



# CHEMISTRY DEPARTMENT **NMR** NEWSLETTER

SEPT 2003

---

## Table of Contents:

1. NMR USERS TRAINING SESSIONS
2. NEW BOOKING NMR SCHEDULER
3. NEW NMR WORKSTATION IN A239
4. DELETION OF NMR USER FILES ON AV300/400
5. NEW 600 AND 400Mhz NMRs DUE TO ARRIVE
6. LATEST NMR PREDICTION SOFTWARE INSTALLED
7. NICK'S TOPIC...LINEAR PREDICTION OF 2D DATA
8. SPECTROMETER CAPABILITIES

---

NMR NEWSLETTER  
BY NICK BURLINSON

NMR Facility  
Rm D140 x23084

---

NMR Facility Personnel

Liane Darge  
Marietta Austria  
Nick Burlinson

## 1. NMR USERS TRAINING SESSIONS:

The next nmr training sessions will begin the **week of Sept 29**. Both INTRODUCTORY and ADVANCED sessions will be run on the AV300/400/AMX500 spectrometers. Please sign up for these upcoming two day/two hour sessions on the sheets posted on bulletin board in NMR FACILITY in D140.

Students who sign up for the users course should be ready to acquire and process nmr spectra as part of their research...procedures will be forgotten otherwise!!! A basic understanding of FT NMR is essential. Good references to read over before class are found in chapters 1-3 of [REF 3] or the first chapter of [REF 2] or chapters 2-4 of [REF 1]. See below.

### REFERENCES:

1. Derome, A. , 'Modern NMR Techniques for Chemistry Research' Pergamon Press Chp 2-4 1987.
2. Sanders,J. K. M., and Hunter, B. K. 'Modern NMR Spectroscopy' A guide for Chemists, 2<sup>nd</sup> Ed Oxford Press 1993 chp 1
3. Claridge,Timothy, 'High-Resolution NMR Techniques in Organic Chemistry', Pergamon Press 1999 Chp 1-3. (**a very good new ref text for the organic nmr user!!**) this book is an update of ref 1.
4. Nelson, John H. , 'Nuclear Magnetic Resonance Spectroscopy' Prentice Hall 2003 Chp 1,2. (lots of chemical shift/coupling tables...for organics and inorganics)

## 2. NEW 'BOOKING' NMR SCHEDULER

The nmr facility this month has finally gone over to a new scheduler for nmr booking of spectrometer times. **For now the only spectrometer affected is the AV400** in D140. The regular users of this nmr need to get signed up with 'username' and passwd to be able to book on-line (see Marietta or Liane for registration sheets and a quick on-line tutorial ). The booking system is an internet based ASP called "BOOK KING SCHEDULER" and runs off a server in Victoria BC. Its fast and can be accessed from any computer anywhere running an up to date browser (IE or Netscape).

**The booking of the AV300 nmr will stay 'paper based'** for now and the other nmr's are prebooked anyway.

Walkup times stay the same for AV300/400 and are still paper based for recording your time on the spectrometer...**please record the actual usage times in tenth's of an hour and sign the log book. Recently the recorded walkup time is only about 60% of the actual walkup time used???**

The major difference in the booking of the AV400 using the new scheduler is that it can be done up to 14 days ahead, at any time, instead of starting on Wed 9AM to book only the next week. There is a limit of two outstanding booking's per user in that period. All would appreciate it if 'overnight' bookings began later in the evening (from 8PM on)

to allow users access to some one-half to two hour bookings in the early evening after walkup time is over.

It may take a bit of getting use to the new interface but hopefully it will make things easier for us all. Book King is willing to make some modifications to the scheduler in the future...your suggestions are welcome...let me know if there are problems.

### 3. NEW NMR WORKSTATION IN A239

A new workstation has been set up in A239 in A-block next to Prof Sherman and Tanner's offices (thanks to Jason Gozjolko, David Bains, Prof Derek Gates, and Prof Laurel Schafer).

The key to unlock A239 is the same as the key for the nmr facility at D140/144. Log on as "user" with "d140" as password (same as other workstations). Files can be transferred using WS-FTP protocol from the AV300, AV400, or AMX500 the same way as the workstations in D140 (NMR Facility).

Remember to save only raw data on the nmr spectrometers (ie.delete processed data before log off ..ie. save only fids) before you transfer them to a workstation. After processing and archiving( to ZIP or CDR) remember to delete your files on the workstation. All files are copied to "guest" directory, and therefore files are not protected on workstations...anyone can delete or copy them.

### 4. DELETION OF NMR USER FILES ON AV300/400

While we are on this subject of file deletion...a few comments on file management on the AV300/400 spectrometers (ie the SGI unix computers). As you accumulate experiments, that are stored under your username in the directory /u/data/<username>, you will eventually run out of space at ~100Megabytes, especially if you are doing 2D experiments and not deleting processed data files. You can see how much space is left in your file by opening a new unix window (blue screen) on your desktop and typing **>quota -v <username>**. If your data file becomes completely full you might not be able to even delete (named or processed files) inside of XWINNMR, in which case the administrator or technician will have to delete the files in the background (unix blue screen). If you used incorrect characters in your filenames (eg. - ,+,:;,\*?,<>#,@,%^^&,(,)=, etc) unix will not allow deletion of files as well!!!! So please use only alpha/numerics in file names. Please be careful when deleting files on unix operating systems...**once deleted there is no recourse to retrieving those files!** Read my user notes on this before attempting deletion.

### 5. NEW 600 AND 400MHz BRUKER SPECTROMETERS

The new 600MHz spectrometer with preliminary BBI-Z tunable probe and a new 400MHz with a BBO-Z probe are due to arrive soon and should be up and running end of this term. In the next six months a Bruker Cryo-probe will be installed in the 600 and will greatly improve sensitivity at the C13/H1 Rf coils that are held at ~26 Kelvin during acquisition of nmr signal from room temp samples!!

## 6. ACD's NMR PREDICTION SOFTWARE

Thanks to CHORSE funding ... (ala Prof. C. Orvig and Dr. W. Scott of the departments new Centre for Higher Order Structure Elucidation)... the NMR Facility now has running on a workstation in D140 the latest C13 and H1 nmr prediction software from Advanced Chemistry Development Inc (ACD) in Toronto. Try it out! You can draw most organic/ and many inorganic structures and ask for the C13 or H1 nmr spectrum. It uses a look-up table of over 100,000 compounds to do this prediction.

## 7. USING LINEAR PREDICTION TO PROCESS 2D HMQC/HMBC DATA

For nmr structure elucidation of compounds with 25 or more carbons with closely spaced and overlapping proton resonances, 2D HMQC (or HSQC) and HMBC experiments have now become routine. These heteronuclear correlation nmr experiments give one bond HC connectivity (in HMQC/HSQC) and two and three bond HC connectivity (in HMBC), helping make structural assignments.

The majority of these 2D experiments are done using an inverse probe. The acquired fids, collected along the "f2 axis", are proton frequencies and the second dimension (f1 axis) are a time incremented set of fids that contain the carbon information incoded in phase and amplitude modulation of the proton frequencies. This time incremented (f1) axis appears to involve a compromise between resolution and experiment time since doubling the number of time incremented spectra (default is 256) more than doubles the total experiment time. This need for compromise can be avoided by using the technique of 'linear prediction' (LP). This is a processing technique and can be applied to any raw data files 1D or 2D.

The forward linear prediction (LPfr) is usually only applied to the f1 dimension of a 2D data set for obvious reasons, since this is where the least amount of digitization is, (i.e. 1024 points (TD2) in f2 and 256 points (TD1) in f1 dimension). The LPfr algorithm looks at the fid and continues to predict the digital points in time from the end of the fid. The parameters are set in `>edp` in XWINNMR... e.g. `ME_mod=LPfr; NCOEF=100; LPBIN=1K` (for 4 fold prediction if TD1=256). Remember, SI (in f1) is 1K which means that without LP the f1 dimension is being 'zero filled' from the 256<sup>th</sup> point up to 1024<sup>th</sup> point. Page P164 in XWINNMR's processing manual explains this in more detail, as does Ref 5 below.

Ref 5: Reynolds, W.F. *Mag. Res. Chem.* **35**, 505-519 (1997)

The spectra below show variations on processing, using LP for a 2D HMQC for strychnine (30mg in CDCl<sub>3</sub>) but note TD1=only 122 increments collected in f1; ns=4; d1=1s (**total acquisition time ~10 min!**).

**Fig 7a.** LPfr=off (both H1 and C13 profiles are 1D spectra imported from standard 32K fids)

**Fig 7b.** LPfr=on (NCOEF=50; LPBIN=1K; SI=1K for TD1 (i.e. f1 axis only)) (C13 profile is now the 2D positive projection across f1 axis (i.e. the sum of the contours in C13 dimension) with obvious resolution improvement along f1 axis by LP).

**Fig 7c.** LPfr=on (in TD2 SI=2K; LPBIN=1500; NCOEF=100) and (in TD1 SI=2K; LPBIN=1K; NCOEF=50) and WDW=SINE/TRAF (now LP is applied to both f1 and f2 dimensions and **both** profiles are the 2D positive projections along f1 (C13) and f2 (H1)). Note the excellent H1 resolution in the projection by using the 'window functions' WDW=SINE (in f2) and TRAF (in f1).

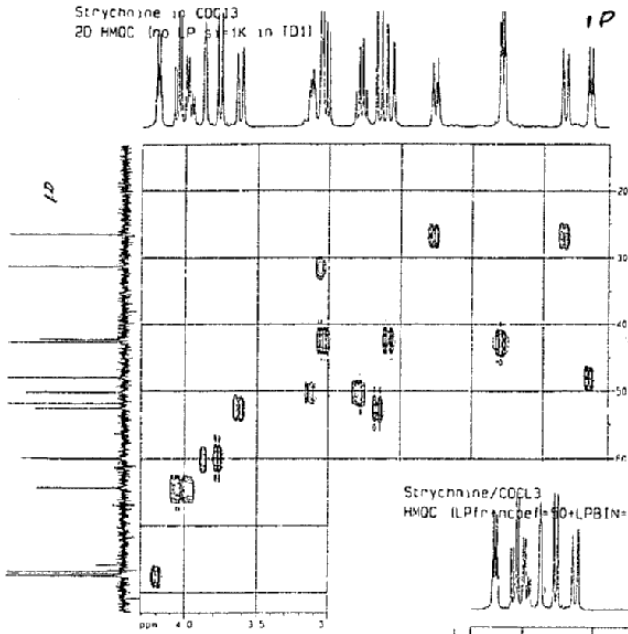


Fig. 7a

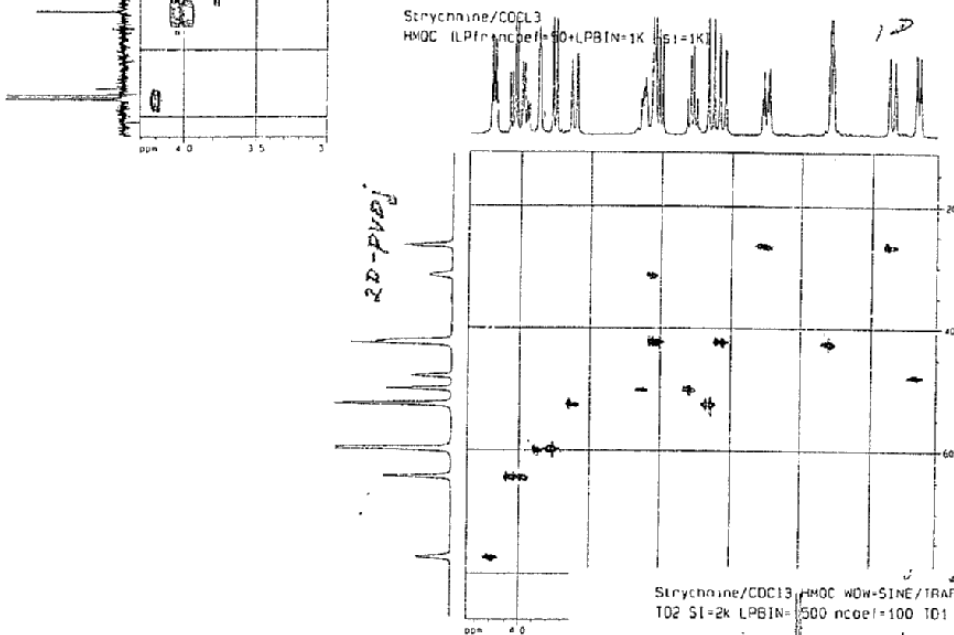


Fig. 7b

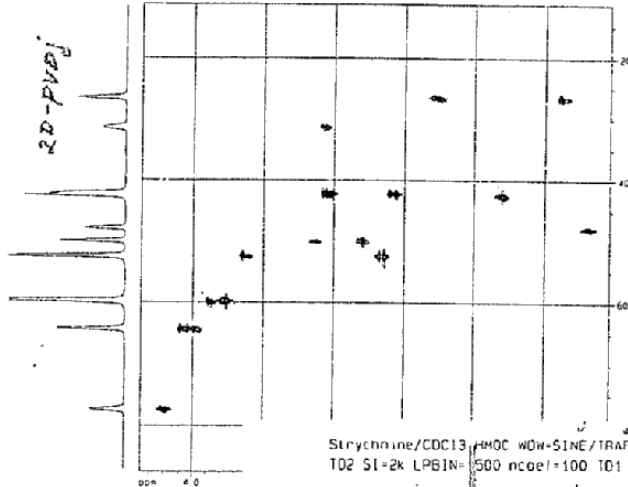
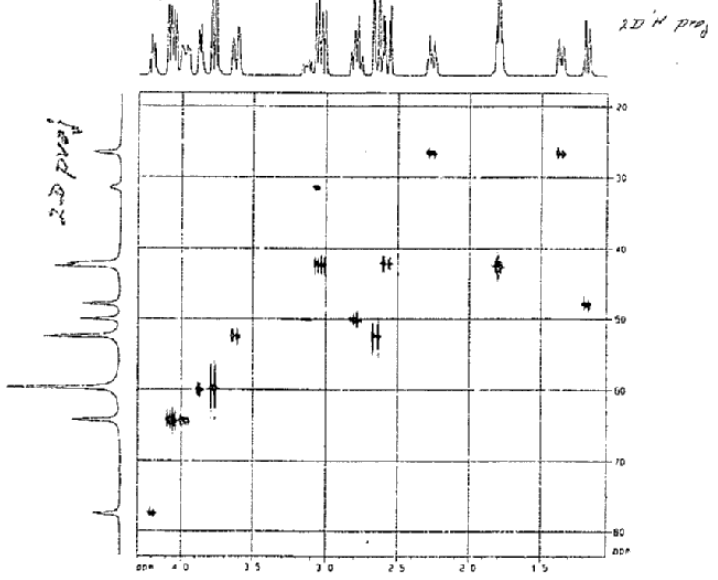


Fig. 7c

**It's important to note here that I acquired a 2D HMQC, a 1D-1H and a 1D-13C\* spectrum all in one experiment in just 10 minutes!!!!...now that's efficient use of a spectrometer!**

Note: the 13C projections in Fig. 7b and Fig. 7c are only a partial carbon spectrum for strychnine since it will only contain carbons attached to protons by one bond, however a 2D-HMBC with LP should give all carbons!



## 8. SPECTROMETER CAPABILITIES

- I. **Bruker Avance 300 Spectrometer.**
- Bruker QNP 5mm probe (auto-switchable quad nucleus probe for obs  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ , and  $^{19}\text{F}$ )
  - VT range -150 to +180°C
  - All Standard 1D and 2D exps
  - Gradient/Shape pulse capability
  - Running XWINNMR software ver.3.0 on SGI O2/UNIX computer
- II. **Bruker Avance 400 Spectrometer**
- Bruker 5mm BBI-Z (inverse broadband probe with Z-gradient coil and Rf broadbanded coil tunable from  $^{109}\text{Ag}$  to  $^{31}\text{P}$ )
  - VT range -150 to +180°C
  - All Standard 1D, 2D exps plus 2D gradient-HMQC, -HMBC, -NOESY, TOCSY, -HSQC, -COSY, etc
  - X nucleus decoupling
  - $^{19}\text{F}$  observe using proton coil (therefore can't decouple H)
  - selective/shaped pulses with PFG's for 1D TOCSY, 1D COSY, 1D NOESY
  - XWINNMR ver 3.0 on SGI O2/UNIX computer
- III. **Bruker WH-400 Spectrometer**
- normal 5mm fixed  $^1\text{H}$  probe with  $^1\text{H}$  decoupler.
  - $^1\text{H}$  spectra only.
  - mainly used for high resolution 1D-proton, 2D-COSY, , and homonuclear. decoupling.
  - can do  $T_1$ 's,  $T_2$ 's, presaturation of  $\text{H}_2\text{O}$  peak, etc.
  - variable temp. is broken
  - DISNMR software on Aspect 3000 system.
  - networked to Aspect 1000 workstation via Lightnet.
- IV. **Bruker AM-400 Spectrometer** (Rm. D107A)
- normal  $^1\text{H}$ ,  $^{13}\text{C}$  (fixed freq.) 5 mm probe with  $^1\text{H}$  and  $^{13}\text{C}$  decouplers.
  - set up mainly to do  $^{13}\text{C}\{\text{H}\}$
  - field drifts : ???
  - DISNMR software on Aspect 3000.
  - networked to Aspect 1000 workstation.
- V. **Bruker AC-200E Spectrometer**
- barcode, automated sample exchanger.
  - normal 5mm  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ,  $^{19}\text{F}$  (fix freq.) probe.
  - five days a week in automation mode.  
weekends - manual use available.
  - DISNMR software on Aspect 3000 system.
  - networked to same Aspect 1000 workstation

- VI. **Bruker AMX-500 Spectrometer** (Rm E161)
- a) Bruker 5 mm BBI-Z (same as in Avance 400)
  - b) Third channel
  - c) VT range -150 to +180°C
  - d) XWINNMR ver 2.5 software on SGI Indy/UNIX system
  - e) no <sup>19</sup>F obs
  - f) networked by LAN to PC's
  - g) normal 5mm BB probe (never used)
  - h) HRMAS probe <sup>1</sup>H and <sup>13</sup>C observe only (deuterium lock)
- with MAS controller unit
- VII. Due in Nov 03 a new **Bruker Avance 400** magnet (with normal broadband probe with Z-gradient coil (ie BBO-Z )) and a **Bruker Avance 600** magnet with a BBI-Z probe and a dual H/C13 cryoprobe).