, 180°; ϕ_3 = 0°, 180°, 90°, 270°, 270°, 90°, 180°, 0°; ϕ_r(H) = 0°, 180°, 180°, 0°; ϕ_r(C) = 0°, 0°, 180°, 180°, 180°, 180°, 0°, 0°.

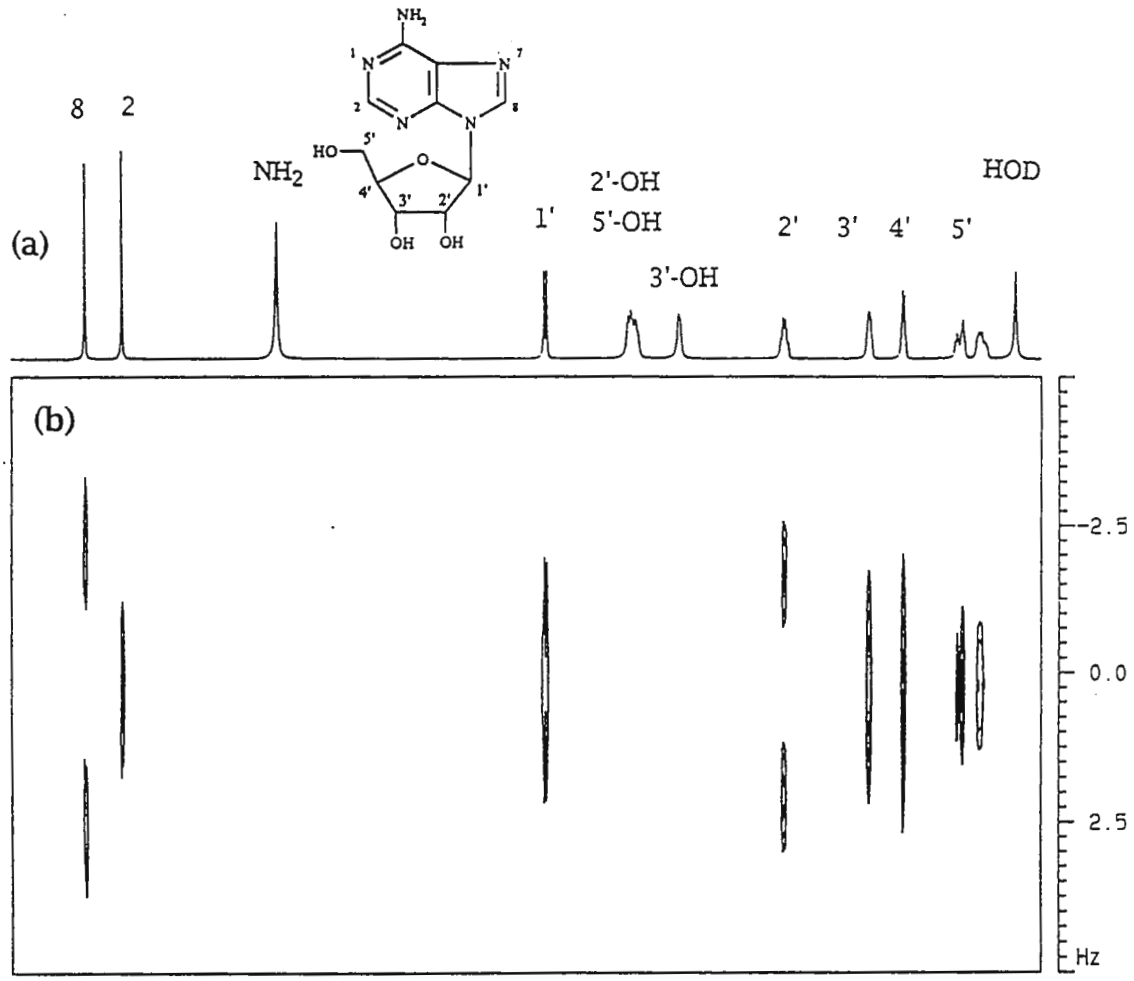

FIG. 2. Assignment and measurement of the long range ^{1}H-^{13}C coupling constants in adenosine. (a) 400 MHz ^{1}H NMR spectrum with assignments, (b) inverse-detected selective heteronuclear J-resolved spectrum with ^{1}H decoupling during acquisition.

Non-Cosmic Curiosity Strikes Again

In response to my inquiry about the photograph which appeared on page 22 of ***Newsletter No. 440*** (May 1995), Paul Stanley reports that "NMR Avenue refers (sadly) to the Natal Mounted Regiment, but I am told they use steel-lined breeches and very strong magnets to keep them on their horses!"

BLS

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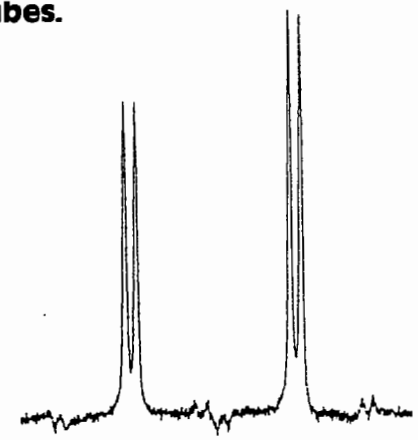
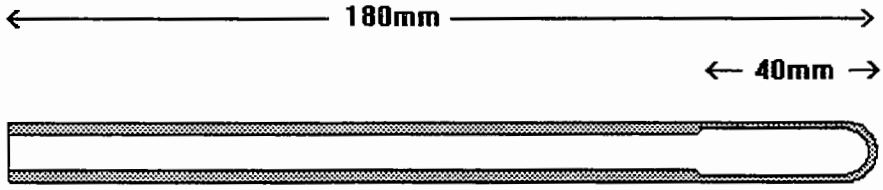
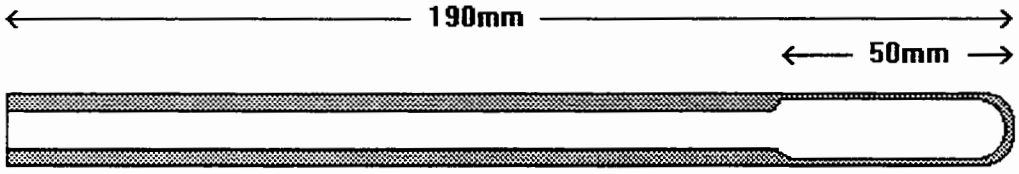


Fig.1a Fig.1b

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



PST-001 and PST-002



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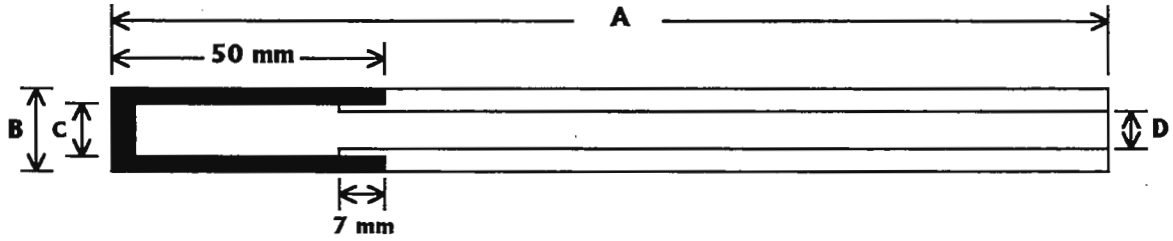

	A Length (mm)	B OD (mm)	C ID (mm)	D OD (mm)	Camber (μ)
Si-005	180	4.965 + 0 − 0.005	4.0 ± 0.1	2.5	± 0.02
Si-010	190	10.0 + 0 − 0.01	9.0 ± 0.1	6.5	± 0.02

Type	Diameter	Price for 5 tubes
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Dr. B.L.Shapiro
NMR News Letter
966 Elsinore Court
Palo Alto, CA 94303

May 24, 1995
(received 5/30/95)

Use of associative arrays for assignment software tools

Dear Dr Shapiro,

Our laboratory, the *Centre de Biologie Structurale* in Montpellier, has been created about 2 years ago, and as the title says, it is devoted to structural biology. Several physical methods are present in the CBS, and NMR is currently the largest. This is the first contribution of the CBS to your NMR Newsletter.

In our laboratory, we have found out recently that the computer object known as "associative array" (AA)[1] turns out to be a very convenient data structure for the storing and handling of the information involved in protein assignment.

Probably, we should first present what AA's are. AA's at first glance look like traditional arrays, as defined in languages like C or FORTRAN. However the main difference resides in the fact that any string can be used for indexing, rather than just integer numbers. This means that (e.g.) `TAB[1], TAB[12], TAB[Ala]` are valid entries of the same array. Another difference with "traditional" arrays, is that entries are allocated when needed. Thus in the example given above, the entries 2..11 need not to exist. AA's are usually used for character string storage, without any lack of generality, since a string can always code for a number.

Conventional data structure can be easily built using AA. To show this versatility, three examples will be given here. First, lookup tables can easily be constructed, for instance a table giving the three letters code of an amino-acid from the one letter code :

```
AALOOKUP["Y"] = "Tyr"
```

AA's can also be used to build n_dimensional arrays, as any separator can be included into the key. A simple assignment can thus be stored as : (here with ", " but any other separator can be used) :

```
ASSIGN["res_name, spin_name"] = "Peak id"
```

where res_name is the residue name (e.g. Ala10) and spin_name the spin name (e.g. Halpha).

Similarly, composite data can be stored in an AA, since the information is stored as a string. For instance the following structure

```
PEAK["pk_id"] = "ppm1, ppm2, res_name1, spin_name1, res_name2, spin_name2"
```

can be used to store all the information related to an assigned peak. In this case `pk_id` can simply be a numeral running on all the peaks. A simple field extraction routine on the content of the array element can then isolate one of the information elements.

Yet another data structure which can be realised with AA's is a chained list. An example is given here of a sequential assignment, obtained from a 3D HMQC-NOESY ^{15}N-^{1}H experiment, assuming 2 peak lists : a list for the 2D HMQC and a list for the 3D HMQC-NOESY.

```
PKASSIGN["2dpk_i"] = "3dpkauto, 3dpkai, 3dpkai+1, 2dpki+1"
```

where `2dpk` are id of peaks in the 2D list, and `3dpk` in the 3D list. In this structure, starting from peaks in the 2D list, pointers are stored which point to peaks in the 3D experiment (the HNi-Ni-HNi autopeak; the HNi-Ni-Hαi and the HNi-Ni-Hαi+1 peaks) as well as to peaks in the 2D experiment (the HNi+1-Ni+1 peak).

Such a data structure holds most of the peak assignment in a convenient manner. It can easily be used as a starting point for plotting strip charts or for extending the assignment on the side chain signals.

Another advantage of this approach is that, since entries are created when needed, and data are parsed at will, the same array can be used for storing different kind of information :

```
AALOOKUP["Y"] = "Tyr"
AALOOKUP["Tyr"] = "Y"
```

will store the 3-letters 1-letter conversion both ways.

Thus we can see that AA's show a flexibility unseen in traditional computer languages (there is in C no simple way of storing a generic data-tree with a-priori an unlimited number of siblings per node).

AA's are also very easy to implement in a interpreted language. Indeed, such a language needs a hash table for storing the allocated variables as they appear. This hash table can then be as simply used to store the variable name `VAR1` as well as `TAB1[ENTRY]`.

This hash table implementation results in a very fast access to the stored information. For instance, the residue name lookup table : `AALOOKUP["Y"]` presented above permits look-up in one memory access, compared to the slower C-like implementation

```
TAB[i].1 = "Y"; TAB[i].3 = "Tyr";
```

which would need a scanning of the list.

An additional possibility, found for instance in the perl language, consists in overlaying the AA data structure to the very simple data-base file format known as the DBM format (typically found in UNIX). The DBM entries consist in a textual field, indexed with a single string. When the AA and the DBM file have been connected, accessing the entry in the DBM file is done by accessing the related element in the array. This provides a very convenient way of storing on file the complete data-structure (a definitely missing feature of a language like C)

AA's as described here, with the overlay on DBM data-base files, have been implemented in the new version of our NMR processing program Gifa[2] . The possibility of such an assignment process is currently being investigated.

Sincerely,

Marc A. Delsuc.

Thérèse E. Malliavin

---

(1) found for instance in the computer languages 'awk' or 'perl'

(2) the Gifa software is freely accessible at the following address : ftp://tome.cbs.univ-montp1.fr/pub

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

23 May 1995
(received 6/3/95)

^{31}P NMR Compositional Analysis of Erythrocyte Membrane Phospholipids using Detergent

Dear Dr Shapiro

We wanted to explore the use of ^{31}P NMR to quantify the phospholipids of erythrocyte membranes, but Eder *et al.* [*1*] had already shown that recovery of phospholipids by using extraction methods is very variable indeed. The extent of extraction is influenced by: (1) the nature of the solvents; (2) the duration of extraction process; (3) the temperature; and (4) the form of mechanical treatment of the sample. Faced with this dilemma we explored various approaches and came up with a rapid, simple one-step procedure for quantitative analysis of phospholipid classes. The method requires minimal sample handling and the whole spectral analysis needs only a short time (~14 min) for completion. The significant feature of the method is its accuracy over the conventional analysis of erythrocyte phospholipids; in effect we achieve 100% recoverability of all the phospholipids simultaneously, because they never actually leave the sample in the first place! They are simply rendered NMR visible by dissolution in detergent micelles.

Detergents were introduced to phospholipid analysis of plasma quite some time ago [*2*] but not to cells, as far as we know. We changed many of the parameters of the previous method in adapting it for use with cells. For example, the high haemoglobin content of erythrocytes could potentially reduce the spectral resolution by virtue of releasing paramagnetic Fe^{3+}, so we use EDTA in the 'extraction' mixture.

The method is as follows: Erythrocytes are washed three times in isotonic saline (154 mM NaCl, 277 K, 5 vol) then subjected to tip sonication (Model B-12 Sonifier, Branson Sonic Power Co., CT) for 10 s. After sonication, 2.5 ml of erythrocytes with a hematocrit that can vary between 0.30 and 0.53, is transferred to a 10-mm NMR tube, and 0.5 ml Na cholate (with 5 mM EDTA) in D_2O is added with a final Na cholate concentration of 200 mM. The samples are bath sonicated (Model B-220, Branson) for 2-5 min prior to NMR measurements. Figure 1 shows a ^{31}P NMR spectrum obtained from a sample of detergent-treated human haemolysate. It is evident that several resonances can be assigned to the various phospholipid classes, whereas these resonances are totally absent in the relevant section of the ^{31}P NMR spectrum of untreated human erythrocytes. We are using the method to investigate correlations of phospholipid profiles with various clinical states and in different animals in a comparative biochemical study of phospholipid metabolism.

Yours sincerely,

Hossein Nouri-Sorkhabi Vanessa Moran Philip Kuchel

1. Eder, K., Reichlmayr-Lais, A. M., and Kirchgebner, M. (1993) *Clin. Chim. Acta* 219, 93-104.
2. Bradamante, S., Barchiesi, E., Barenghi, L., and Zoppi, F. (1990) *Anal. Biochem.* 185, 299-303.

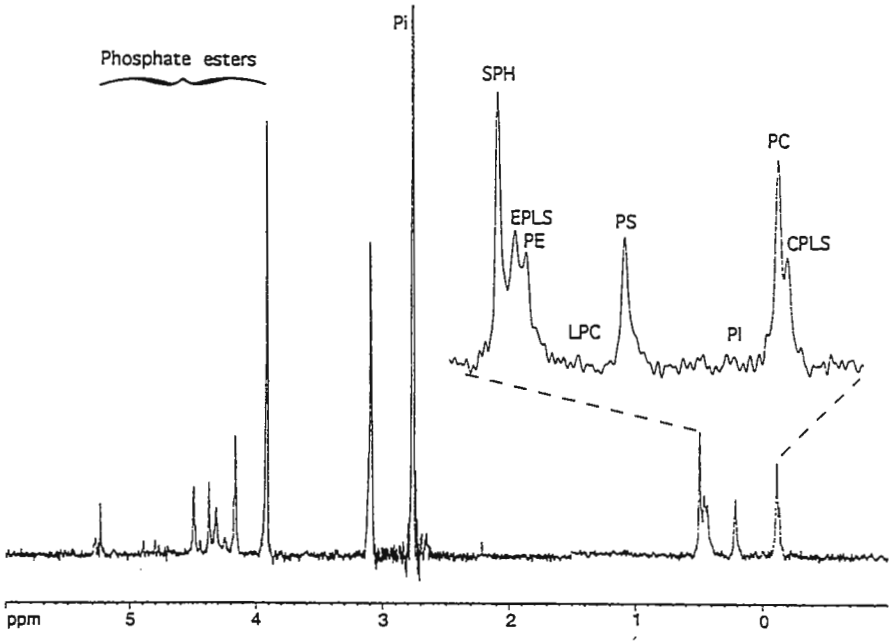

FIG. 1. ^{31}P NMR spectrum of a sample of human erythrocytes treated with sodium cholate. Resonance assignments for the phospholipids, indicated on the spectrum, were confirmed by adding the authentic compounds. Abbreviations: CPLS, phosphatidylcholine plasmalogen; PC, phosphatidylcholine; PI, phosphstidylinositol; PS, phosphatidylserine; LPC, lysophophtidylcholine; PE, phosphatidylethanolamine; EPLS, phosphatidylethanolamine plasmalogen; SPH, sphingomyelin and; P_i, inorganic phosphate.

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Washington
WASHINGTON·UNIVERSITY·IN·ST·LOUIS

Department of Physics

June 5, 1995

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

Measuring Site Occupancies in Metal-Deuterides Using MAS

Dear Dr. Shapiro,

One of the outstanding problems in the field of transition metal-hydrides is determining the occupancies of inequivalent interstitial hydrogen sites. Unfortunately, x-ray diffraction is only sensitive to the positions of the metal atoms; thus, a variety of other experimental techniques have been used. No technique has proven entirely satisfactory, and there remain significant disagreements over the site occupancies in a number of metal-hydrides. We thought that it would be fun to use magic-angle spinning to resolve chemical/Knight shift differences between interstitials on inequivalent sites, since determining the site occupancies from well-resolved lines in an NMR spectrum is pretty straightforward. We have promising results to report from a magic-angle spinning study of yttrium-dideuteride (YD_2).

There are several line-broadening interactions which are important in metal-hydrides: dipole-dipole, anisotropic chemical and Knight shifts, first-order quadrupole (for deuterium), and magnetic susceptibility. This last broadening is unusually important in metal-hydrides because of their typically large electronic susceptibilities from d-electrons and the necessarily powder state of metallic NMR samples. The most difficult interaction to remove, however, is proton-proton dipolar since this results in a homogeneous broadening. To remove the ~30 kHz of like-spin dipolar width in YH_2 would require MAS rates above 30 kHz -- higher than the currently available spinning rates.

Thus we chose to look at metal-*deuterides*. Here the like-spin dipolar broadening is smaller by a factor of ~25 and easily removed by MAS at 2 kHz or faster. In Fig. 1, the ^2D spectrum of $YD_{1.98}$ at 194 K shows only one line due to D atoms on tetrahedral (T) sites in the face-centered cubic Y lattice. But for $YD_{2.08}$ (Fig. 2), there are more D atoms than there are T-sites, so some of the octahedral (O) sites are also occupied; the D atoms on O-sites yield the shifted line, 28 ppm up-frequency from the T-site line. The magnitude of the shift shows it is at least partly a Knight shift.

Thus, MAS of metal-deuterides appears to be a promising technique for identifying and quantifying the occupancies of inequivalent interstitial sites. We feel this will be particularly interesting in alloys and compounds (e.g. ABD_x) in which a great variety of sites exist.

But there is more detail present in the $YD_{2.08}$ spectrum. First, as temperature is increased above ~230 K the O-site line and most of the T-site sidebands disappear (Fig. 3). This is due to thermally activated T-O interchange averaging the T and O resonances. Further, the only sites with substantial EFG (and hence sideband intensity) are T-sites with occupied O nearest neighbors, which destroy the local cubic symmetry. These T_O sites have not

only substantial EFG but a *slightly* different Knight shift, which is apparent from the fact that the center frequency of the sidebands is approximately 150 Hz up-frequency from the center of the T-site line.

We've also had fun with inversion-transfer: we selectively invert the T-site line and then monitor the rate of magnetization transfer to the O-site line. We find that this rate is thermally-activated. Hence, we have directly measured the T-O interchange rate.

A technical note: Before we began this project we thought that spinning a metal powder would be difficult because the induced eddy currents would have a braking effect on the spinner. In fact, this effect proved to be fairly minor. However, we did find that the probe de-tuned whenever we started spinning. Apparently the metal particles made better electrical contact during MAS due to the large forces between the sample and the walls of the rotor. Diluting the powdered metal with an insulating powder (MgO) greatly reduced this problem.

Please credit this to the account of R.E. Norberg.

Sincerely,

Mark S. Conradi

Natalie Adolphi

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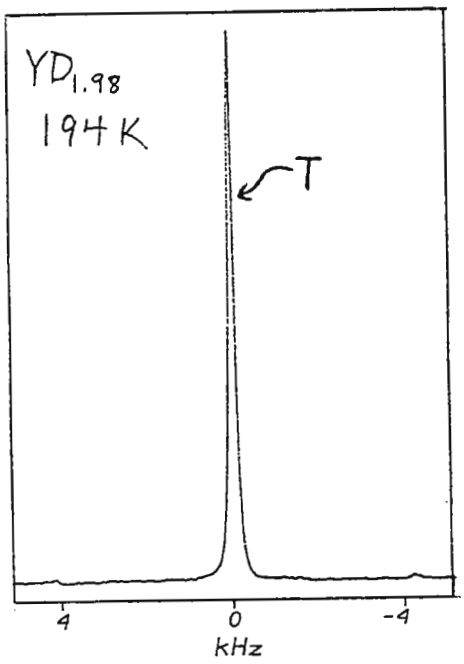


Fig. 1

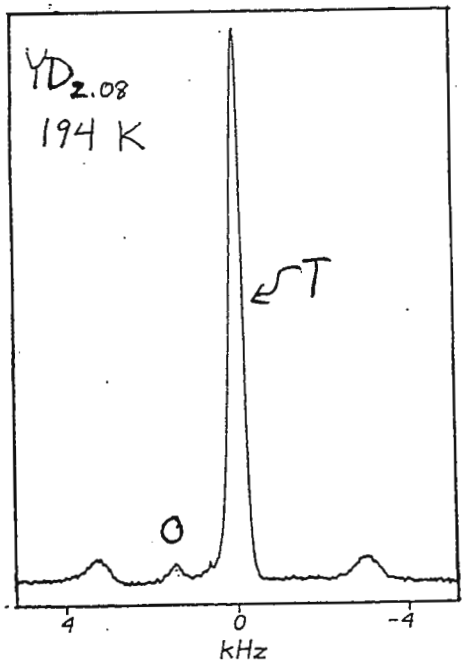


Fig. 2

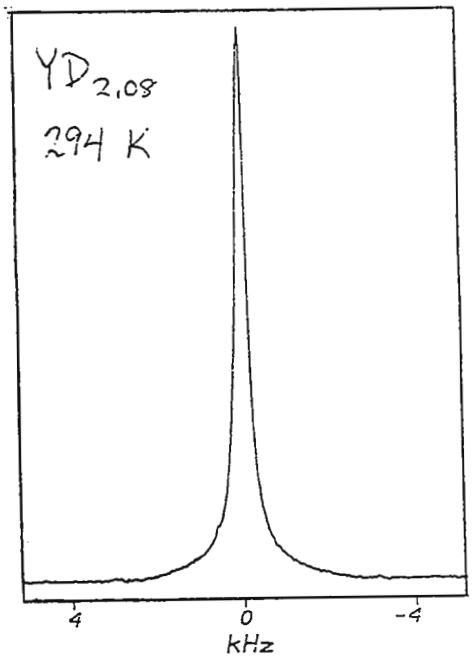


Fig. 3

University of Alberta
Edmonton
Canada T6G 2H7

Department of Biochemistry
474 Medical Sciences Building, Telephone (403) 492-5460
Fax (403) 492-0886

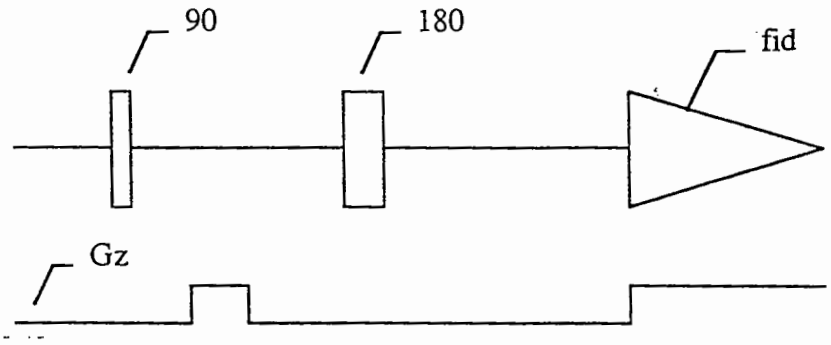
May 24, 1995
(received 6/2/95)

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

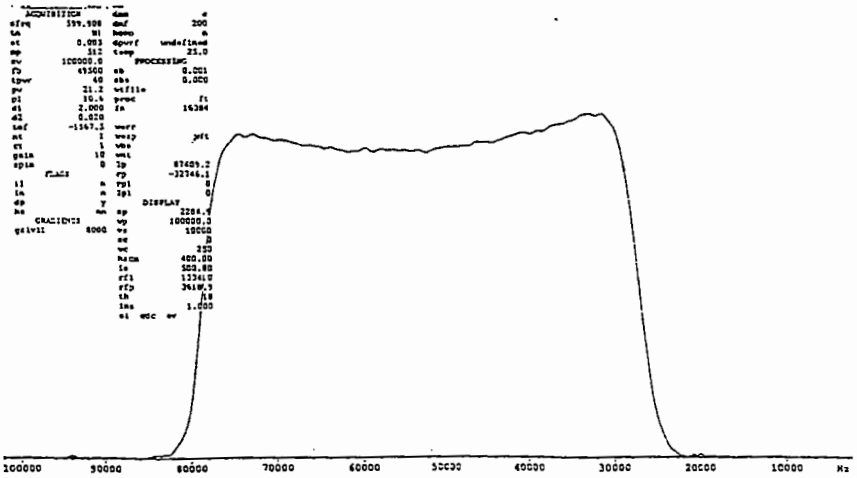
Title: Determination of gradient strength and center of gradient coil

Dear Barry:

When we received the Triple Resonance PFG probe for our Varian Unity 600, we thought it would be interesting to see how close the centre of the gradient coil was to the centre of the receiver coil, and whether we could independently measure the strength of the gradient. We used the 'profile' pulse sequence provided by Varian:

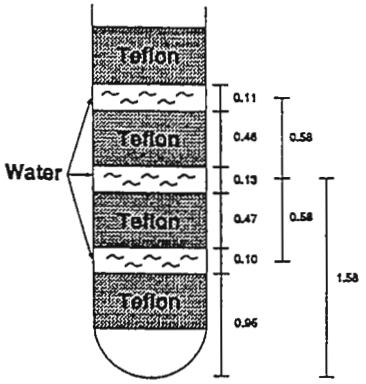


which is the same as described by Laird Trimble from Merck Frosst [1]. Using a sample of HDO, we obtained the following spectrum.

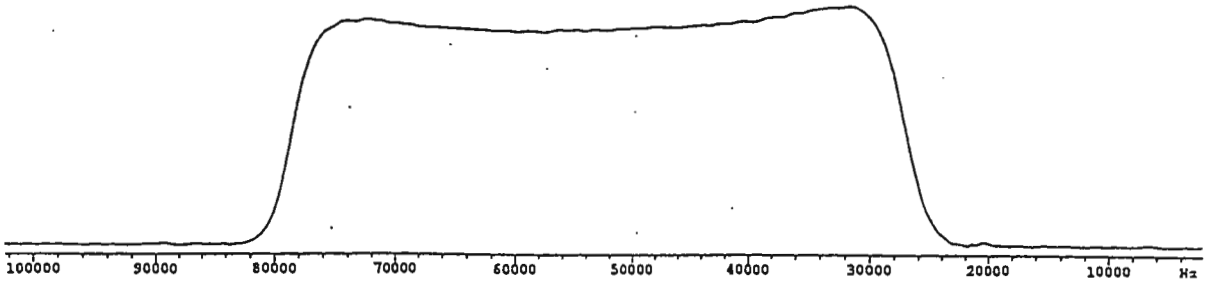


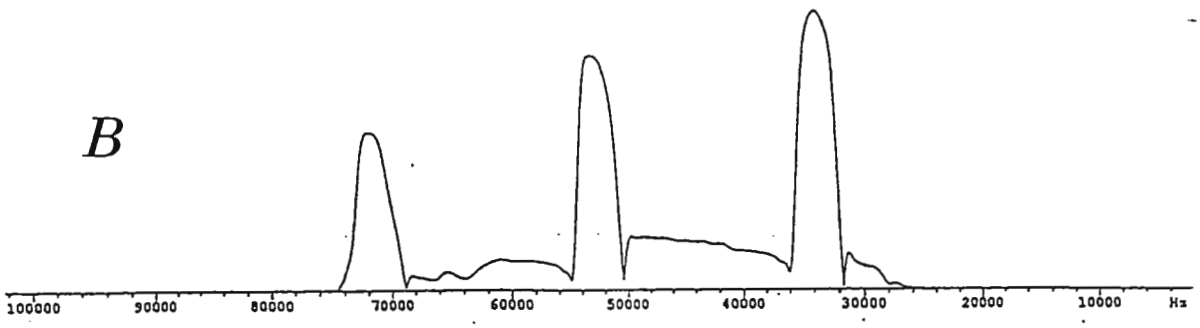
[1] The NMR newsletter , No. 439 , April 1995

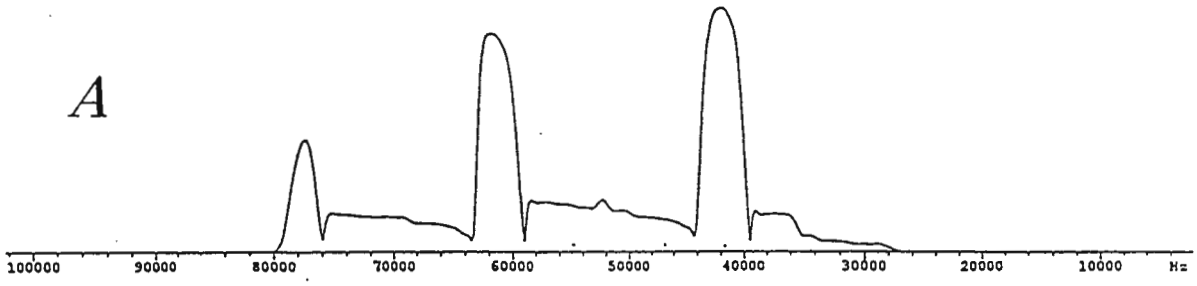
We then constructed a phantom consisting of H_2O separated by teflon plugs made from pieces of a Wilmad capillary tube holder. Three of the plugs have a hole up the middle and the bottom one is a solid portion.



Using the 'profile' pulse sequence we obtained the following spectra when the phantom was placed 2.5 mm below the center of the receiving coil, (A)and when centered in the gradient coil (B). We used gradient settings of ± 8000 DAC units out of a maximum of 32767 DAC units.





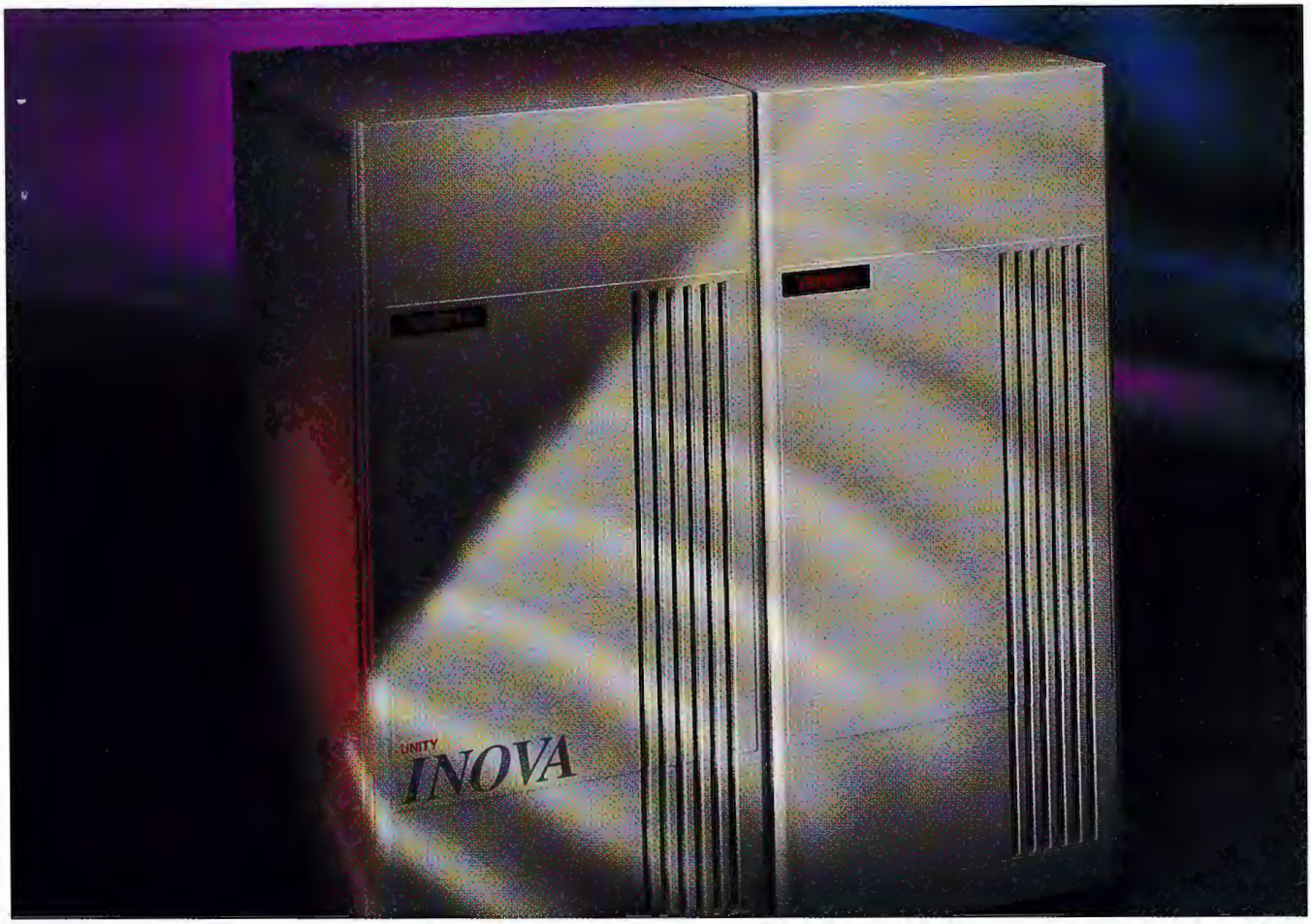


This experiment allows us to calculate the Gz. field gradient strength at 30.8 G/cm @ a setting of 32000 DAC units and determine that the gradient coil and the receiver coil were centered to within ± 0.1 mm which is within the accuracy of our measurement.

Sincerely,

Gerry McQuaid Stéphane Gagné Brian Sykes

From the First Name in NMR Comes the Latest Word in NMR: *INOVA*



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MAG-8402/420

ALBERT EINSTEIN COLLEGE OF MEDICINE
Department of Physiology and Biophysics
Bronx, New York 10461

June 9, 1995
(received 6/12/95)

Dr. B.L. Shapiro
The NMR Newsletter
Palo Alto, CA 94303

Dear Barry:

^{1}H-NMR Reveals Mg^{2+}-Dependent Changes in Fatty Acid Unsaturation of Vascular Smooth Muscle Cells

^{1}H-NMR is a comprehensive technique for monitoring lipid composition of cells and tissues (e.g. 1,2). By applying ion-exchange chromatographic procedures prior to the NMR assay, lipids can be quantitatively separated into fractions according to their polarity. This improves ^{1}H-NMR analysis of individual lipids both quantitatively and qualitatively because of reduced overlap and separation of low abundance lipids from one another. Fig 1 illustrates the ^{1}H-NMR spectrum of total lipid extracted from a segment of cerebrovascular smooth muscle after an 18 h incubation in medium containing 1.2 mM Mg^{2+}. ^{1}H-NMR allows direct measurement of fatty acid unsaturation (5.34 ppm) and plasmalogen (5.70 ppm) in lipids extracted from as little as 5 mg wet wt. of smooth muscle cells.

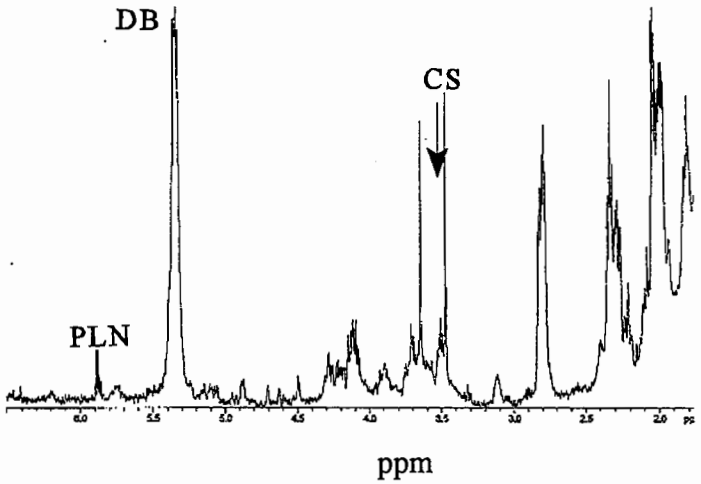

Fig 1. ^{1}H-NMR spectrum of crude lipids extracted from cerebrovascular smooth muscle helical strips. Lipids extracted from 10 mg tissue are dissolved in 1.0 ml $CDCl_3$. Useful peaks in crude extracts include plasmalogen (PLN), fatty acid double bonds (DB) and cholesterol (CS).

Total lipids were extracted by a modification of the method of Bligh and Dyer (4) and were separated on Aminopropylsllyl minicolumns (Alltech Assoc., Deerfield, IL) into: a) neutral lipids and 1,2-diacylglycerol, b) free fatty acids, c) neutral/basic phospholipids and d) acidic phospholipids. Lipids were dried under N_2 and water and residual solvent removed under vacuum at 65°C. The residue is redissolved in 99.96% $CDCl_3$; the 0.04% $CHCl_3$ present was used as an internal standard. One-pulse spectra are taken on a Varian VXR-500 NMR spectrometer operating at a proton frequency of 500 MHZ. All spectra are taken at 25°C using

a 60° pulse, spectral width of 5000 Hz, repetition time of 10 s, 8K data points. 256 acquisitions were required to attain adequate signal:noise ratios.

Using ^{1}H-NMR, we find that fatty acid unsaturation in vascular smooth muscle cells changes as a function of extracellular Mg^{2+} concentrations (Fig 2). Cultured cells from rat aorta were incubated in medium 0.17, 0.3, 0.6, 1.2 and 4.8 mM Mg^{2+} for 18 h and lipids extracted as described above. Fatty acid saturation doubled when vascular smooth muscle cells from rat aorta were changed from a medium containing 1.2 mM Mg^{2+} ion concentration to 0.17 mM Mg^{2+}. A similar Mg^{2+}-dependent increased fatty acid saturation was seen for segments of dog cerebrovascular smooth muscle (data not shown). These results demonstrate that the level of fatty acid unsaturation is sensitive to changes in $[Mg^{2+}]_o$ concentrations over the human patho-physiological range (0.3 to 0.8 mM).

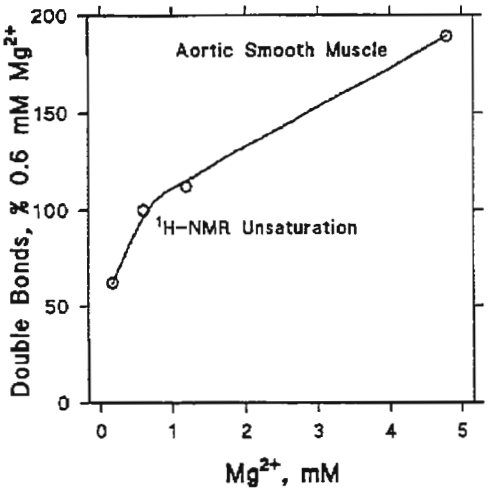

Fig 2. Effect of $[Mg^{2+}]_o$ on the saturated fatty acid content of rat aortic smooth muscle cell cultures. Primary cell cultures were incubated for 18 h in media containing the Mg^{2+} concentrations indicated.

Low serum Mg^{2+} is correlated with increased risk of cardiovascular disease; normalizing magnesium reduces vascular tension and arrhythmias (cf. 3). This study shows that reducing $[Mg^{2+}]_o$ increases fatty acid saturation in aortic and cerebral vascular smooth muscle membranes. These Mg^{2+}-induced phospholipid changes in vascular smooth muscle cell membranes may be pivotal in intracellular signaling pathways that control vasomotor tone, reactivity and pathological states such as atherogenesis. Supported by Research Grants AA08674, HD10463 and DK32030.

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2. Choi,GTY; Casu,M; Gibbons,WA (1993) Bioch. J. 290: 717.
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5. Horrocks,LA, Yeo,YK, Harder,HW, Mozzi,R, Goracci,G (1986) Adv. Cyclic Nucleotide Res. 20: 263.
6. Altura,BM, Barbour,RL, Dowd,TL, Wu,F, Altura,BT, Gupta,RK: (1993) Biochim. Biophys. Acta 1182:329.

Best regards,

Gene Morrill, GA
Adele Kostellow, AB
Raj Gupta, RK

This work was carried out in collaboration with Drs. B.M. and B.T Altura, Department of Physiology, SUNY Health Sciences Center, Brooklyn, NY.

BRUKER

PROGRESS IN DIGITAL FILTERING

ON-THE-FLY IN-LINE DIGITAL FILTERING ON THE AVANCE™

All spectrometers in the *AVANCE* continuum utilize real time oversampling and digital filtering for sampling rates of 400 kHz or less. Dedicated very fast digital signal processors (DSPs) are placed in-line on the Receiver Control Unit (RCU), which is located in the *AVANCE* VME acquisition bus, and receives the digitized signal from the ADC. The DSPs on the RCU are extremely fast and can execute up to 100 million mathematical operations per second (not just 100 MIPS). In this manner oversampling, digital filtering, and on-the-fly decimation can be utilized for all high resolution and CP/MAS acquisitions on the *AVANCE* series; all the benefits of oversampling and digital filtering, such as improved dynamic range, steep filter cutoffs, flat baselines, improved signal-to-noise, etc., are provided at all times, without the need for increased data storage or additional operator-intensive manipulations.

Bruker has invested heavily into fundamental digital filtering research, and has developed a unique and novel window function with extremely steep cutoffs. Figure 1 shows various window functions that have been described in the literature. As can be seen, the proprietary *AVANCE* window function provides much steeper cutoffs, and thus, suppression of unwanted signals, than traditional window functions such as the Blackman window function. This is essential for optimal data quality and absence of artifacts.

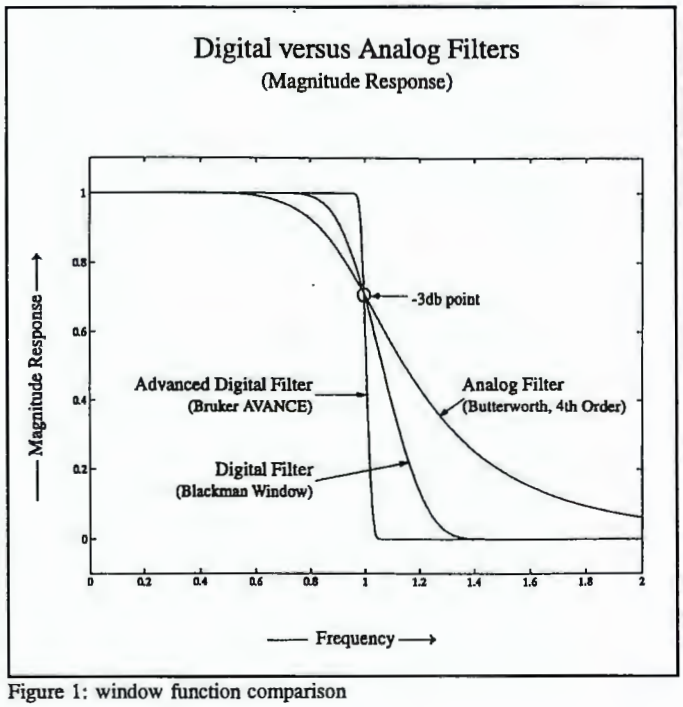
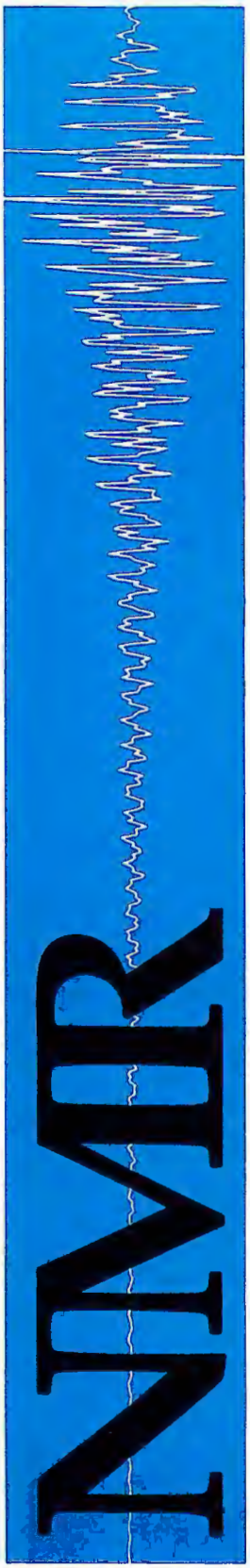


Figure 1: window function comparison



BRUKER

DIGITAL NOTCH FILTER

In response to customer demand, Bruker now provides a digital notch filter on the *AVANCE* series. Figure 2 shows the spectrum of lysozyme A) with and B) without the digital notch filter. The digital notch filter applied in the time domain can be utilized for the suppression of unwanted signals, for instance water, or other high intensity peaks.

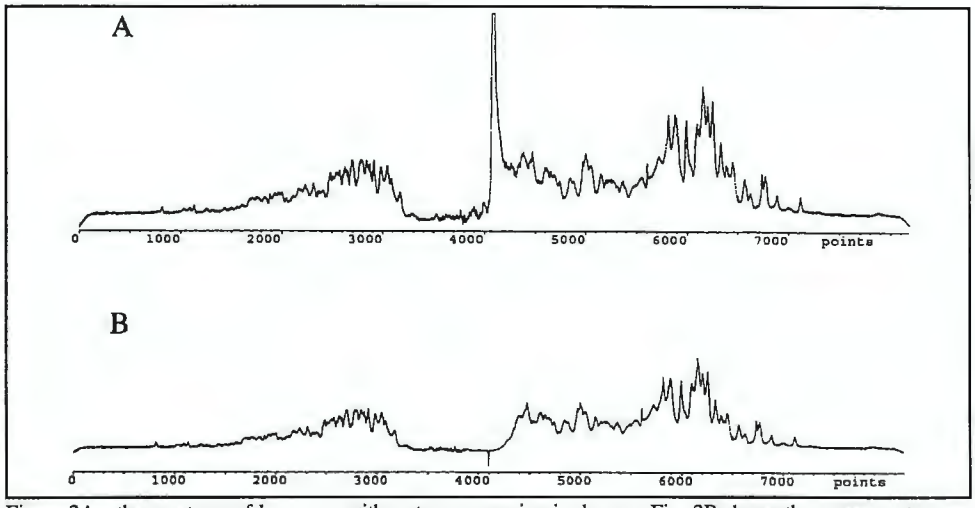


Figure 2A: the spectrum of lysozyme with water suppression is shown. Fig. 2B shows the same spectrum, after digital notch filter (200 Hz band stop), centered on the water resonance, was applied.

OFF-LINE DIGITAL FILTER SOFTWARE FOR AM, AMX AND AVANCE CUSTOMERS

Many customers have inquired about the ability to utilize digital filtering off-line, on spectrometers not yet equipped with on-line real-time digital filters, or simply to become familiar with the applications and benefits of digital filtering. Bruker suggests to utilize the Signal Processing Toolbox available within the program MATLAB (from The MathWorks, Inc. in Natick, MA, phone: (508)653-1415). The MATLAB Signal Processing Toolbox provides an easy user interface for creating various digital filters, including finite impulse response (FIR) and infinite impulse response (IIR) digital filters. The effect of the number of coefficients (tabs) on the quality of the digital filter, and on computational times can be explored. Moreover, various published window functions are available.

Bruker customers can transfer their AM or AMX data to an off-line Silicon Graphics workstation, or utilize the SGI host computer of an *AVANCE* spectrometer. MATLAB also runs on Macintosh and PC computers and can be used in conjunction with Bruker's popular WIN-NMR™ software packages on these platforms. Data transfer from WIN-NMR or UXNMR to MATLAB is easy and can be done in binary or ASCII form. After the application of digital filters, the results can easily be transferred back to UXNMR or WIN-NMR for Fourier transformation, further processing and plotting.

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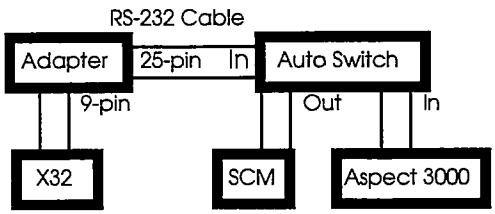
Dr. B.L. Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

June 1, 1995
(received 6/3/95)

Automatic Shimming of Bruker AM Spectrometers With An X32 Workstation

Dear Dr. Shapiro,

We would like to report a procedure we recently developed here at the UCB NMR facility to automatically shim Bruker AM spectrometers with computer controlled tune files and macros on an X32 workstation. This project involves two aspects: the physical connections and the tune files and macros. The physical connections between the two machines are shown in a block diagram on the left. There are two hardware modifications. A 9-pin-to-25-pin adapter connects the DB-9 CONTTY port of the X32 to the standard RS-232 DB-25 SCM port on the AM spectrometer. Its pinouts are listed in the table below. They were obtained by adding two additional connections needed for the auto-switch to the pinouts from our Bruker AMX-300. We thank Henry Luhrs from Bruker, Boston for providing us with the original pinout information. A 2-way RS-232 Serial Data Switch from B&B Electronics of Ottawa, Illinois is used to combine inputs from both the X32 and ASPECT 3000 into one output to the RS-232 ASPECT port of the SCM. This switch detects control signal from either of the two inputs. Since UXNMR communicates with the CONTTY port at the baud rate of 9600, we set both the SCM and ASPECT 3000 to talk at the same rate. After these two hardware modifications, both the X32 and ASPECT 3000 can talk to the SCM without intervention. This enables us to schedule more frequent computer controlled maintenance shimming than manual shimming.



Pinouts for DB9-to-DB25 Converter

9-pin X32		25-pin RS-232	Note
case SHD	NC	1 SHD	
2 RxD	==>	2 TxD	
3 TxD	==>	3 RxD	
4 DTR	==>	5 CTS	for auto-switch
5 GND	==>	7 GND	
6 DSR	==>	20 DTR	diff. from Luhrs
7 RTS	==>	6 DSR	for auto-switch
8 CTS	==>	20 DTR	

As far as the shimming software is concerned, we basically follow the auto shimming guidelines described in "Automatic shim procedure for high resolution NMR spectrometer" by Alain Louis-Joseph in the TAMU NMR Newsletter No. 433, Oct. 1994. However, we have discovered some major problems with the Bruker tune file language, which have also been confirmed by Bruker (psm@durham.bruker.com). Most of the problems involve the SIMPLEX command. The order and spelling of the shims are significant in a SIMPLEX statement. For example: SIMPLEX Z1 Z2 and SIMPLEX Z2 Z access both shims, SIMPLEX Z2 Z1 does not. It shims only Z2! A more severe problem is that non-SIMPLEX commands following a SIMPLEX statement are not executed. Some unexpected results may happen if some loop and other statements are after the SIMPLEX statement. For example, in the tune sequence below, the statement Z3 20 3 is not executed if all the commands are stored in one tune file. Instead, it will continue to execute the SIMPLEX Z3 Z2 Z statement. One way to work around this deficiency is to separate the tune commands into many small blocks and write them into separate tune files so that the SIMPLEX commands are at the end of one or more of these files. In the above example, the first 3 statements are written to Tunefile1 and the last 2 to Tunefile2. Then a UXNMR macro combines these tune files with:

```
Z1 20 3
Z2 20 3
SIMPLEX Z2 Z        } Tunefile1
Z3 20 3
SIMPLEX Z3 Z2 Z     } Tunefile2
```

```
tune Tunefile1
tune Tunefile2.
```

The efficiency of the computer controlled tune programs is comparable to the manual shimming of an experienced NMR operator. For inexperienced operators, it is much easier to use the auto shimming. For probe changes or other shimming from scratch operations, the auto shimming proves to be much easier and quicker for most of our NMR users.

Sincerely,

Hua Yang

S.a.d.i.s.
BRUKER SPECTROSPIN
34, rue de l'Industrie
67166 WISSEMBOURG Cedex FRANCE
Tél. (33) 88 73 68 00
Télex 870 639 BRUSPIN
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3, avenue du Général de Gaulle
91090 LISSES
Tél. (33) 1 69 89 85 20
Télécopieur (33) 1 60 86 34 90

Wissembourg, May 26th 1995
(received 6/10/95)

Dear Barry,

Since, on line DIGITAL FILTERING is available on the BRUKER AVANCE® spectrometers, one of the most exciting feature is the use of this facility for SEMI-SOFT and SOFT COSY experiment recording in a very easy manner. The selectivity in the frequency (F_2) domain is obtained by just setting the spectral width and the Carrier frequency. The F_2 selected frequency domain is obtained without backfolding over the user wanted range as shown in figure 1. Nevertheless care must be taken against the frequency F_1 domain if a nucleus I_A which resonates outside of the choosen spectral width is correlated with a nucleus I_B which resonates inside of the choosen spectral width we found a "cross peak" at the frequencies $\nu_2 = \nu I_B$ and $\nu_1 = \nu I_A$ which can be back folded in the F_1 dimension if the F_2 and F_1 spectral width are the same. This was the case in the example shown in figure 1c) for the anomeric proton of ATP which resonates at 6.05 ppm and is backfolded to 5.38 ppm in the F1 direction as far as the spectral width in the F_1 domain was choosen equal to 1200 Hz and in the F_2 domain to 600 Hz. To overcome this drawback it's sufficient to use a selective pulse[1,2] instide of the first Hardpulse used in a COSY or DQF-COSY experiment. We have used for this purpose the BIDAZ selective pulse which was a combination of two DANTE-Z[1] pulse trains. A accurate selectivity (figure 2) is obtained in a very easy manner as far as only two parameters have to be setted namely the wanted F_1 spectral width and the Carrier frequency for the F_1 frequency domain (the other parameters are calculated in an automation routine namely the power of the needed 180 degree pulse and the delay between the pulses in the pulse train). The Carrier frequencies in the F_2 and F_1 domain can be the same (two dimensional map around the diagonal) or different (two dimensional map outside of the diagonal).

In this way it is very easy to obtain high resolution 2D parts of a complicated two dimensional COSY or DQF-COSY map. This can be very helpful for spectral assignement. The obtained resolution increase can be used for a more accurate coupling constant determination as is needed for sugar ring conformations in DNA or steroids. This is shown in the following table for ATP where the knowledge of the fraction of $C_{2'}$ endo and $C_{3'}$ endo conformations is strongly dependent from the accuracy of the coupling constant determination.

	Coupling Constants
$^3JH_{3'}$-$H_{4'}$	3.4 + 0.7[3] / 3.6 + 0.1[4]
$^3JH_{3'}$-$H_{2'}$	6.9 + 0.7[3] / 6.7 + 0.1[4]
$^3JH_{4'}$-$H_{3'}$	3.5 + 0.7[3] / 3.7 + 0.1[4]

Sincerely,

Dr Philippe LUX Dr Christian BREVARD

---

(1) C.Roumestand, D.Canet, N.Mahieu and F.Toma *Journal of Magnetic Resonance*, Serie A 106, (1994) p 168-181.

(2) E.Kupce, R.Freeman *Journal of Magnetic Resonance*, Serie A 112, (1995) p 134-137.

(3) Extracted from the complete 2D map (figure 1 a, b) with a resolution of 0.7 Hz/point in the F_2 dimension.

(4) Extracted from the restricted 2D map (figure 1 c, d) with a resolution of 0.1 Hz/point in the F_2 dimension..

Figure 1 : ^1H-^1H DQF-COSY spectrum of ATP in D_2O (with presaturation) at 300 MHz : a) Spectral width ($F_2 = F_1 = 10$ ppm) , b) Region plot of a) showing the $H_{2'}$,$H_{3'}$,$H_{4'}$ and $H_{5'}$, $H_{5''}$ region, c) Spectral width ($F_2 = F_1 = 2$ ppm), d) Region plot of c) showing the $H_{2'}$,$H_{3'}$,$H_{4'}$ and $H_{5'}$, $H_{5''}$ region.

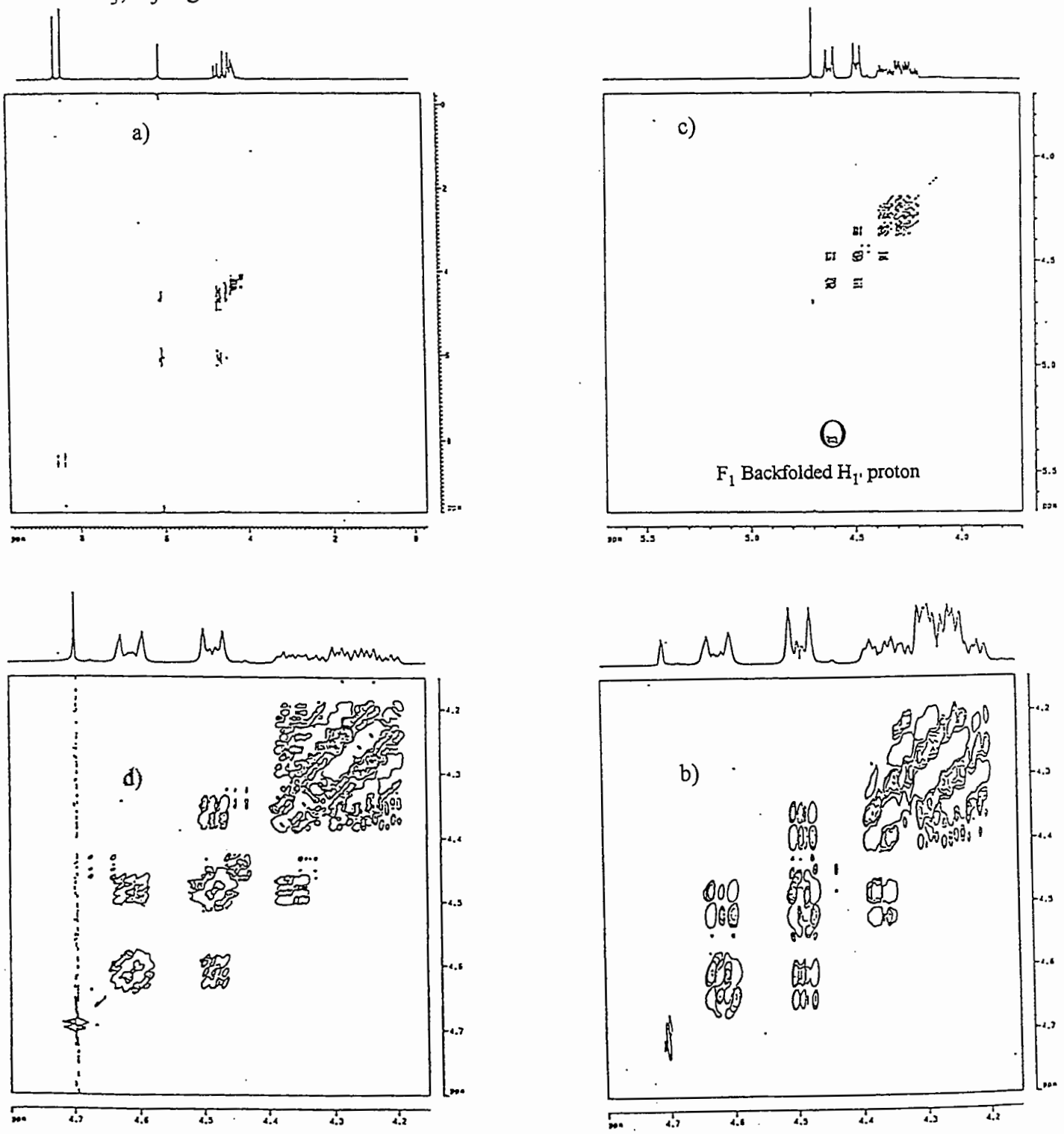
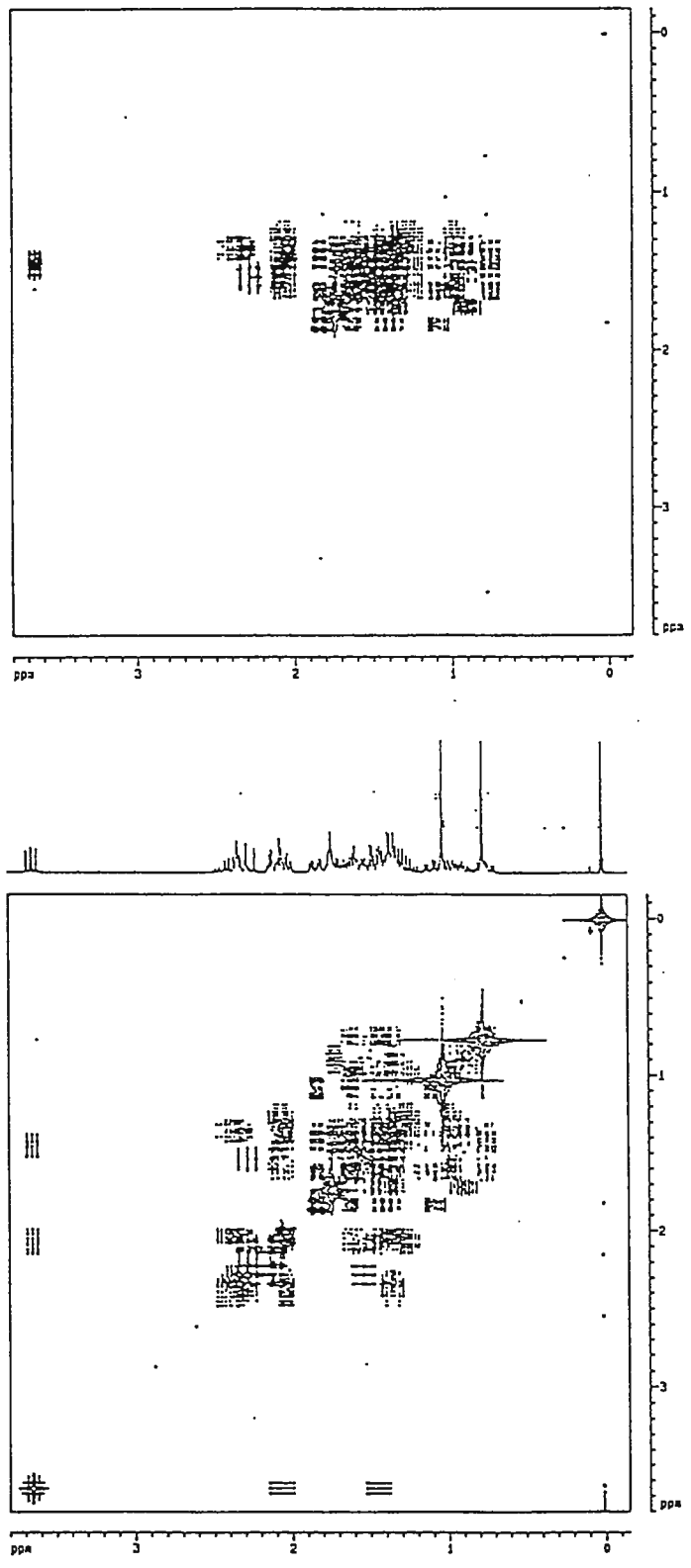


Figure 2 : bottom , ^{1}H-^{1}H non phased COSY experiment recorded on 100 mM Androstan using Homospoil Gradients (lenght = 3 ms, recovery time = 4 ms, Amplitude 1/-1). Spectral Width in the F_2 and F_1 domain = 3.95 ppm. top , the same experiment recorded in the same condition by replacing the first 90 degree pulse by a BIDAZ pulse train (n = 2.5, 180 deg. = 245 µs, τ = 250 µs) selective over 250 Hz.



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May 1, 1995
(received 6/13/95)

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

Dear Dr. Shapiro:

NMR ANALYSES OF EMULSIONS AND DISPERSIONS

In hopes that you will reactivate our subscription after a lengthy tardiness in making a contribution, we'd like to present a few simple methods for the NMR analysis of emulsions and dispersions. Emulsions and dispersions are frequently encountered in specialty chemical product lines. As a specialty chemical company, we are called upon to analyze many different types of emulsions and dispersions. Recent methods have been implemented for the spectroscopic examination of these colloidal systems to provide compositional data. *In situ* analyses and separation methods have provided useful information for our research efforts on emulsion and dispersion technology.

Normally, the NMR spectra of colloidal particles, as present in emulsions and dispersions, are severely attenuated owing to solid-state effects, e.g, diminished molecular motion resulting in dipolar and anisotropic broadening. The addition of a diluent, or the application of heat, are two methods by which the solid-state behavior of the particle is overcome to produce a 'liquid-like' state. Enhanced colloid mobility is attained by these approaches, resulting in a dramatic signal improvement for the emulsion/dispersion. The advantage of a such a nondestructive technique is that it can provide quantitation of the emulsion/dispersion components directly *in situ*.

A third approach involves a breaking of the emulsion/dispersion by ultracentrifugation. This separation technique has been devised to obtain two fractions; an aqueous fraction, containing surfactants and other additives, and a solid organic fraction. Analysis of both fractions by NMR has provided an alternative analytical tool to effectively determine the components of competitive emulsion/dispersion products.

As an example, two spectra of a paper chemical emulsion are shown on the next page. The 'before heat' ^{13}C spectrum (bottom) is useful for providing information on the types of additives, e.g, starch, which are dissolved in solution. In comparison, a heated ^{13}C spectrum (top) provides, not only the additives, but information on the colloidal components as well. In this fashion, we are able to determine the emulsion composition in a nondestructive manner, eliminating wet chemical efforts.

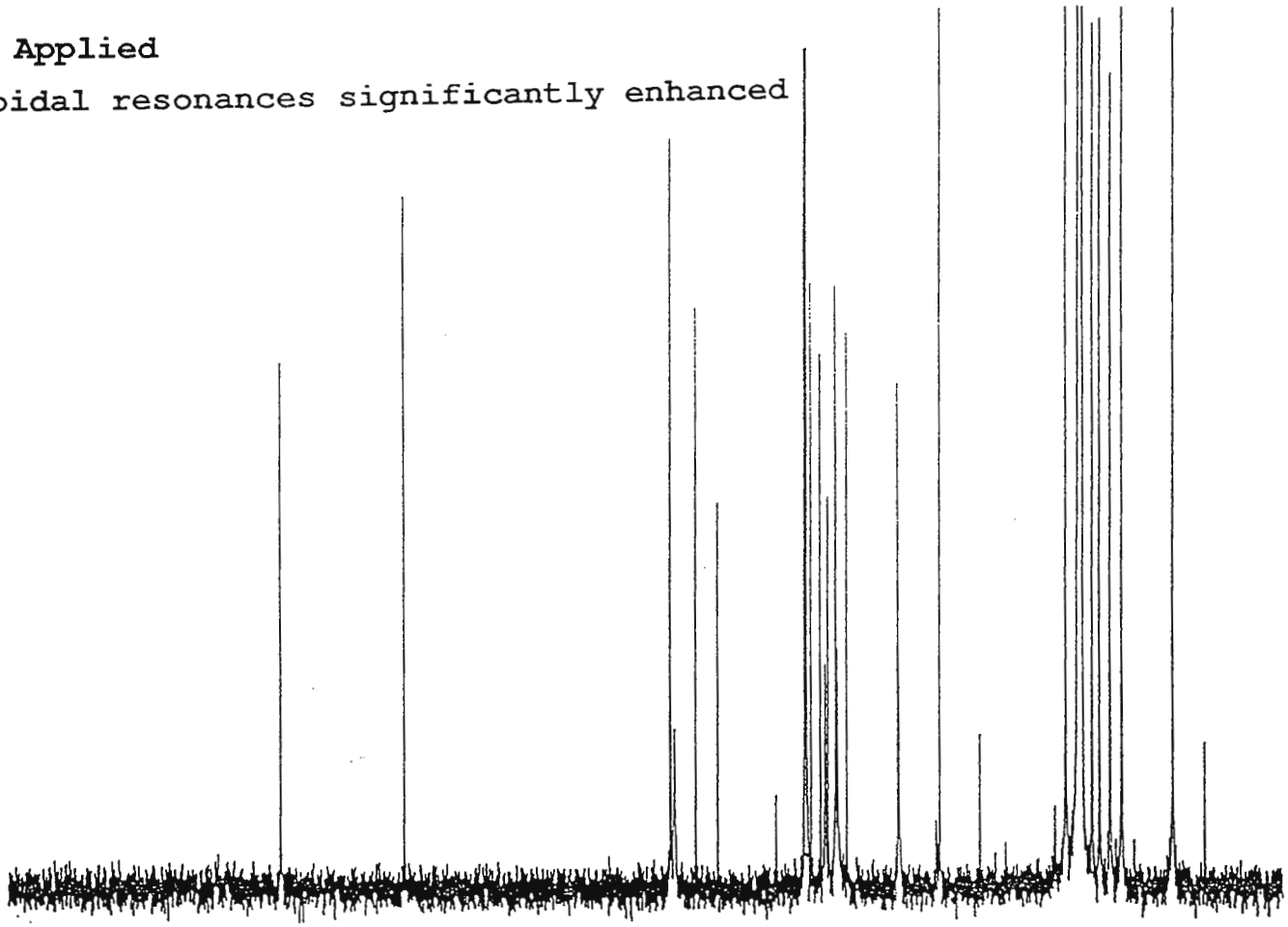
Sincerely,

Ernest Laletas

13C NMR Spectra of a Paper Chemicals Emulsion

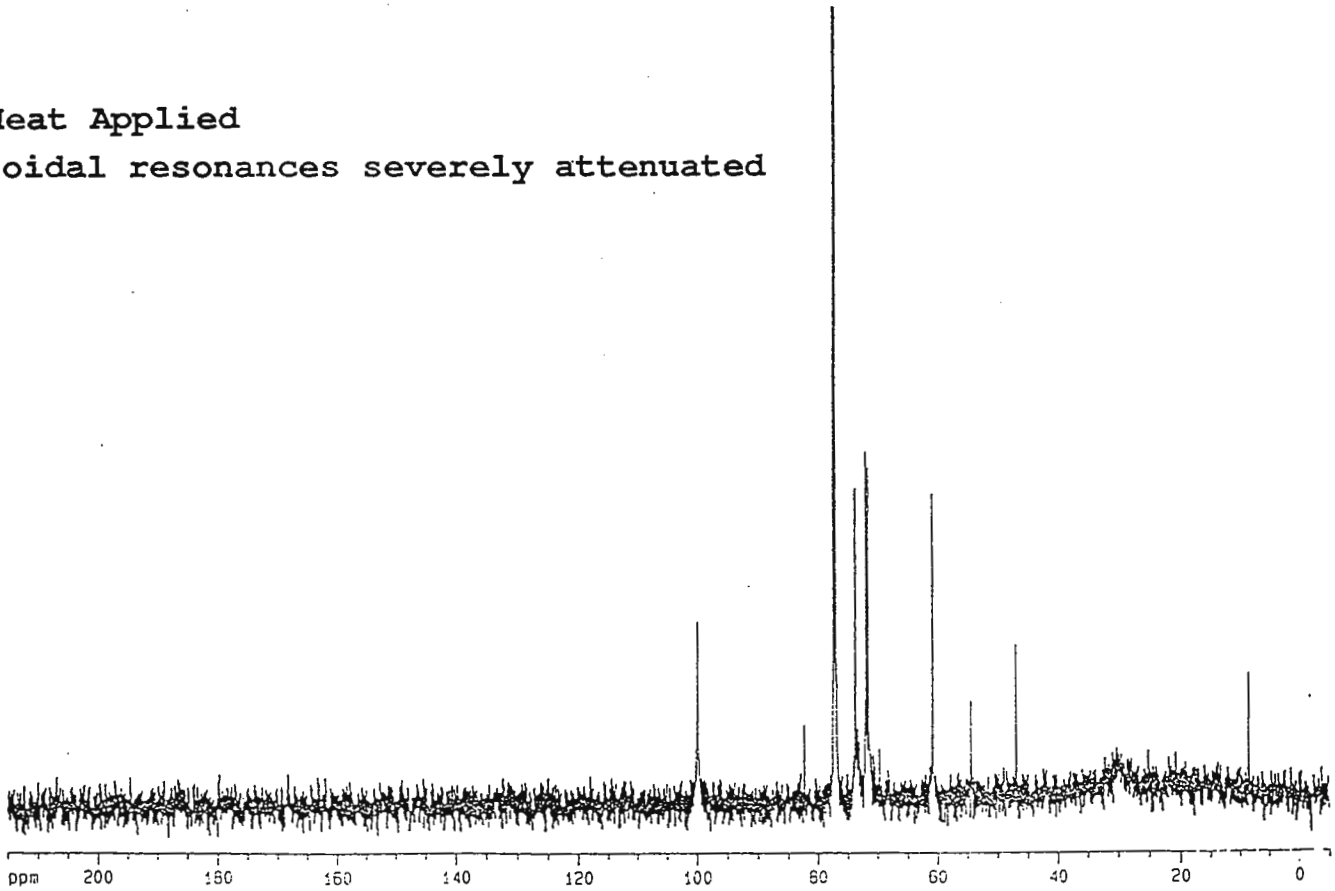
Heat Applied

colloidal resonances significantly enhanced

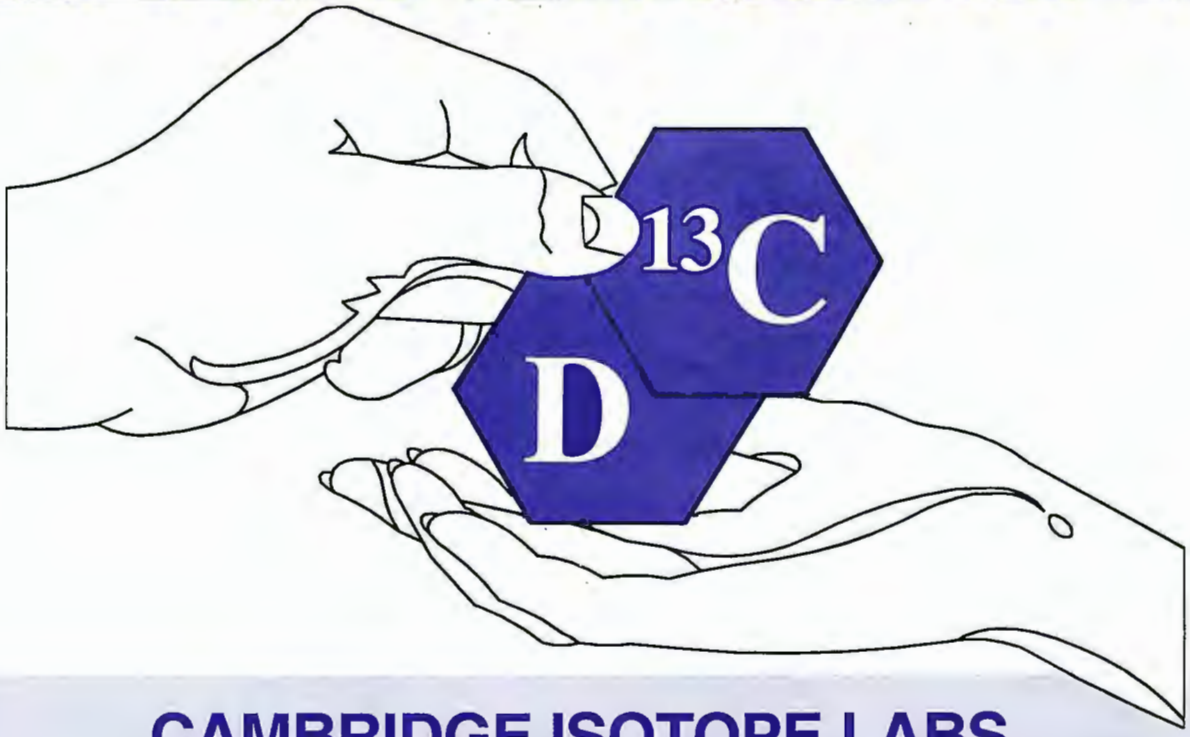


No Heat Applied

colloidal resonances severely attenuated



Your Partner in Research...



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CIL is seeking proposals from researchers who have ideas for new applications, analytical methods, or novel experiments which could expand the body of scientific knowledge in this area. We believe that this program represents the best in cooperative research between private industry and the scientific community.

Deadline for applications is August 15, 1995. Please call to apply.

CIL

CAMBRIDGE ISOTOPE LABORATORIES
50 Frontage Road, Andover, Massachusetts 01810 USA

800-322-1174 or 508-749-8000 (USA) 508-749-2768 (Fax) 800-643-7239 (Canada)

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In order to be considered for a CIL grant, an application must be submitted to CIL containing the following information:

1. Biographical sketch of principal investigator and names and titles of all other researchers who will work with the labeled material (students, postdocs, collaborators, etc.).
2. Description of compound and quantity desired. Refer to the "List of Available Compounds". The awards may be worth up to $10,000 based on CIL catalog prices.
3. Expected timeline for completion of project.
4. Description of facility(ies) where all parts of research will be carried out (synthesis, analysis, etc.).
5. Description of proposed research with all appropriate references (not more than 1000 words). Refer to "Proposed Research Topics".
6. Statement describing the value of the research. The statement should include summaries of prior grant proposals (if applicable) and statements from two colleagues recommending the proposal.

Please send the application to:

Dr. John Aberhart
CIL Research Grant Program
Cambridge Isotope Laboratories, Inc.
50 Frontage Road
Andover, Massachusetts 01810 USA

varian associates / 3120 hansen way, box d-298 / palo alto, ca 94304-1030

Dr. Barry Shapiro
966 Elsinore Court
Palo Alto, CA 94303

June 21, 1995
(received 6/22/95)

Gradient Autoshim

Dear Barry,

There has been some interest in exploiting field and shim mapping techniques to assist in automated shimming. We have developed an approach that is integrated into VNMR software that enables gradient autoshimming with the use of any z-axis PFG probe. It's approach is also compatible with imaging probes and triple-axis PFG probes. For those unable to justify spending the extra money for three-axis PFG amplifiers and probe, this capability offers gradient shimming on hardware they might already have.

The operation is composed of two parts: A one-time shim coil mapping that need not be repeated for subsequent sample shimming, and a two-fid fitting procedure done on the sample of interest. In most cases this latter step will be the only task needed to achieve good shims. If an unrealistic (but often demonstrated!) task of shimming from all zeroed shims is attempted, the two-fid step may be done two or three times before the same end result is obtained. Good shims may be obtained in a matter of a fraction of a half of a minute. This has been our experience for a z-axis triple-resonance PFG probe at 600 MHz using a 500ul 1mM protein sample in 90% H2O. Extension to three-axis probes would, of course, require proportionately longer.

The real message is that good shimming can be obtained on water samples in less than a minute, starting from essentially arbitrary conditions for the z1-z6 shims. The axial z1-z6 shims are the most important shims to adjust for routine applications, and are very sensitive to changes in volume and sample length, whereas transverse gradients are mostly insensitive to volume changes, the biggest adjustments in which may be made manually if necessary. Thus, gradient shimming with a normal z-axis PFG probe is all that is required for most shimming applications.

To give you an idea of the quality of the shimming, Figure 1 shows the presat spectrum of the protein where all the axial gradients are zeroed. Figure 2 shows the effect of setting z1-z6 to maximum (+32767). Figures 3-6 show the presat spectra for various inappropriate starting conditions. Typically, the time required is on the order of 30 seconds for the miserable starting points and 10 seconds for just a "touch up".

Sincerely Yours,

George Gray
NMR Applications Lab

Bayard Fetler
NMR Software Department

varian associates / 3120 hansen way, box d-298 / palo alto, ca 94304-1030

Figure 1. Z1-Z6 Shims Set to Zero

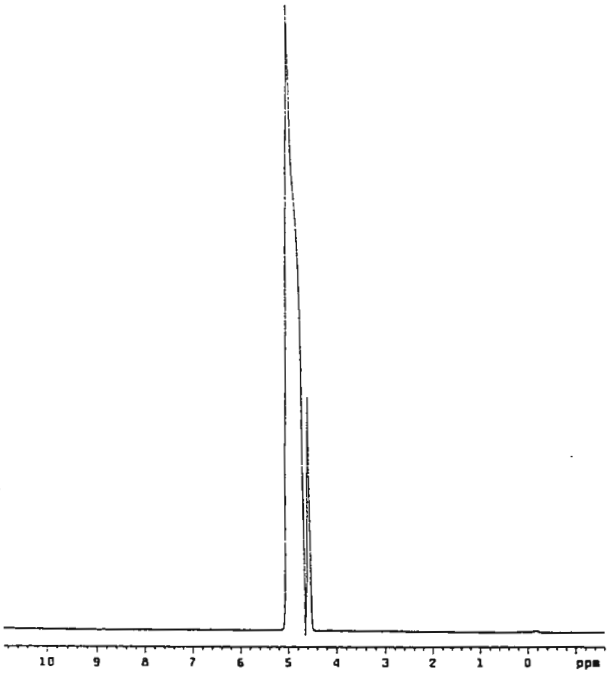

Figure 2: Z1-Z6 Shims set to Full Positive

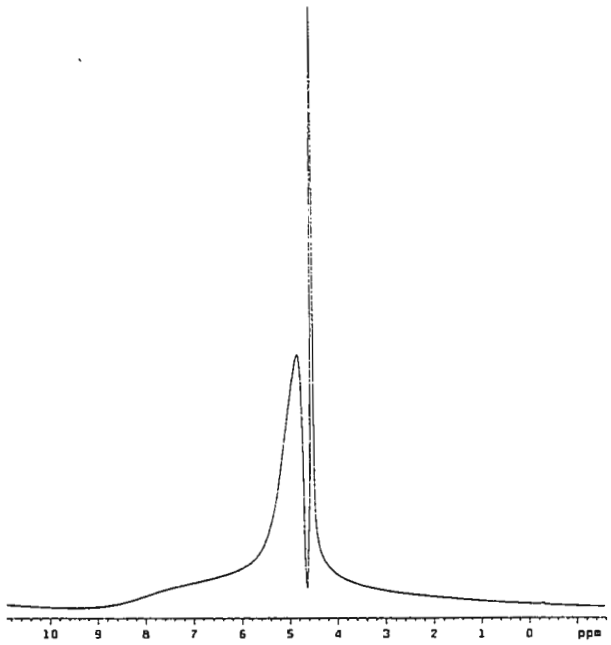

Figure 3. After gradient shimming from Z1-Z6 starting at zero.

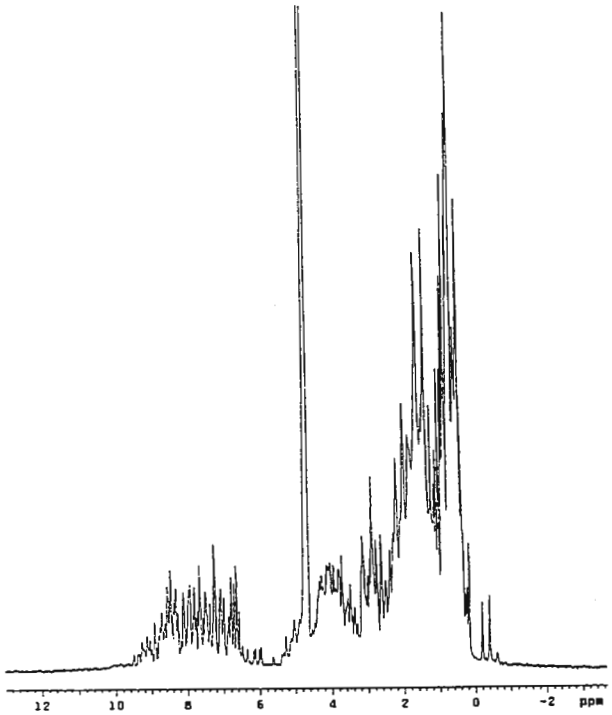

Figure 4. After gradient shimming from Z1-Z6 starting at +32767

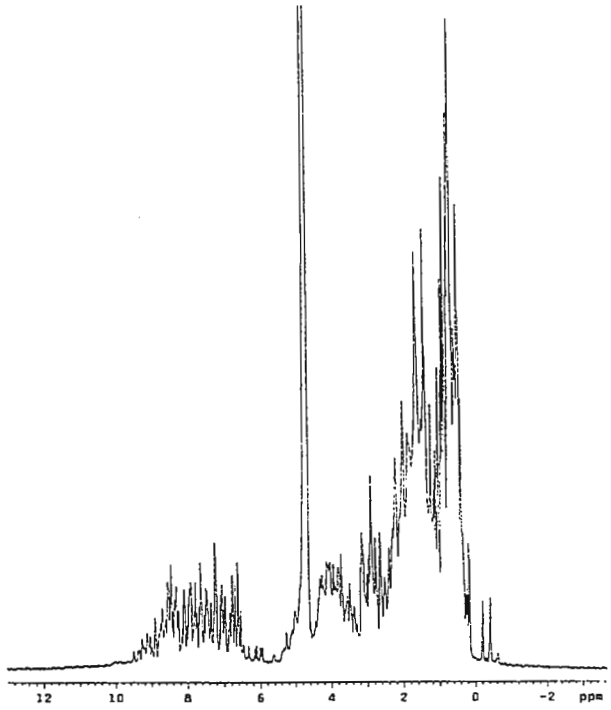

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Figure 5. After gradient shimming from shims optimized for 400 ul

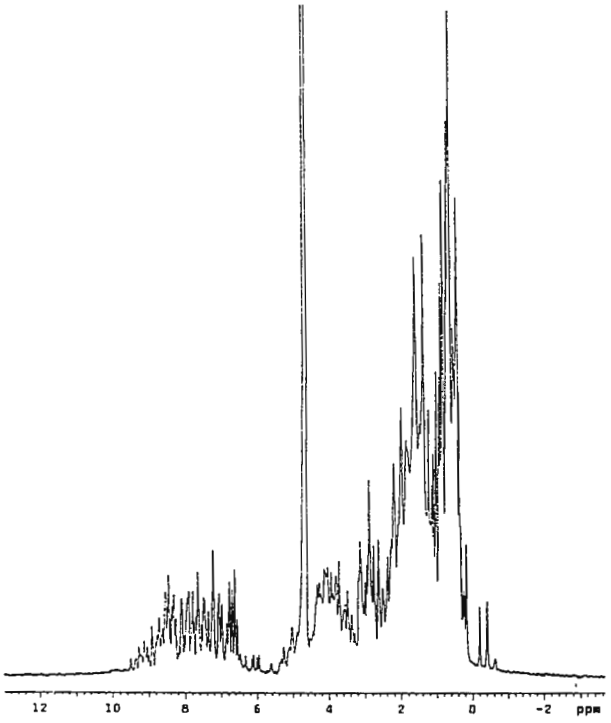


Figure 6. After gradient shimming from shims set for Lineshape Sample

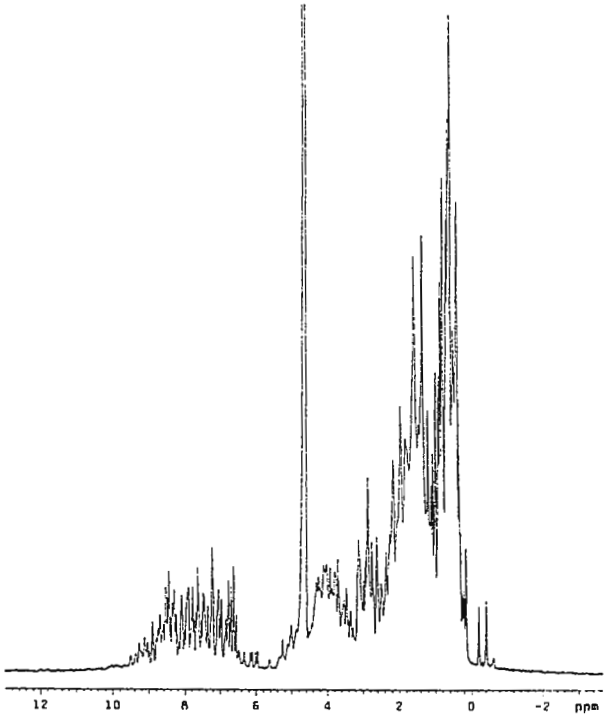
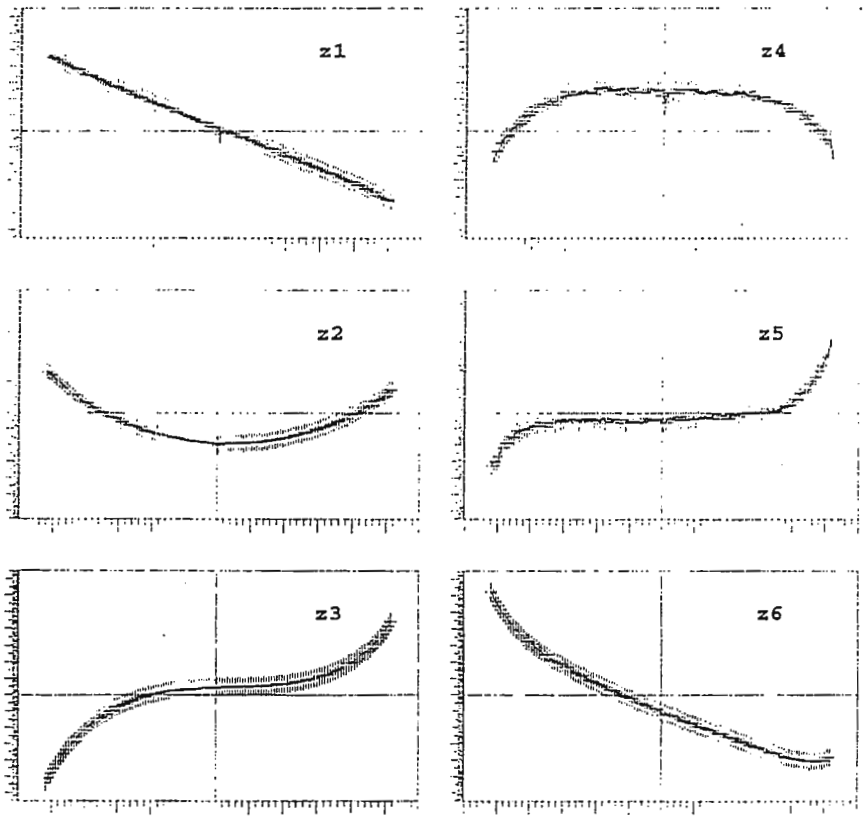


Figure 7. Field Maps of Shims obtained by gradient mapping.



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

June 14, 1995
(received 6/16/95)

Dear Dr. Shapiro,

Title: NMR RECEIVER SENSITIVITY TEST

THE OBJECTIVE OF THIS TEST IS TO RAPIDLY DETERMINE THE SENSITIVITY OF THE RECEIVER INDEPENDENT OF FIELD HOMOGENEITY, PROBE PERFORMANCE, THE TRANSMITTER, ETC.

SEARLE

Spectrometer settings

a. spectral width	3000 Hz
b. Filter bandwidth	3000 Hz
c. Receiver gain	set to maximum, attenuate as required to prevent an ADC overflow
d. Line broadening	0.3 Hz (EM)
e. time domain data points	64k (32k real Fourier transformed data points)
f. One accumulation	

Signal Generator* settings

a. Output frequency	500 to 1,000 Hz away from spectrometer operating frequency
b. Output level	-120 dBm (0.224 microvolts rms)

Connect the signal generator output to the spectrometer preamplifier input, disconnect the transmitter output and terminate it into a 50 ohm load. Acquire one scan, BC, EM, FT, adjust phase. Calculate the signal-to-noise ratio (S:N) using the standard NMR S:N formula, or let the spectrometer software do the calculation.

S:N = Signal x 2.5 / peak-to-peak noise

For a receiver noise figure of 2.5 dB, the results of this test should give a S:N of 250:1, a 3.5 dB noise figure should provide a S:N of 220:1. This test will also provide an indication of the one-pulse quadrature-image suppression.

*The signal generator should be turned on for at least 24 hours prior to this test. The HP 8657A with opt. 001 (high stability time base) works well for this test.

Regards,

Robert W. Dykstra

Notice:

Subscription renewal invoices for the October 1995 - September 1996 year were mailed on June 30, for receipt of payment by September 5. Prompt processing of your invoice will be greatly appreciated.

A small increase in the subscription rate, the first such rise since 1992, is necessary because of a decline in advertising revenue, substantially greater mailing rates, and increased operating costs attendant upon the recent privatization of the Newsletter operation. The subscription rate for the 1995-96 year has been set at $190.00, with the usual 50% discount for academic or personal subscriptions.

It is hoped that advertising revenue will pick up again, and that future increases in the subscription rates can be deferred. If there is anything you can do to engender additional advertising, or if you can arrange for your company or institution to become a Sponsor, this will be most helpful. Details of these categories will be sent immediately on inquiry.

B. L. Shapiro
1 July 1995

Address all Newsletter correspondence to:

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

(415) 493-5971* - *Please call only between 8:00 am and 10:00 pm, Pacific Coast time.*

Deadline Dates

No. 443 (August)	21 July 1995
No. 444 (Sept.)	25 August 1995
No. 445 (October)	22 Sept. 1995
No. 446 (November)	27 Oct. 1995
No. 447 (December)	24 Nov. 1995

*Fax: (415) 493-1348, at any hour. Do not use fax for technical contributions to the Newsletter, for the received fax quality is very inadequate.

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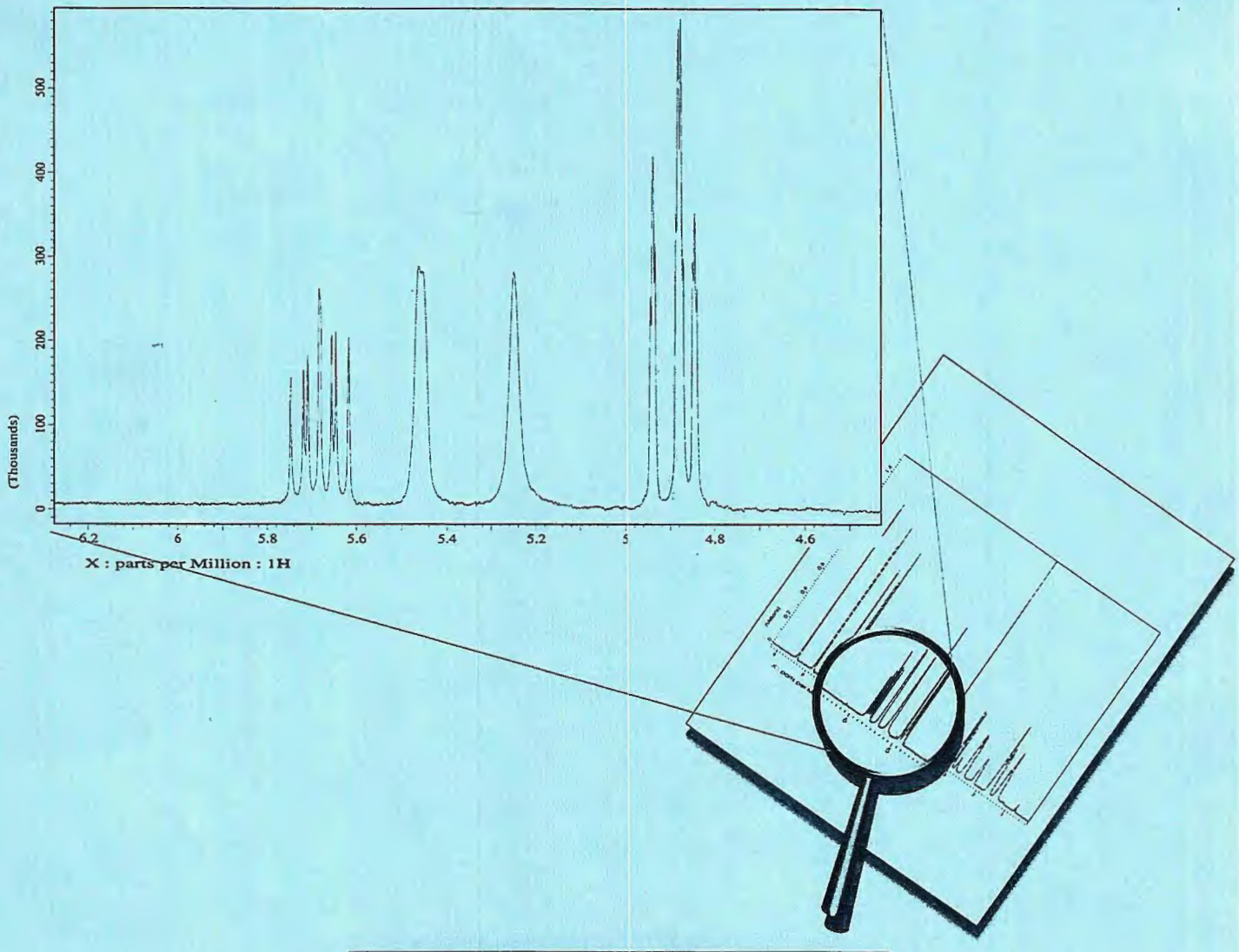

Eclipse NMR *The Better Way!*

This data shows the effect of digital filtering on JEOL USA's Eclipse NMR Spectrometer. The bottom spectrum shows the full spectrum of quinine while the top spectrum shows the same area after digital filtering has been applied. In contrast to the non-filtered area the digital filtered area shows none of the aliasing of the peaks from outside the spectral window.

The advantage of the Eclipse is that there are no "coefficients" or "poles" to choose, one need only choose the spectral window and the Eclipse does all of the work. Consequently digital filtering becomes an easily used option for any NMR experiment.

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