• ELECTRON MICROSCOPES • SEM • ESR • E-BEAM • TEM •

TEM • SAMPLE PREP • MICROPROBES • NMR • MASS SPEC

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Solutions for Innovation

Solids for fun and games

MHF 1/2019

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Setup is Important!

- It is easer to get no signal than to get a signal in solids
  - You can guess at parameters for liquids NMR and get data. It may be poor but it will be data.
  - If you do this for solids you will get exactly what you deserve: NOISE!

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Things to know before you start:

- **Know your chemistry:**
  - **How was the sample prepared?**
    - **Can result in inconsistent results**
  - **What is the proposed structure?**
    - **Can greatly affect NMR parameters**
    - **Molecular weight?**
  - **What is the density?**
    - **Can destroy the probe!**
  - **What nuclei do you want to observe?**
    - **Is the machine capable and will the probe tune?**

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Example from customer:

- **Customer e-mailed and stated they:**
  - Ran Adamantane standard > great signals
  - Ran compound of interest > NO signal
  - Reran Adamantane standard > great signals
- **What is wrong?**
  - My first question: What is the unknown chemical?
  - Customer stated: Salicylic acid

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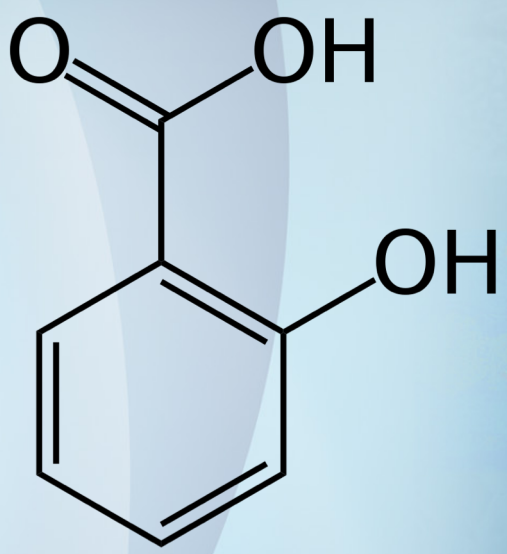
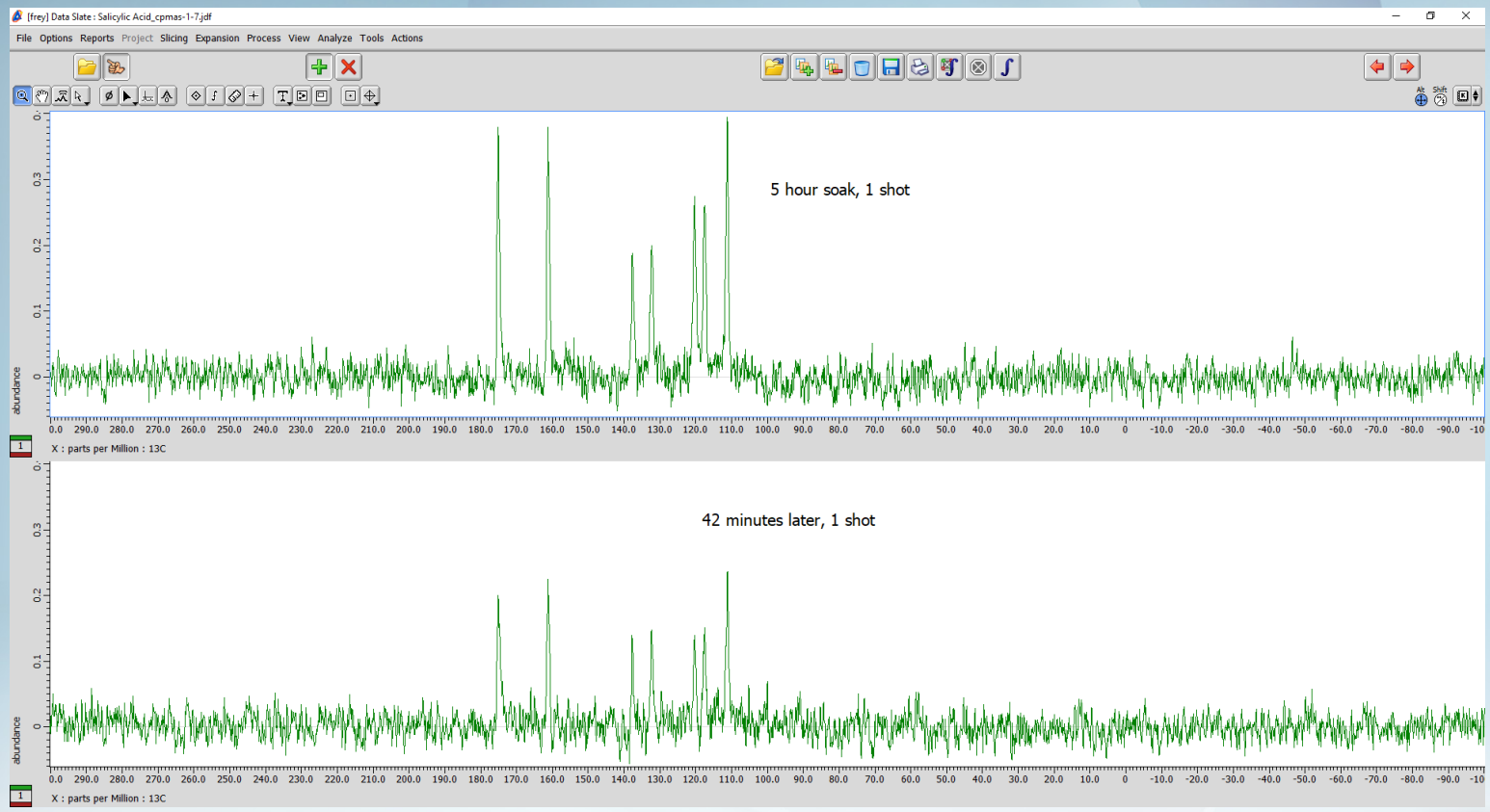
Why No Signals?

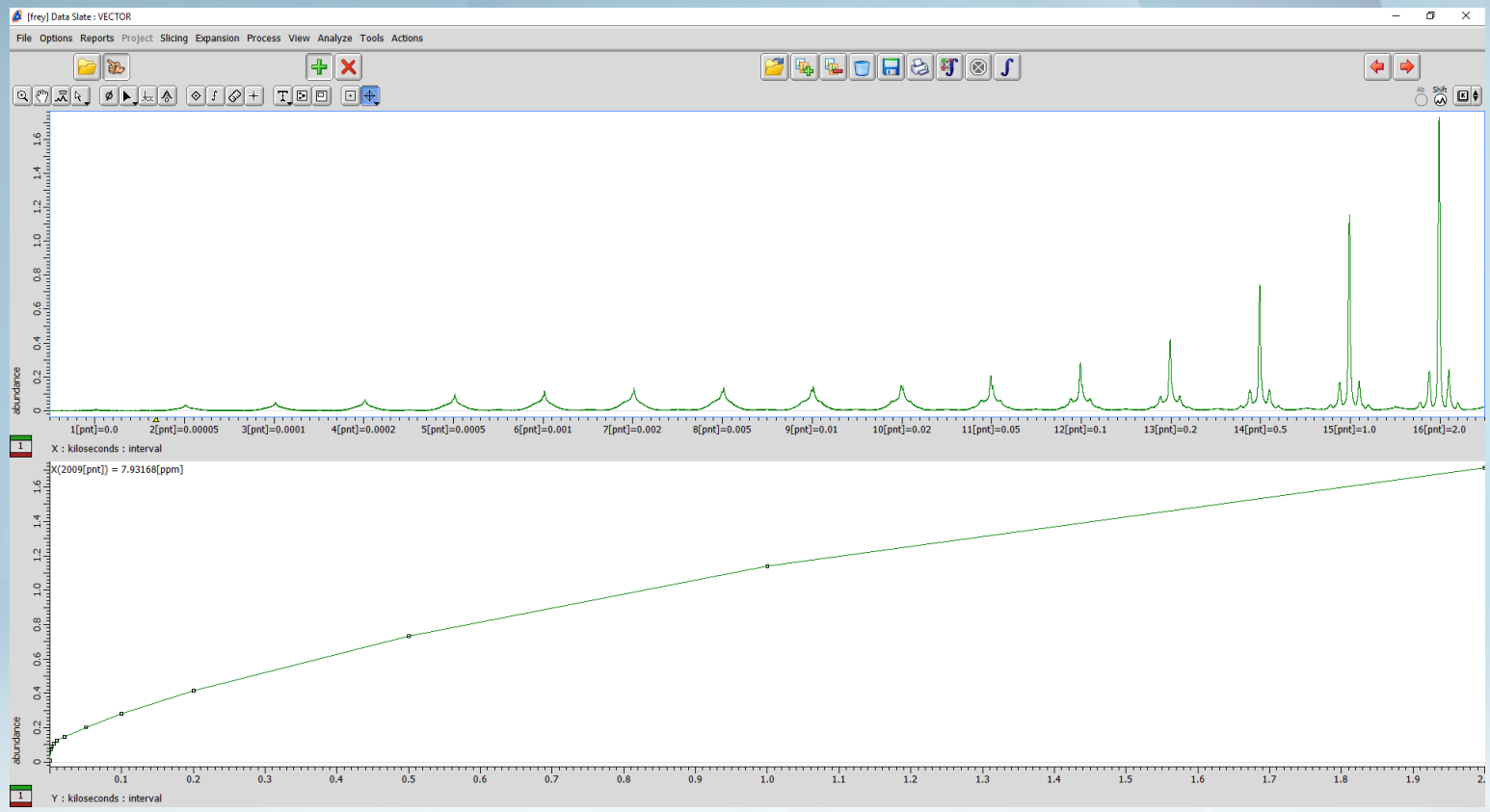
- **What I did:**
  - I made up the sample and put it in the magnet
  - Took 1 CP shot > No signal
  - Let it soak in the magnet 5 hours
  - Took 1 CP shot the next morning > Great Signal!!
  - Waited 1 hour
  - Took 1 CP shot > poor signal
- **Result**
  - The ^{1}H T1 is very very long (hours!).
  - You need internal motion to bring down Proton T1
    - Includes Methyl Groups, Phenyl Rings, soft materials



Know your chemistry



Proton Saturation Revocery



Packing and Spinning Samples

- **Pack loosely**
  - Compressing the sample is usually not necessary
- **Put sample in vial and label the vial!!**
  - You cannot write the sample name on the rotor
- **Test in Bench Spinner**
  - It is less expensive to repair the bench spinner than the MAS NMR probe

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Experiments and sample parameters for setup

- KBr – Magic Angle
- ^{1}H 90 Array – Proton Power
- CP Array – Match condition
- Contact Array – Maximum Signal
- Ramp Array – Equalize CP to all sites

- Examples are for 3.2mm HXMAS probes

- Typical spinning speeds for ^{13}C = ~100 to 125 ppm
  - ^{13}C 1st order spinning sidebands are minimal
  - 400 = 10 to 12.5 kHz
  - 500 = 12.5 to 15 kHz
  - 600 = 15 to 20 kHz

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Standard ^{13}C Setup Sample - AGK

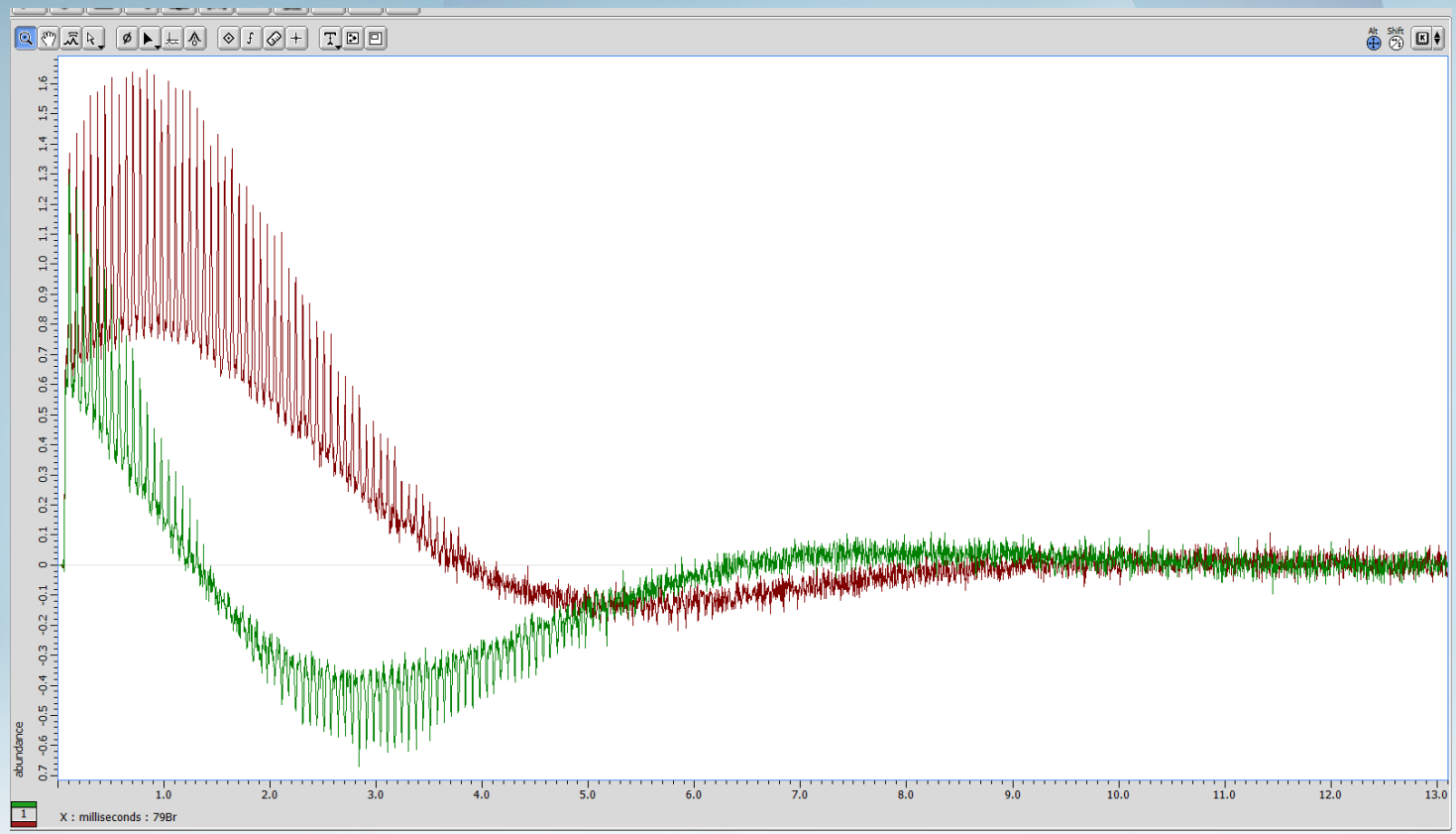
- Mixture of:
  - Adamantane: 227mg
  - Glycine: 500mg
  - KBr: 291mg
- Equal molar in ^{13}C carbon sites
- Saves expense and repacking rotors for multiple standards
- Works for:
  - Setting Magic Angle
  - Setting CP conditions
  - Checking Proton Decoupling
  - Chemical Shift Reference for ^{13}C, Adamantane peak at 37.77 ppm.

- Pure Adamantane will have sharper lines

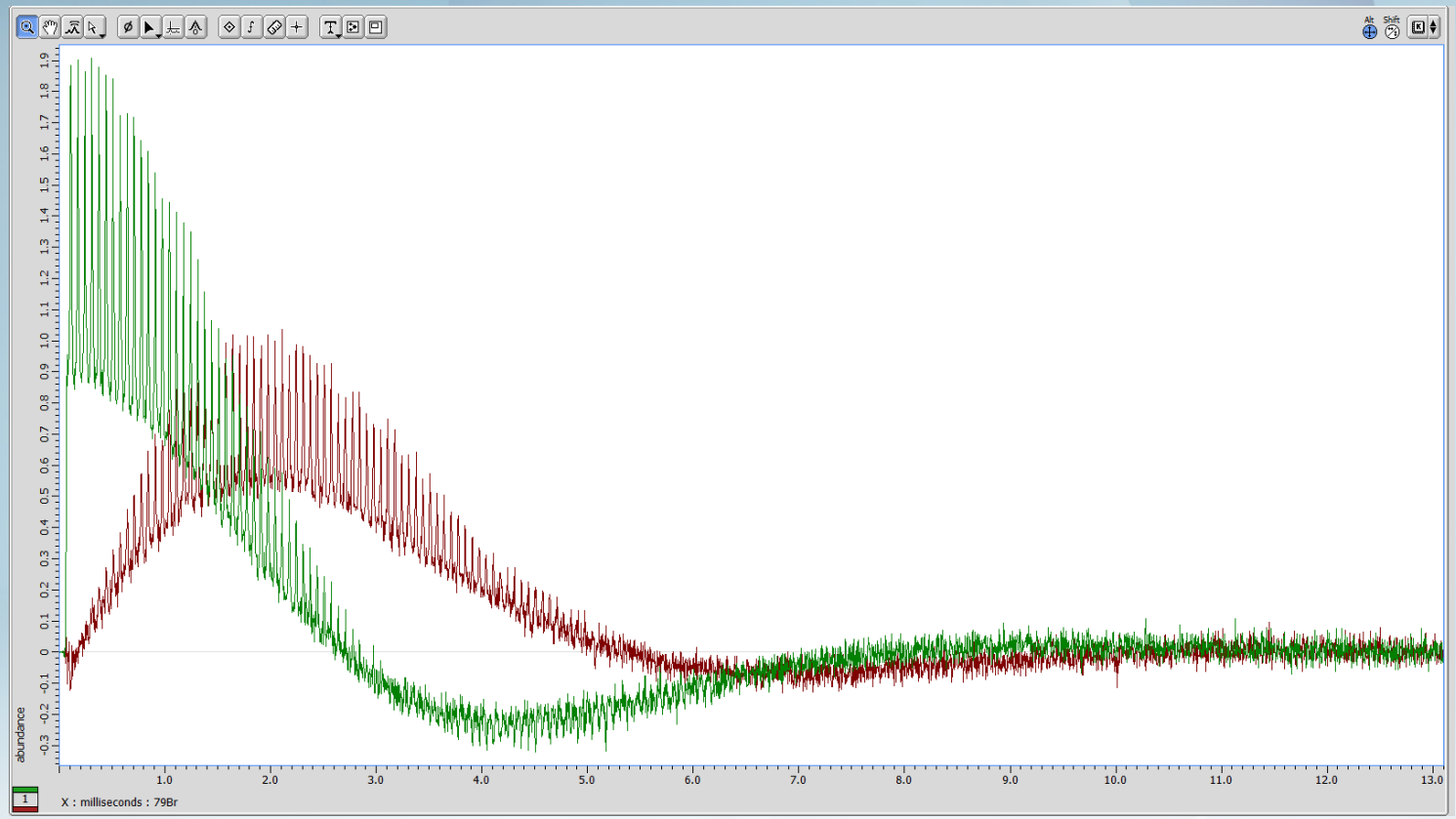
KBr Magic Angle Adjustment

- Use mas_adjust_kbr.jxp experiment
- Load and start the experiment
  - If there are no parameters for ^{79}Br use ^{13}C values
  - Tune probe
- Set up monitor:
  - Process DC balance
  - Press Shift-2 to display imaginary data (red)
  - Set phase point (Φ p) to 0%
  - Adjust PO to get Imaginary FID (red) to start at 0
  - Adjust P1 to remove oscillations from FID

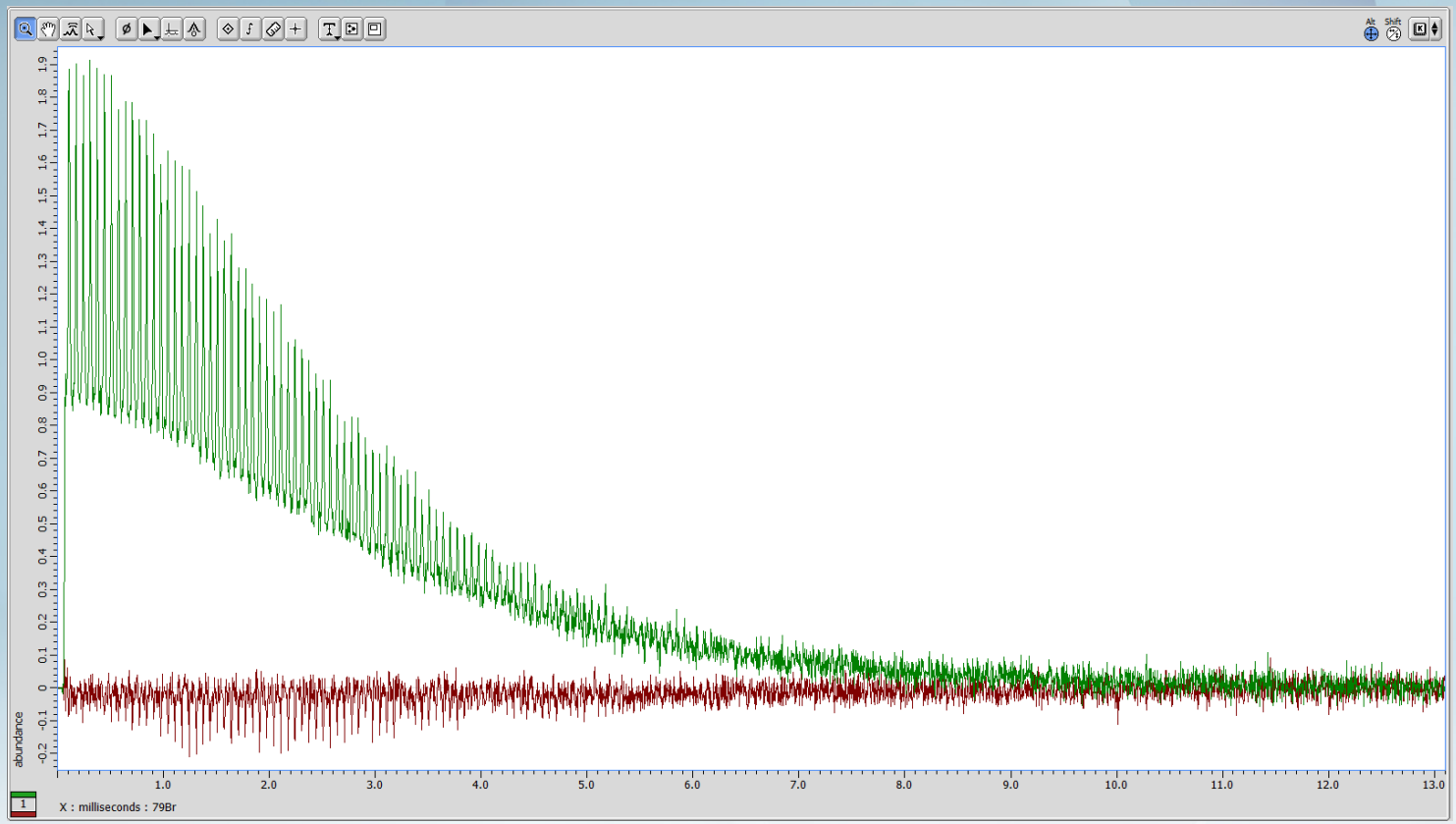
KBr Magic Angle Adjustment 1 – No Adjustment



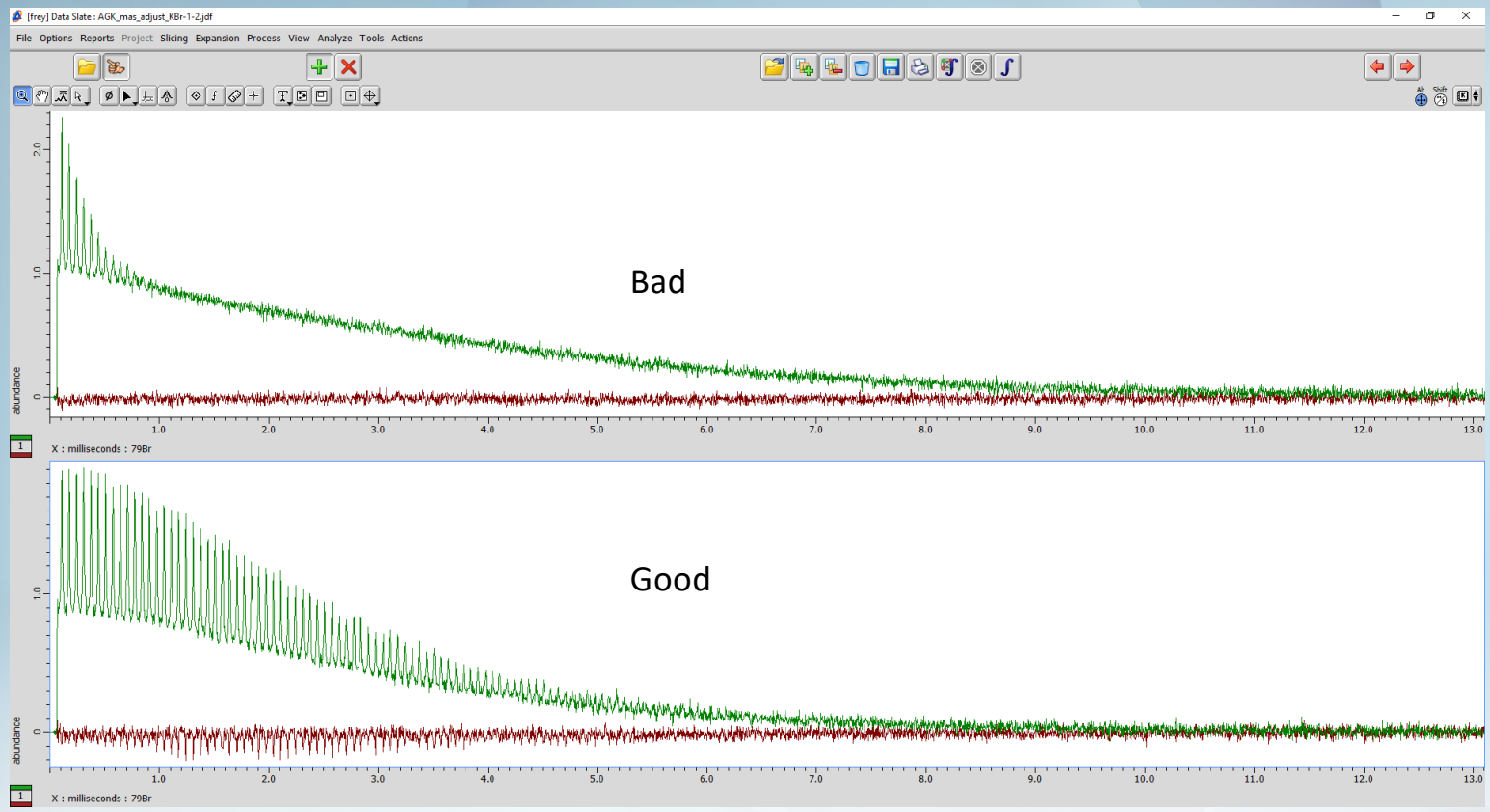
KBr Magic Angle Adjustment 2 – After P0 Adjustment



KBr Magic Angle Adjustment 3 – After P1 Adjustment



KBr Magic Angle Adjustment 4 – Angle Adjustment

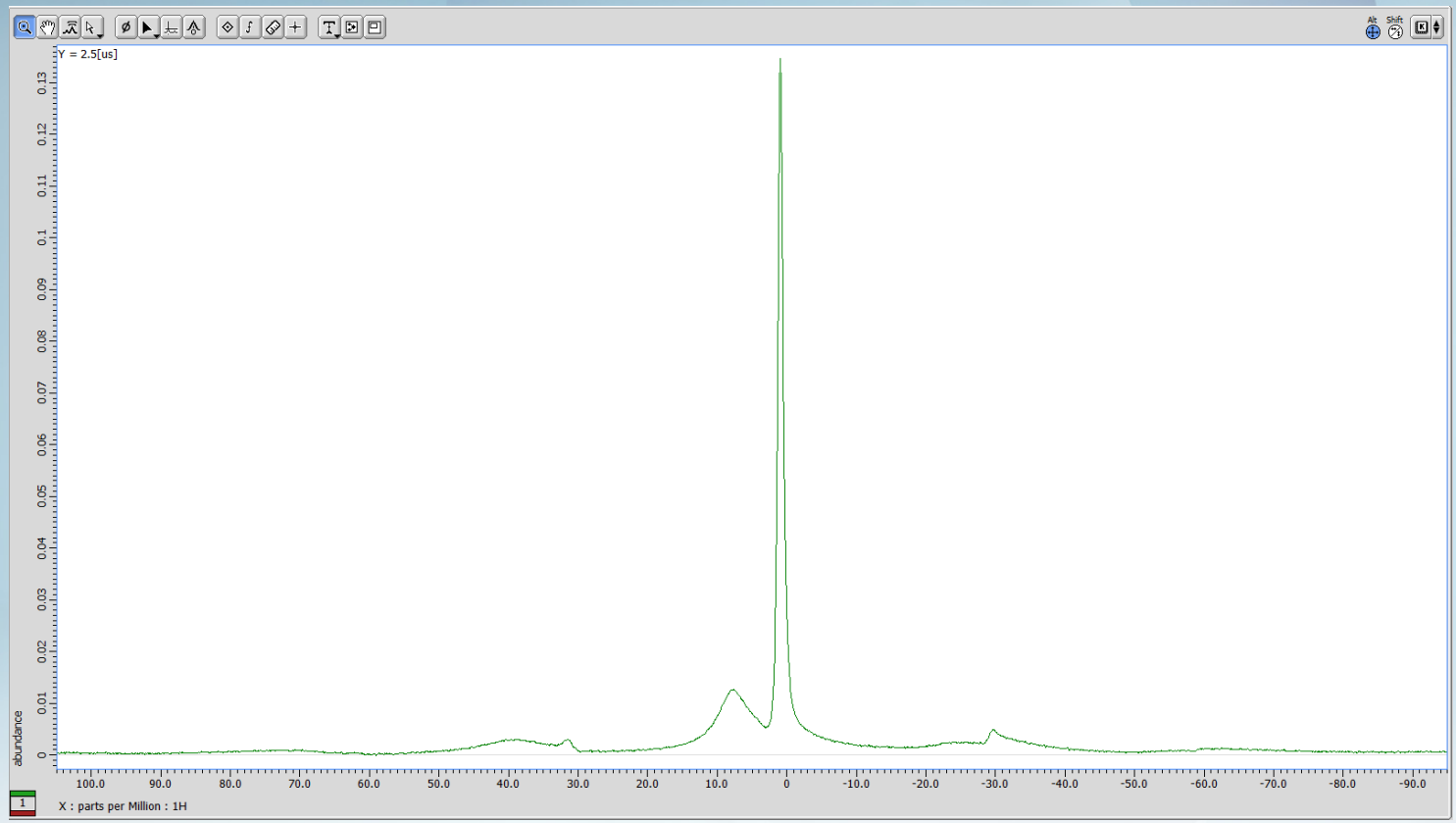


^{1}H 90 Check

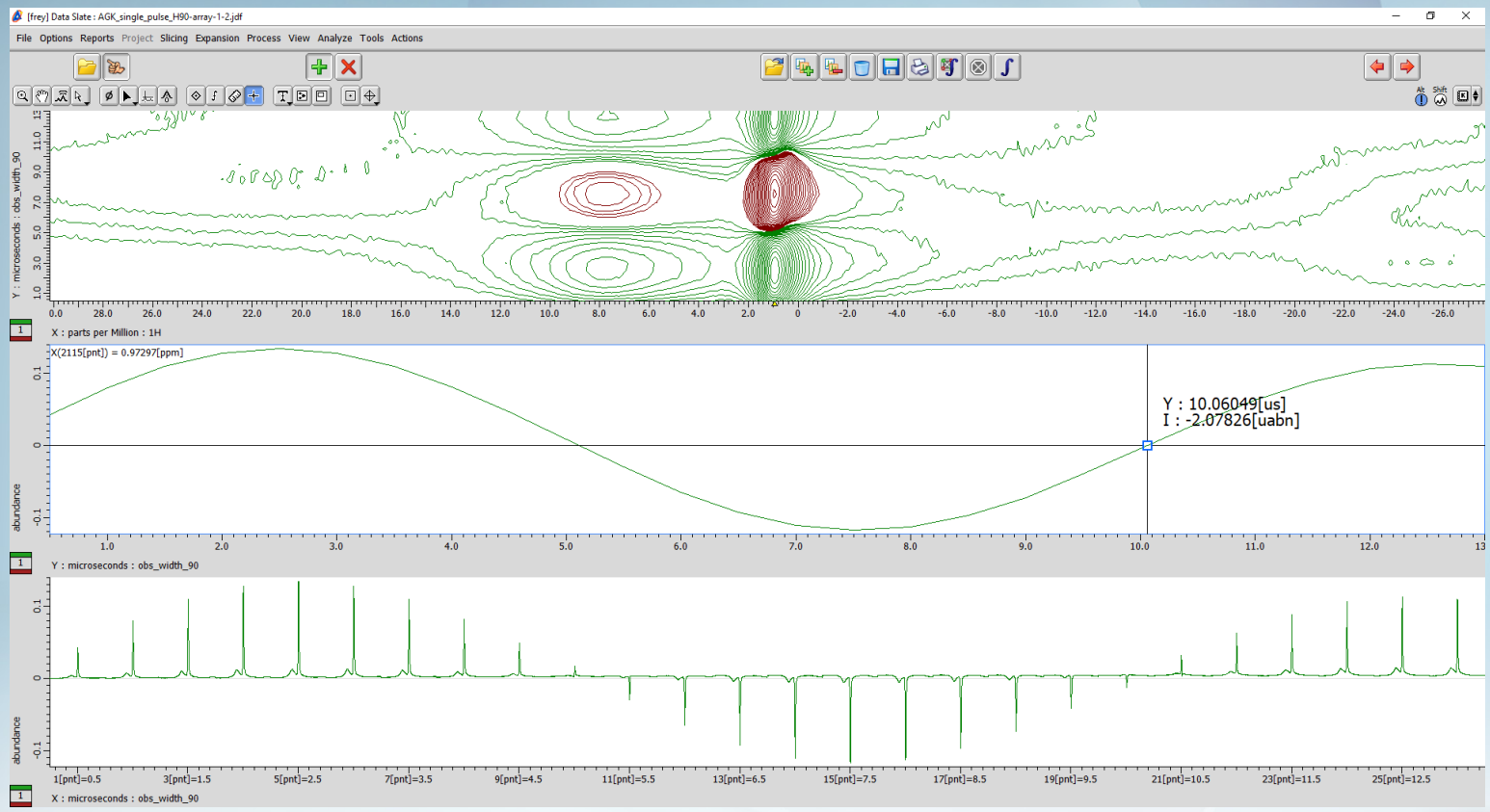
- Use single_pulse_solid.jxp
- Run just like ^{1}H 90 check in liquids

- To make sure ^{1}H decoupling is working properly
  - Power levels are critical in solids

^{1}H spectrum of AGK



^{1}H 90 Array results – H90 = 2.5 us



Setup CPMAS

- CP array to determine CP power
- Contact Array to determine best contact time
- Ramp Array to maximize all signals

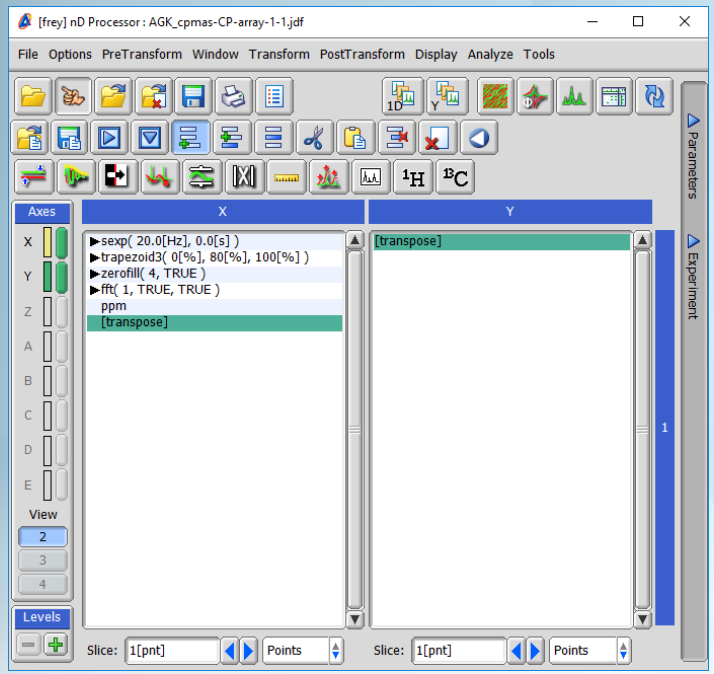
- Use CPMAS cpmas.jxp

Setup CP array

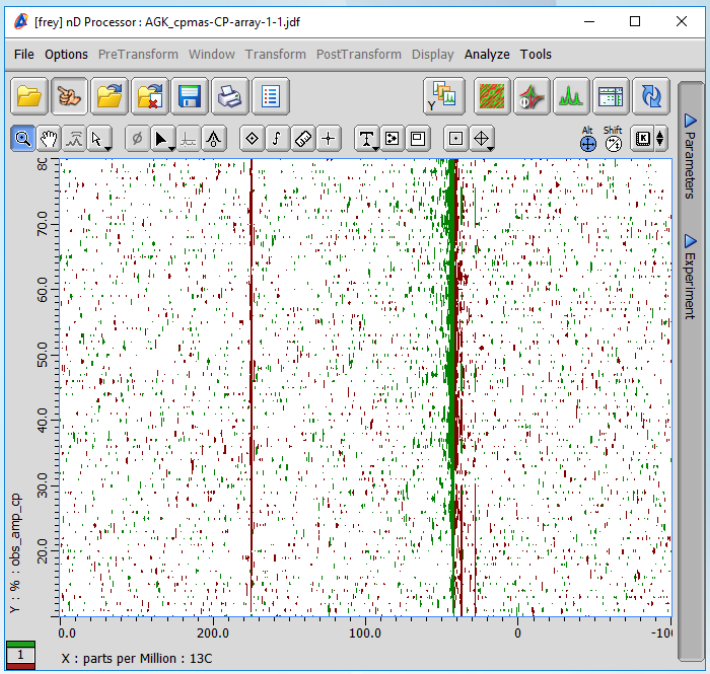
- Scans = 1
- obs_shape_cp = constant_cp
- contact_time = 5 ms
- irr_amp_cp = 50%
- obs_amp_cp = y_acq 10[%]..80[%] : 1[%]

CP -Array

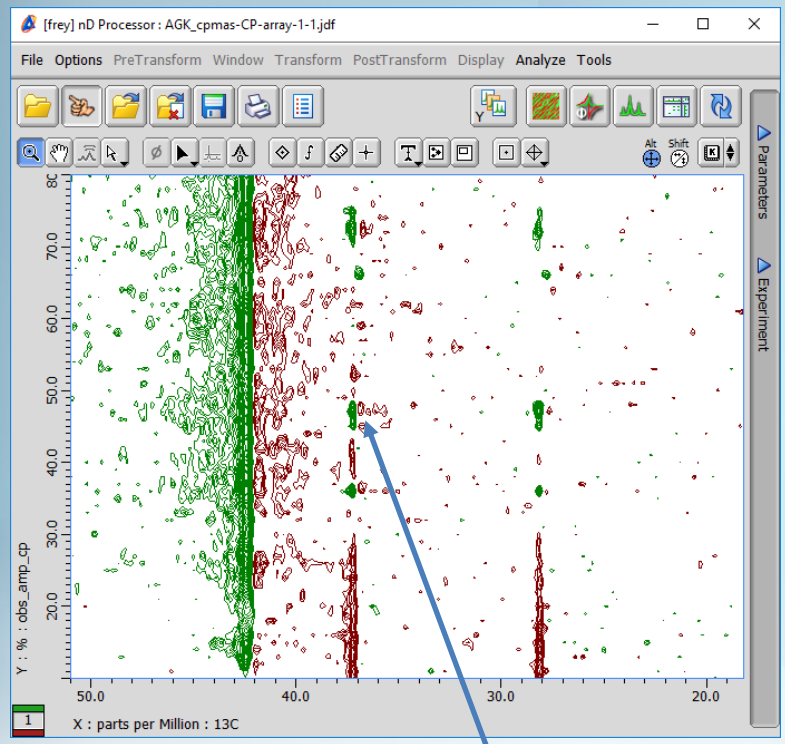
Processing List

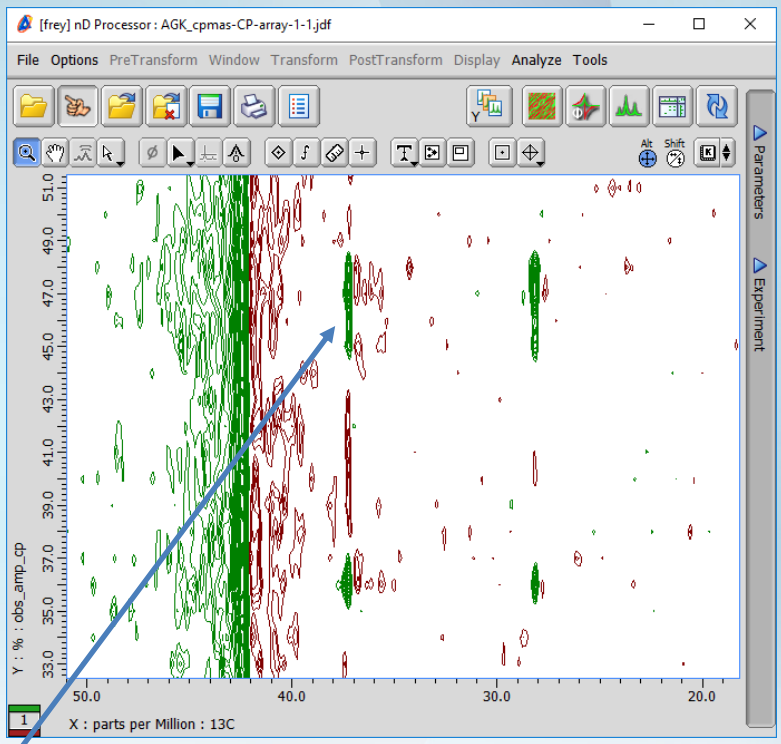


Un-Phased Result



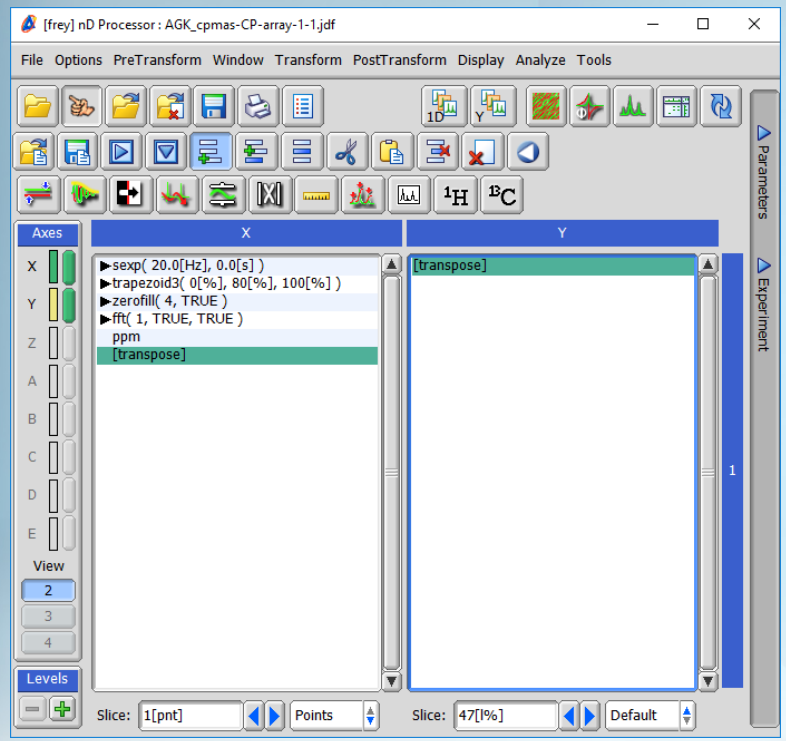
Zoom on Aliphatic region to find Adamantane peaks

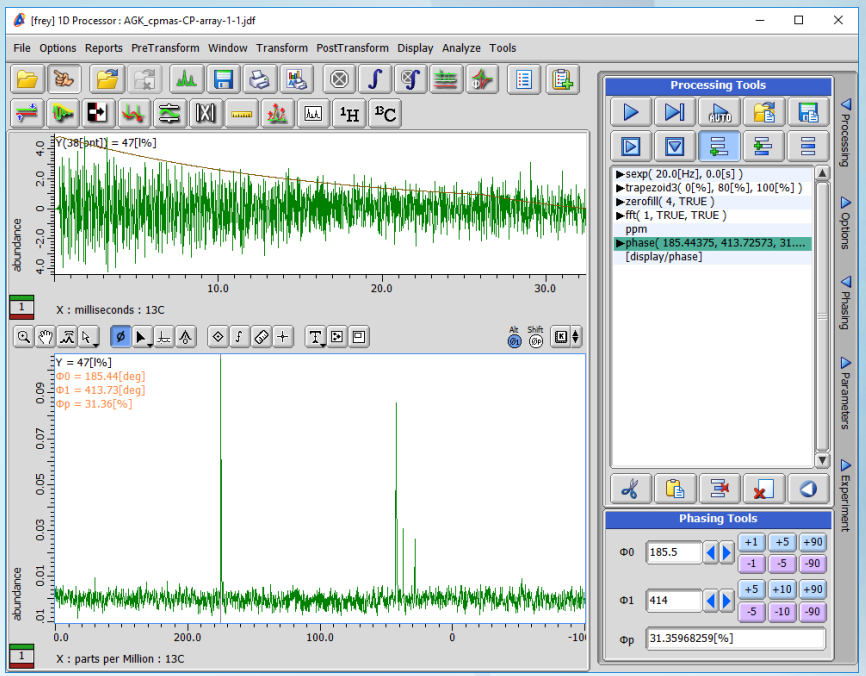




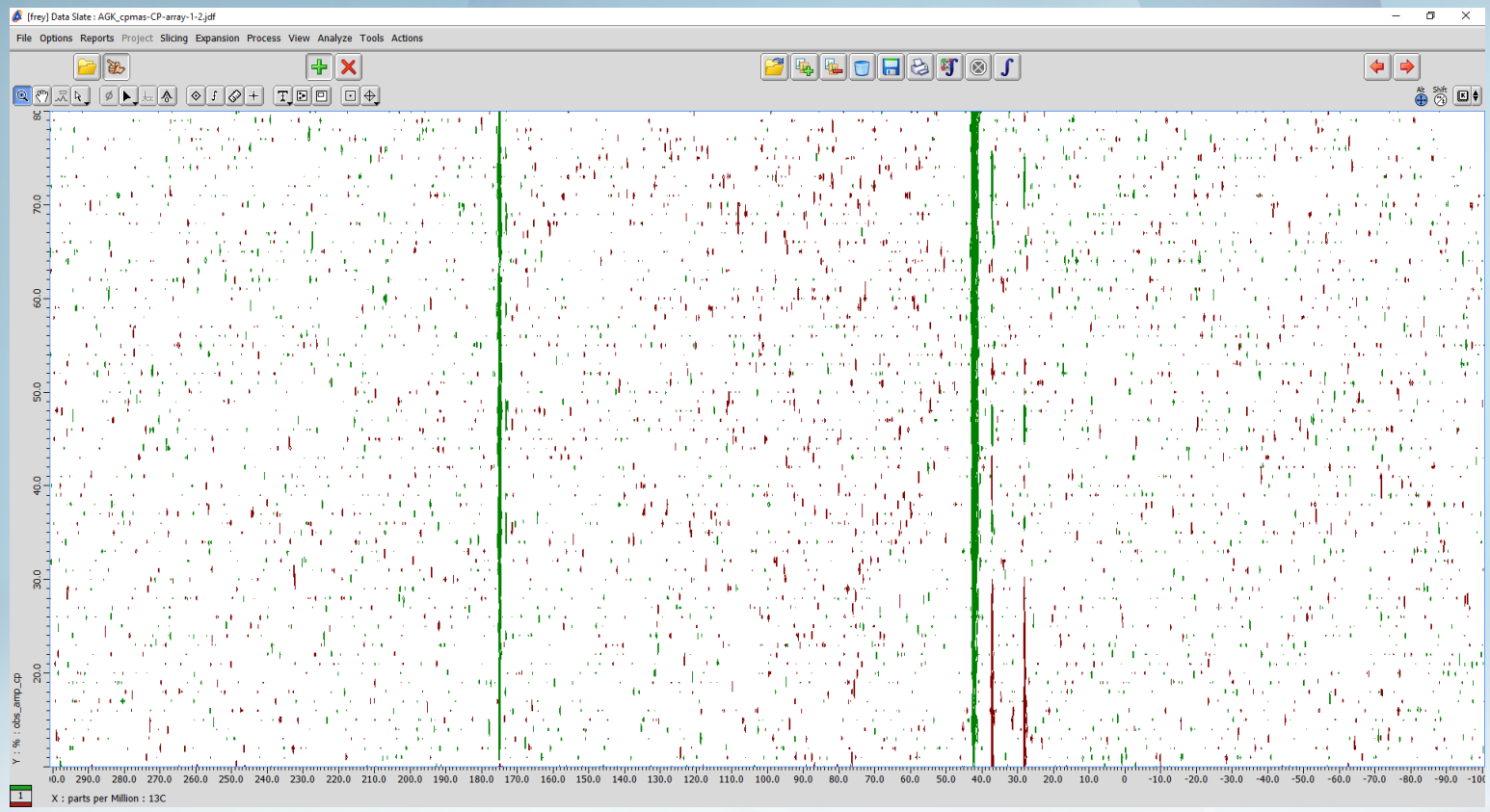
Adamantane peak

Pick slice at 47% to phase



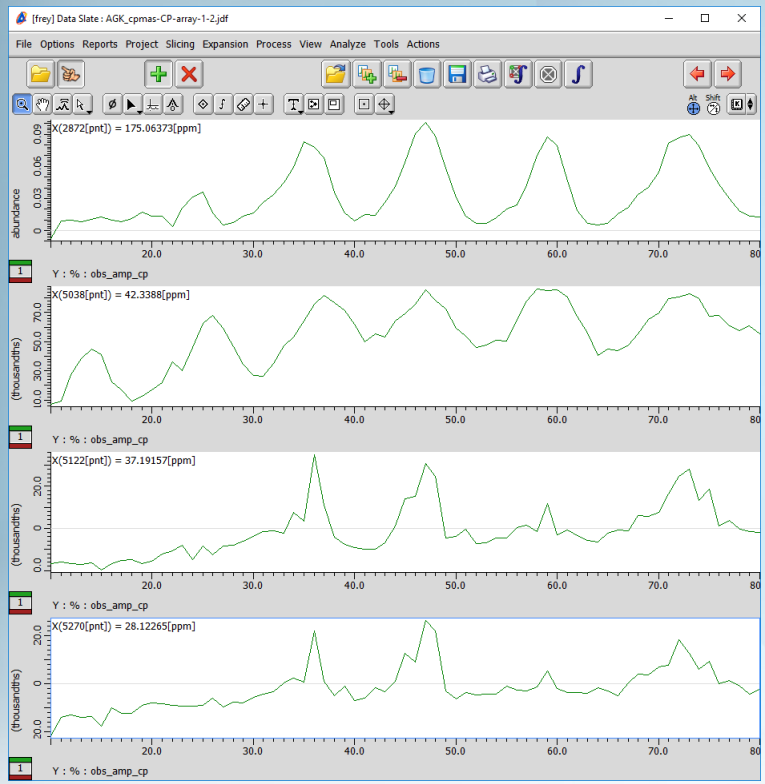


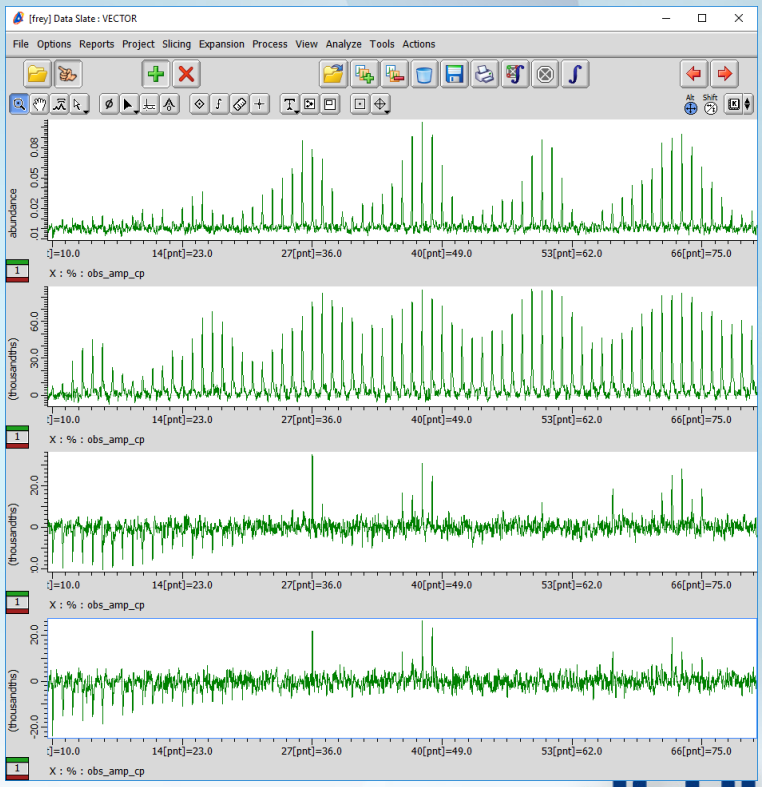
Process the data to Data Slate



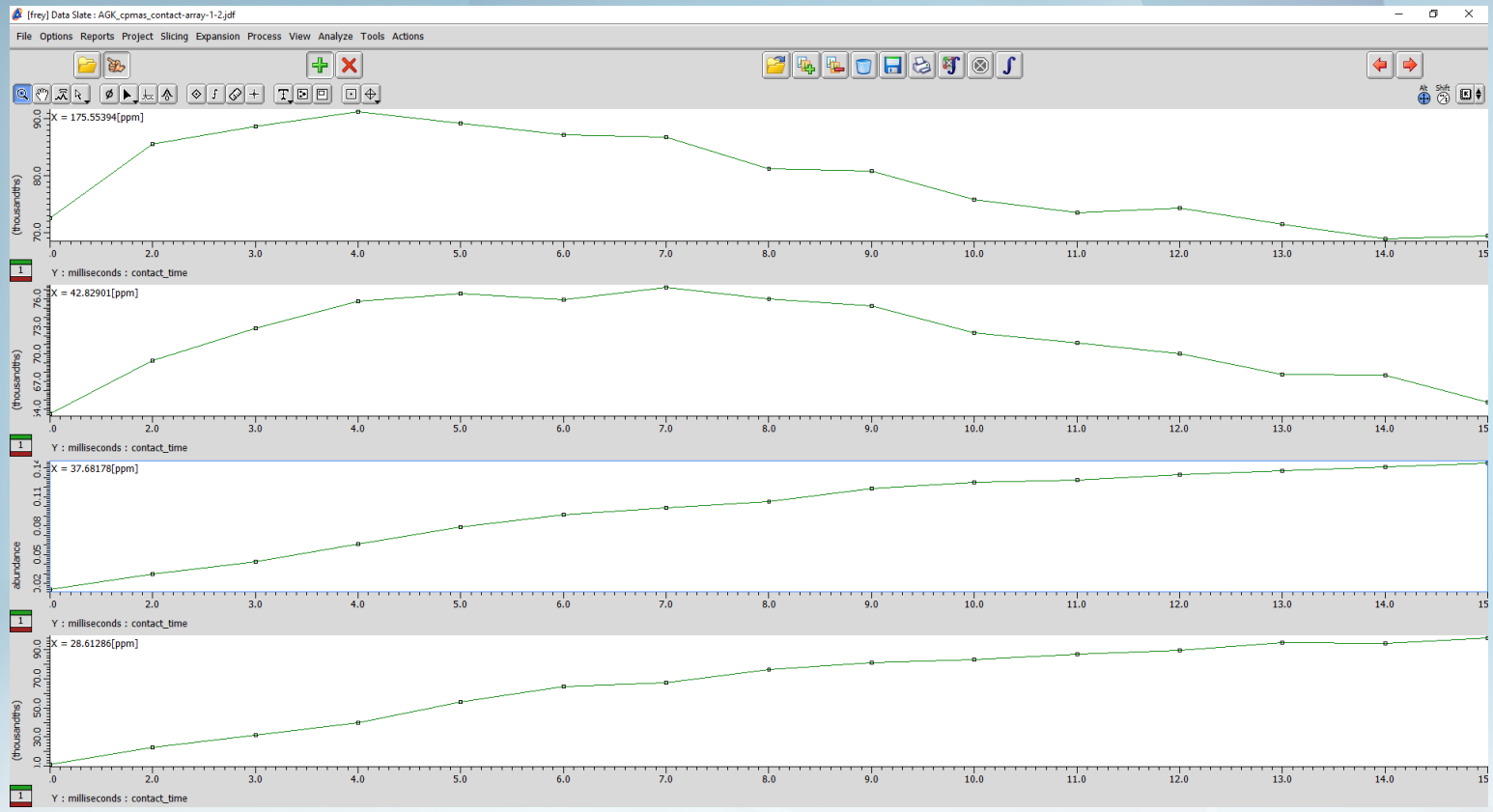
Pick slices or linearize at peak positions

Update obs_amp_cp to use maximum @ 47%

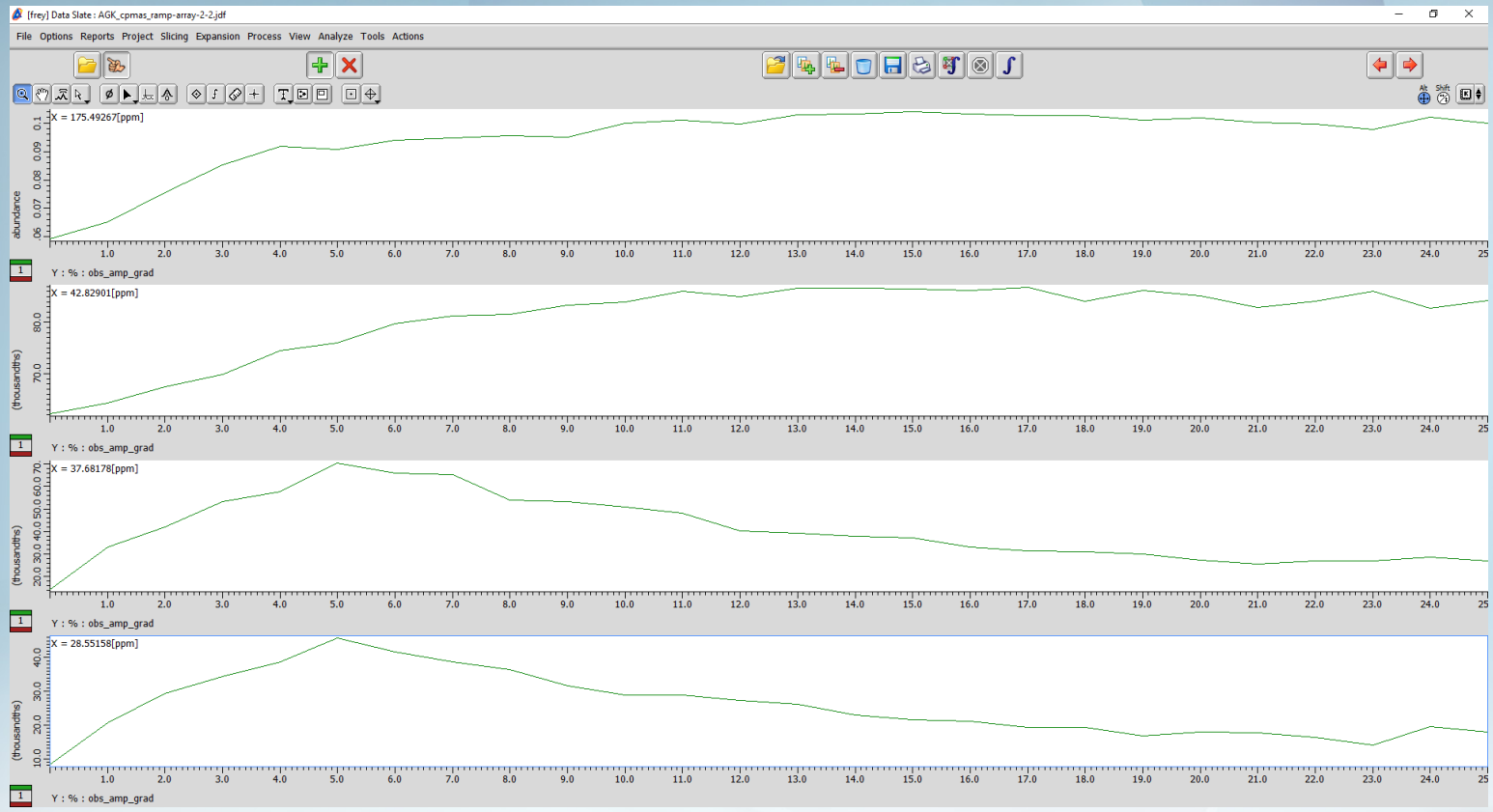




Setup contact array = y_acq {1[ms], 2[ms], 5[ms], 7[ms], 10[ms]}



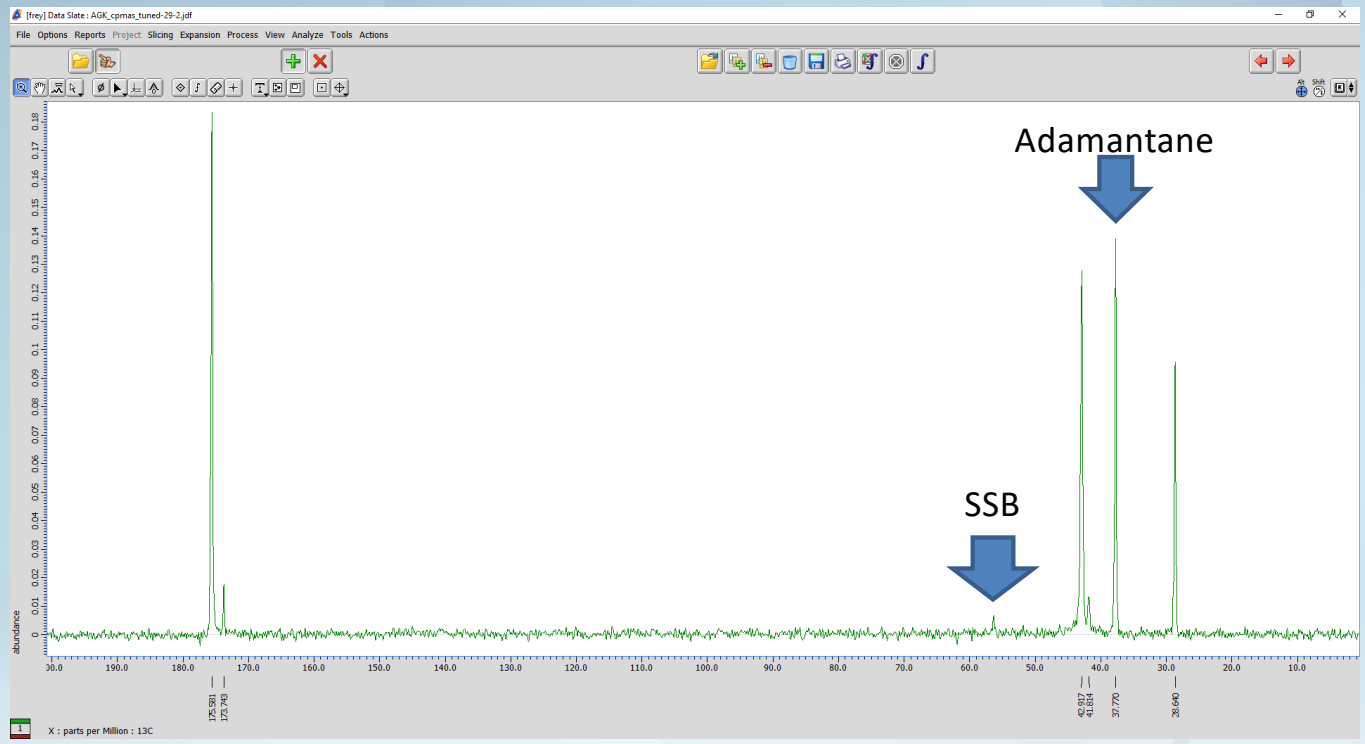
Setup Ramp array = y_acq 0[%]..20[%] : 1[%]



CPMAS Tuned experiment

- Scans = 16
- obs_shape_cp = RAMP_cp
- contact_time = 4 ms
- irr_amp_cp = 50%
- obs_amp_cp = 47%
- obs_amp_grad = 5%

AGK Tuned CPMAS spectrum

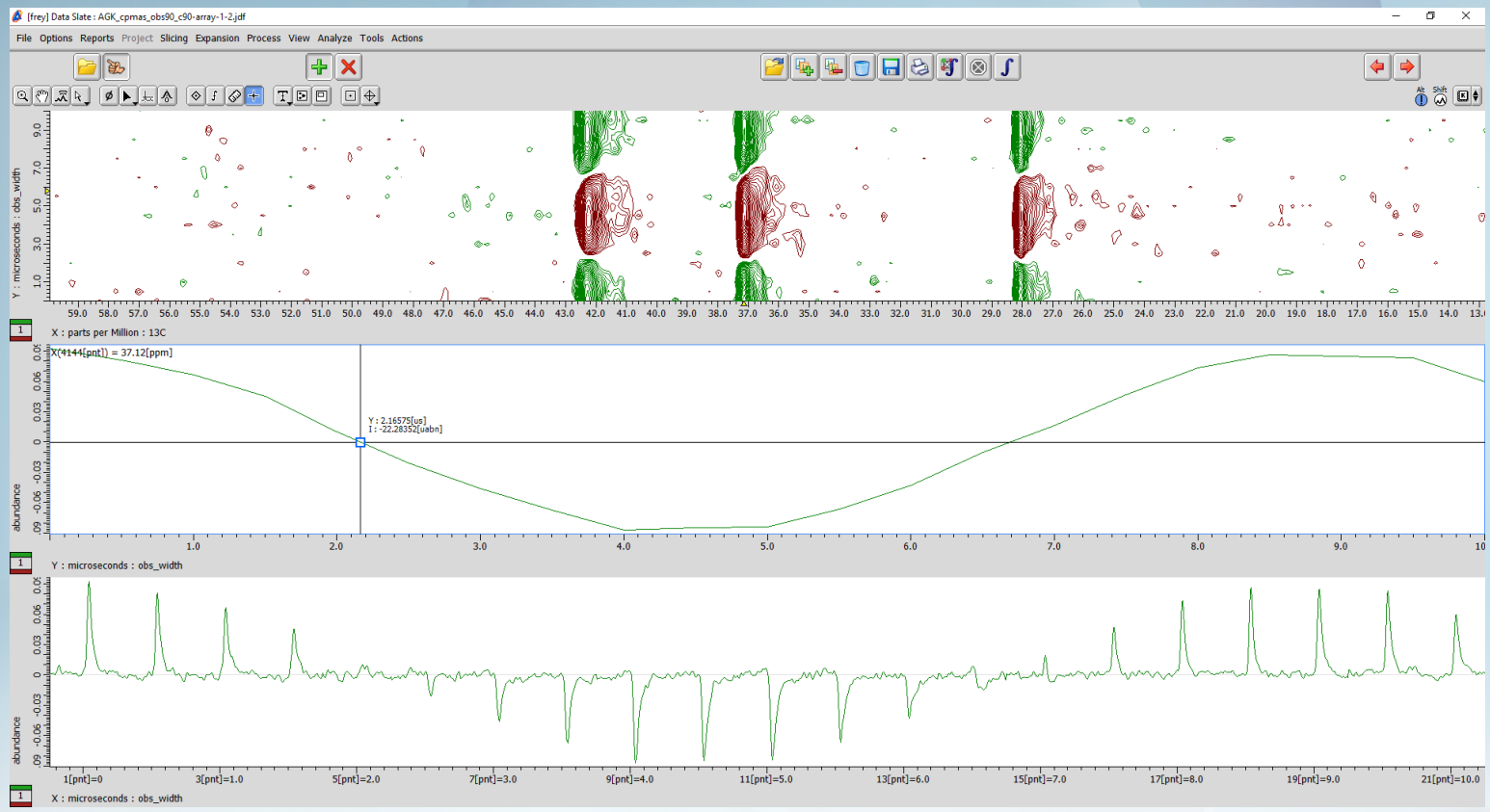


Adamantane peak is also chemical shift reference at 37.77 ppm
Spinning speed 15 kHz

^{13}C 90 via CPMAS

- Use cpmas_obs90.jxp experiment
- Set up standard CP conditions
- Array obs_width = y_acq 0[us]..10[us] : 0.5[us]

^{13}C 90 via CPMAS



Running Samples Standard Procedure

- Run tuned CPMAS of AGK before every sample
- Run sample
- Run tuned CPMAS of AGK after every sample

- This does 3 things:
  - Checks that the machine is operating correctly and the problem is the sample not the spectrometer
  - Provides chemical reference for all spectra.
  - Check if magic angle is drifting

- This only adds a few minutes, but ensures that the instrument is working properly before and after every sample

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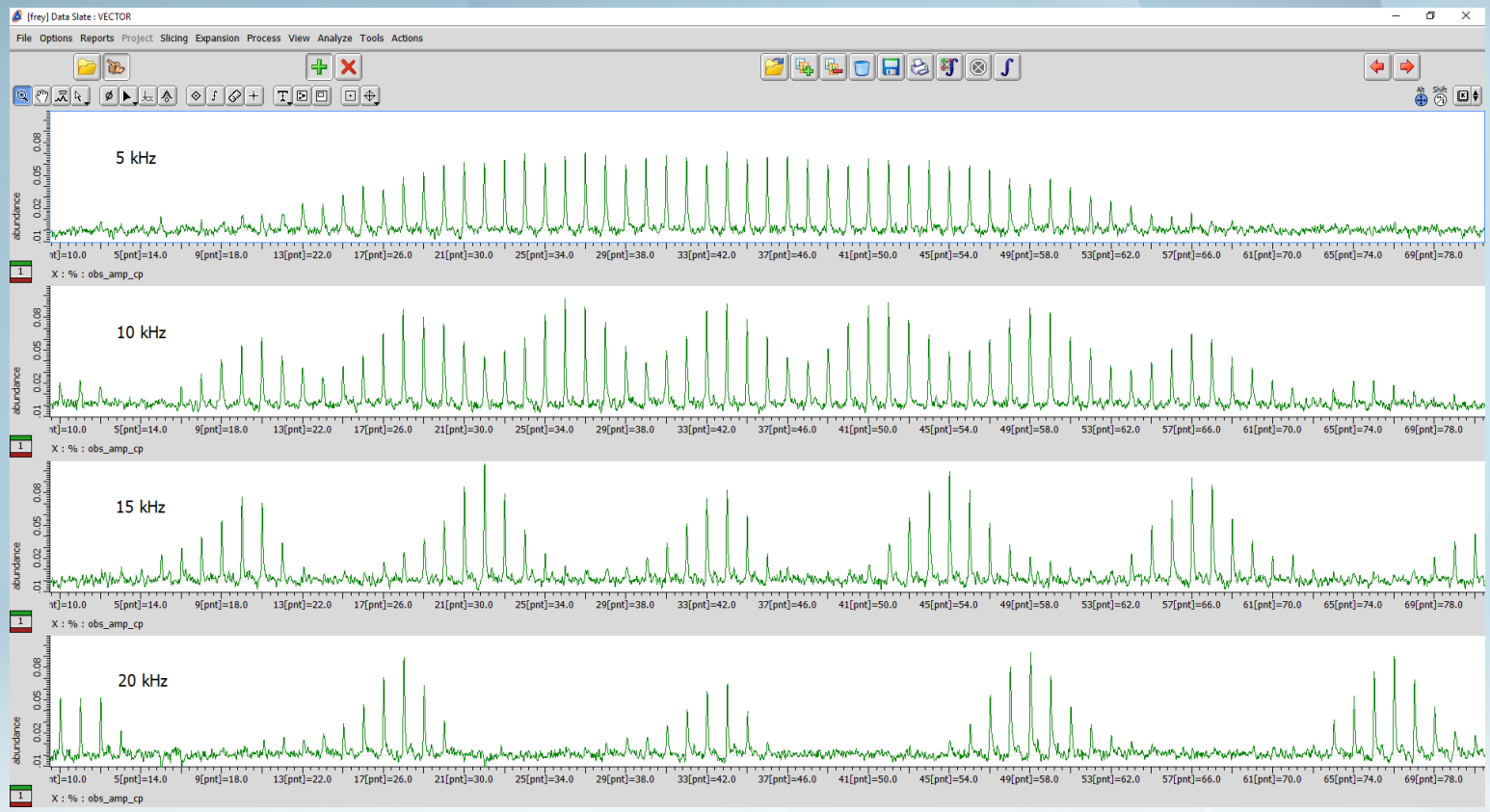
Things to check

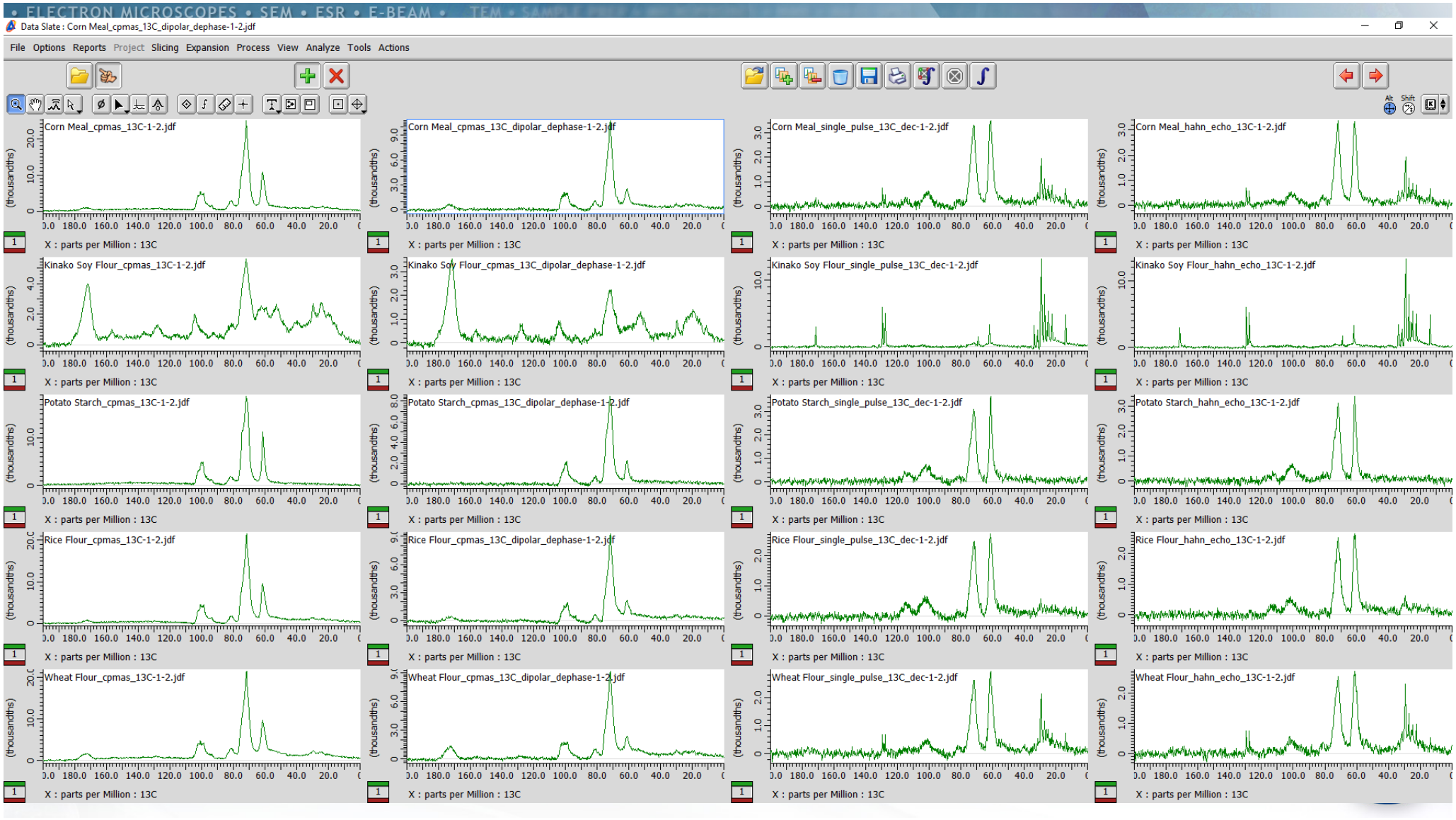
- **If sensitivity on real sample seems low:**
  - **Run quick contact time array on real sample**
  - **Run a quick ^{1}H T1**
- **Rerun the CP obs amp array if spinning speed changes**

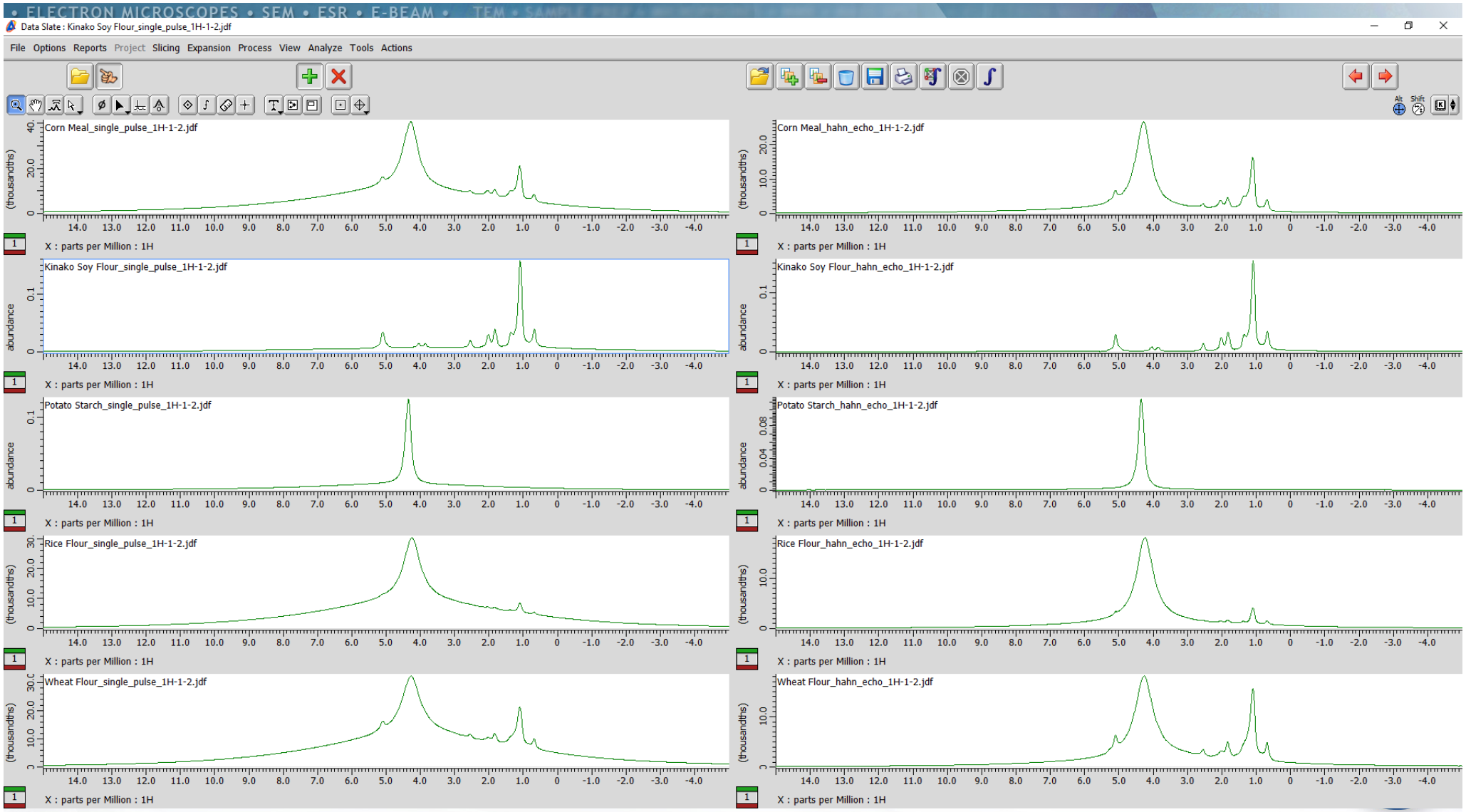
CP Array vs Spinning Speed



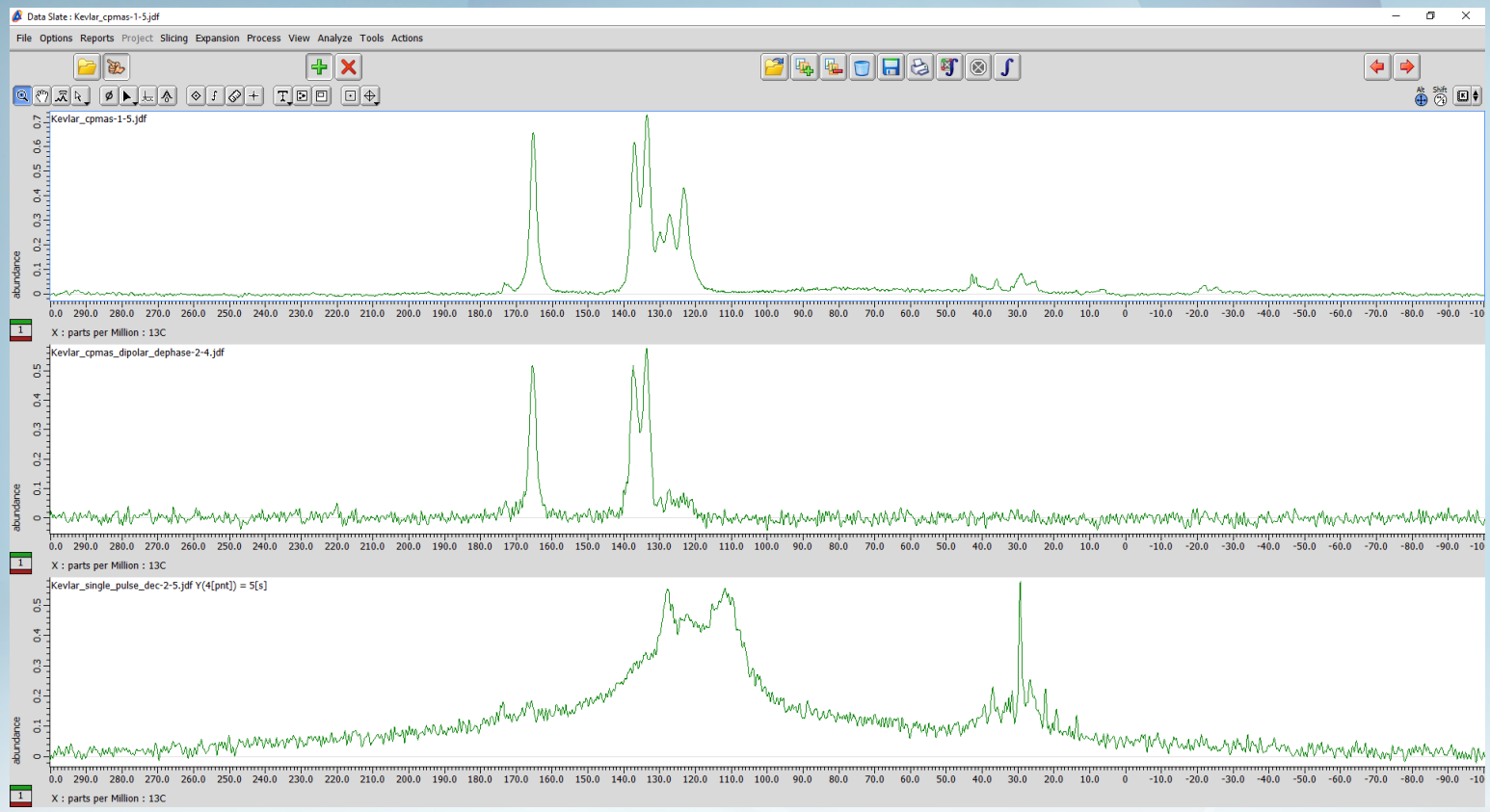
Other Experiments to remember:

- ^{1}H Single Pulse with DEPTH
- ^{1}H Echo
- ^{13}C Single Pulse with DEPTH
- ^{13}C Echo
- ^{13}C CPMAS Dipolar Dephasing

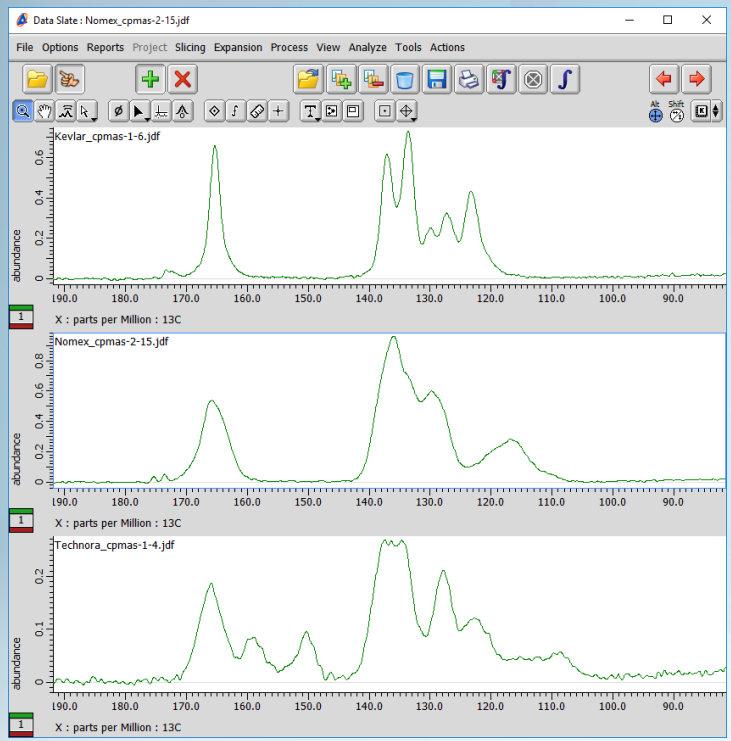

ELECTRON MICROSCOPES • SEM • ESR • E-BEAM • TEM
Data Slate : Corn Meal_cpmas_13C_dipolar_dephase-1-2.jdf
File Options Reports Project Slicing Expansion Process View Analyze Tools Actions
Corn Meal_cpmas_13C-1-2.jdf
Corn Meal_cpmas_13C_dipolar_dephase-1-2.jdf
Corn Meal_single_pulse_13C_dec-1-2.jdf
Corn Meal_hahn_echo_13C-1-2.jdf
Kinako Soy Flour_cpmas_13C-1-2.jdf
Kinako Soy Flour_cpmas_13C_dipolar_dephase-1-2.jdf
Kinako Soy Flour_single_pulse_13C_dec-1-2.jdf
Kinako Soy Flour_hahn_echo_13C-1-2.jdf
Potato Starch_cpmas_13C-1-2.jdf
Potato Starch_cpmas_13C_dipolar_dephase-1-2.jdf
Potato Starch_single_pulse_13C_dec-1-2.jdf
Potato Starch_hahn_echo_13C-1-2.jdf
Rice Flour_cpmas_13C-1-2.jdf
Rice Flour_cpmas_13C_dipolar_dephase-1-2.jdf
Rice Flour_single_pulse_13C_dec-1-2.jdf
Rice Flour_hahn_echo_13C-1-2.jdf
Wheat Flour_cpmas_13C-1-2.jdf
Wheat Flour_cpmas_13C_dipolar_dephase-1-2.jdf
Wheat Flour_single_pulse_13C_dec-1-2.jdf
Wheat Flour_hahn_echo_13C-1-2.jdf
(thousandths)
X : parts per Million : 13C

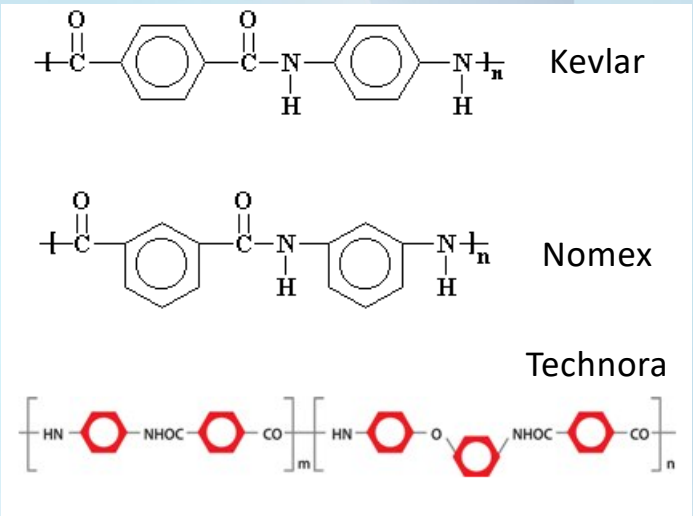

• ELECTRON MICROSCOPES • SEM • ESR • E-BEAM • TEM •
Data Slate : Kinako Soy Flour_single_pulse_1H-1-2.jdf
File Options Reports Project Slicing Expansion Process View Analyze Tools Actions
Corn Meal_single_pulse_1H-1-2.jdf
Corn Meal_hahn_echo_1H-1-2.jdf
Kinako Soy Flour_single_pulse_1H-1-2.jdf
Kinako Soy Flour_hahn_echo_1H-1-2.jdf
Potato Starch_single_pulse_1H-1-2.jdf
Potato Starch_hahn_echo_1H-1-2.jdf
Rice Flour_single_pulse_1H-1-2.jdf
Rice Flour_hahn_echo_1H-1-2.jdf
Wheat Flour_single_pulse_1H-1-2.jdf
Wheat Flour_hahn_echo_1H-1-2.jdf
(thousandths)
abundance
X : parts per Million : 1H

Polymer example - Kevlar



Polymer example – Aramid Fibers

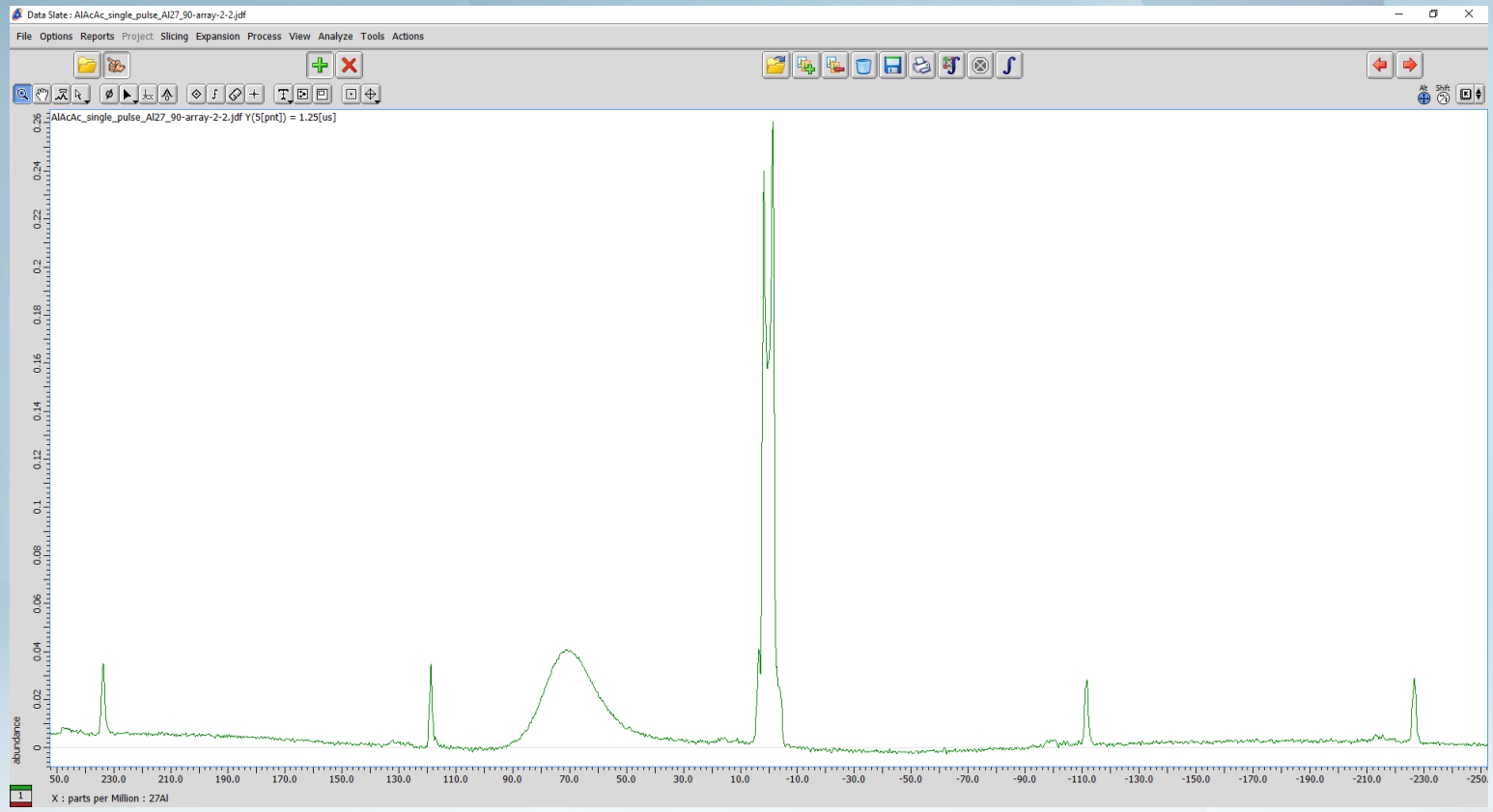




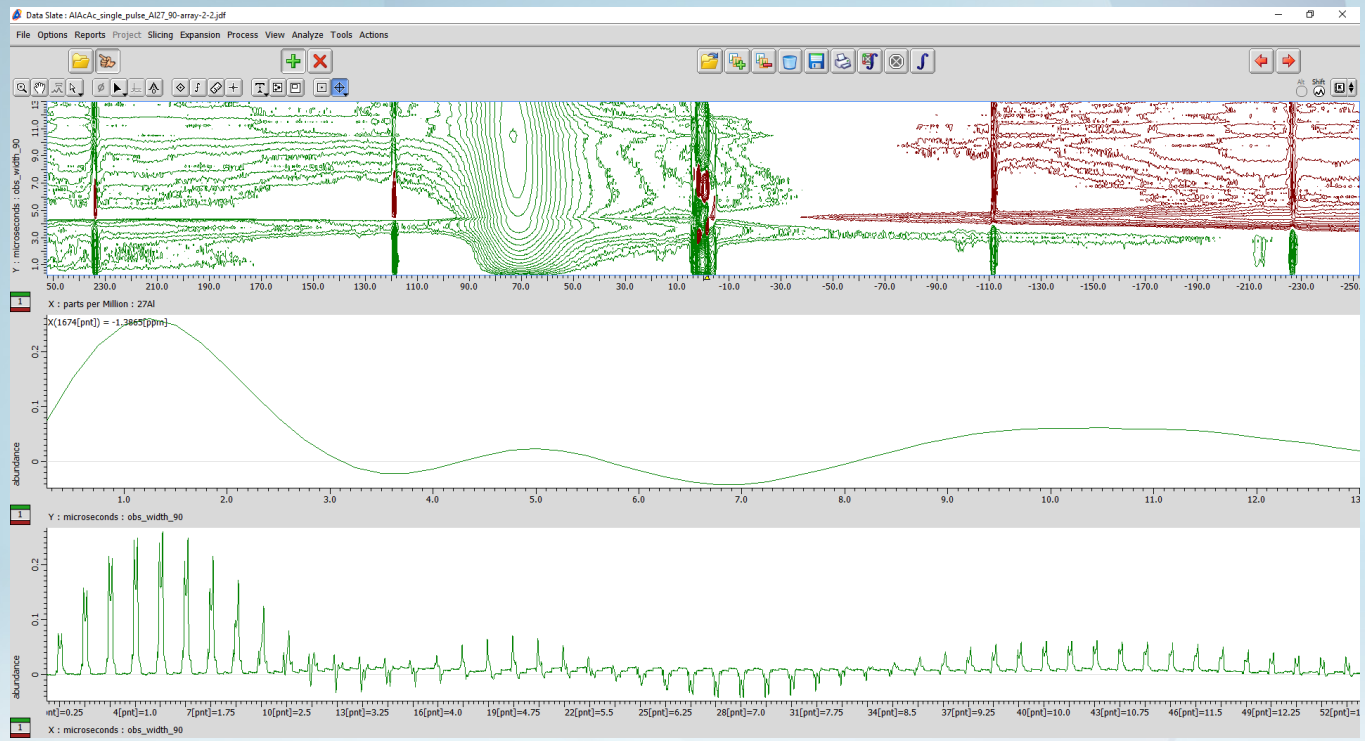
3Q MQMAS Split t_1 Echo with Fast Amplitude Modulation Pulse

- **3 Quantum MQMAS Experiments:**
  - mqmas-s3-3q_fam_split-t1_echo.jxp for Spin 3/2
  - mqmas-s5-3q_fam2_split-t1_echo.jxp for Spin 5/2
  - mqmas-s7-3q_fam2_split-t1_echo.jxp for Spin 7/2
  - mqmas-s9-3q_fam2_split-t1_echo.jxp for Spin 9/2
  - And setup versions
- **Processing lists:**
  - mqmas_split-t1_echo.list
  - mqmas_split-t1_echo_check.list

Easy test sample AlAcAc for ^{27}Al MQMAS

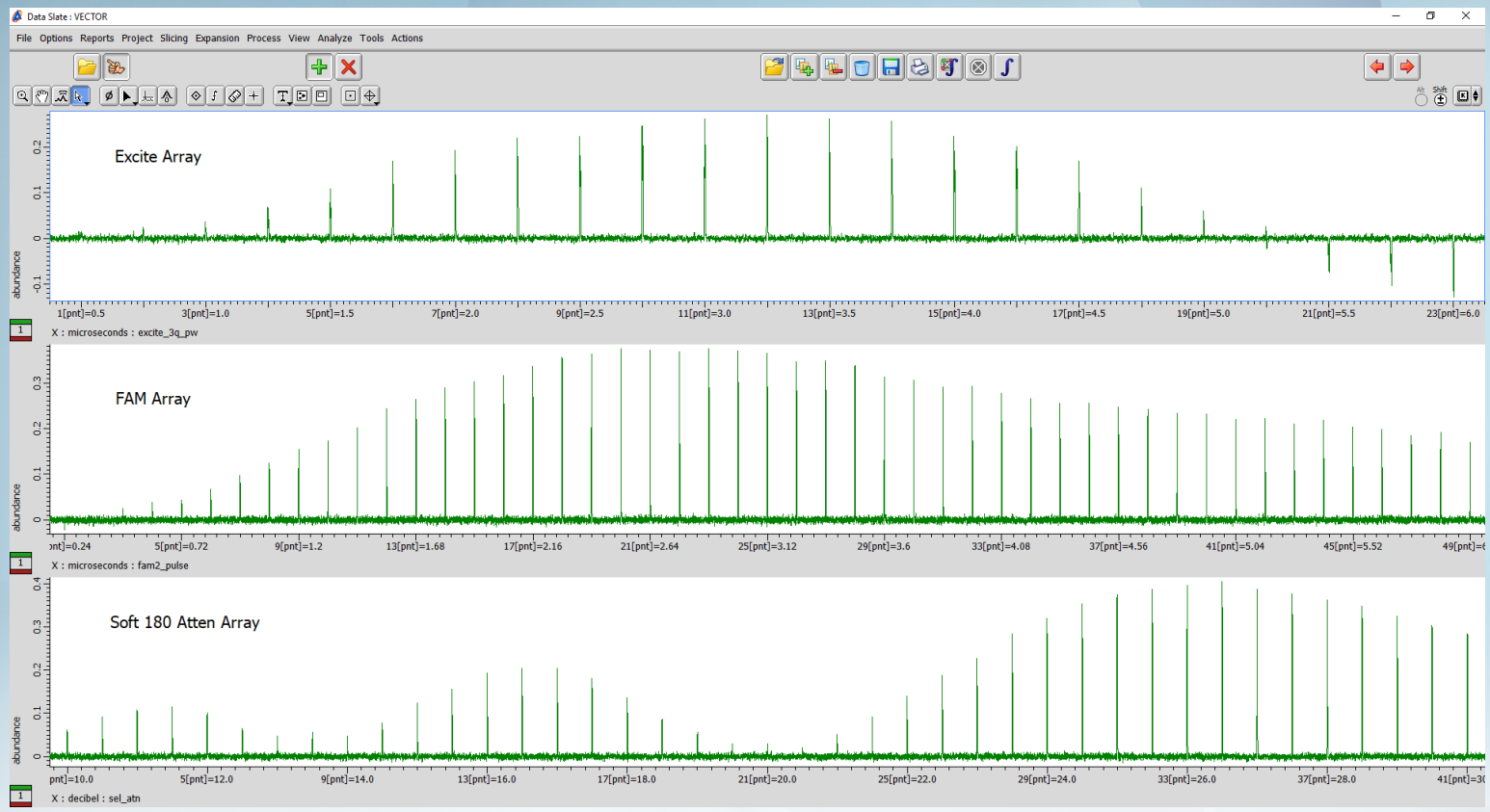


^{27}Al Nutation plot

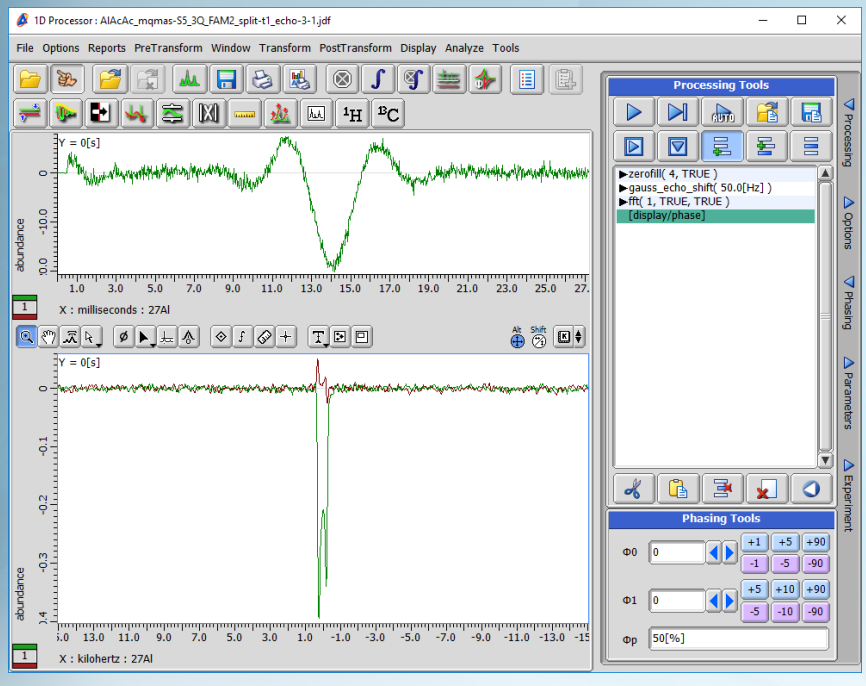


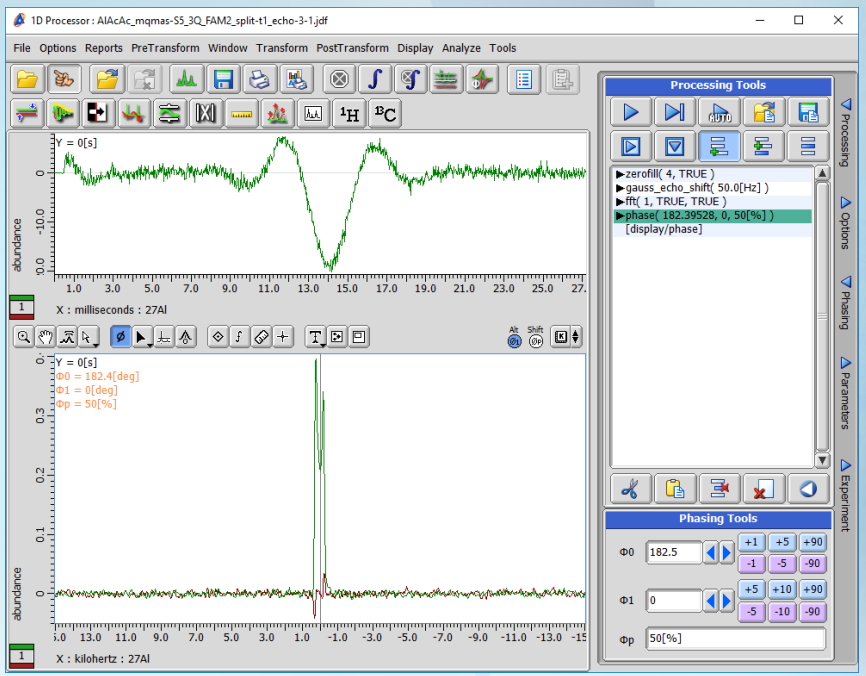
The nutation rate is scaled by the spin, $w_n=(I+1/2)w_{rf}$

Optimize each pulse by arraying

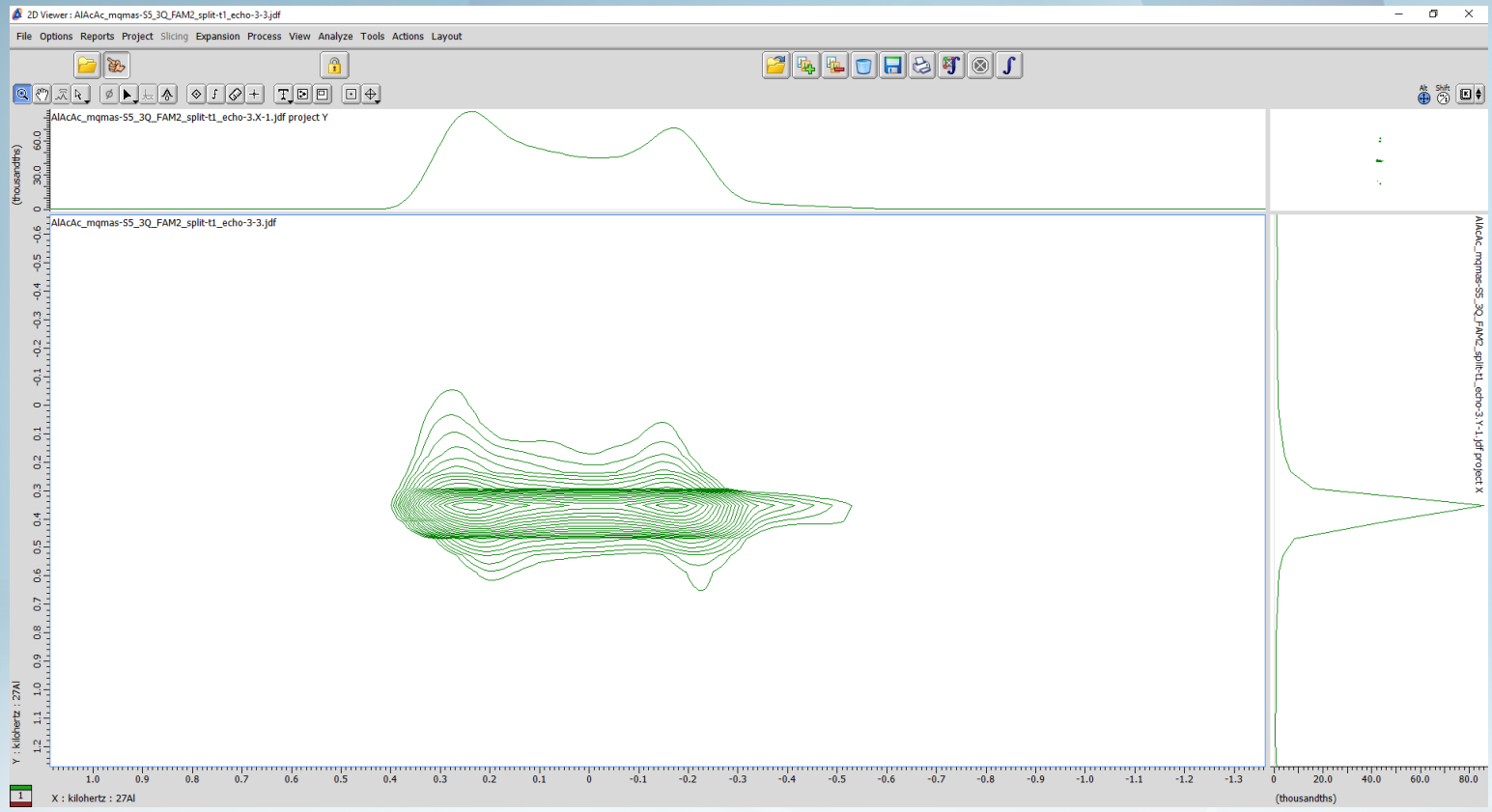


Process and phase the echo

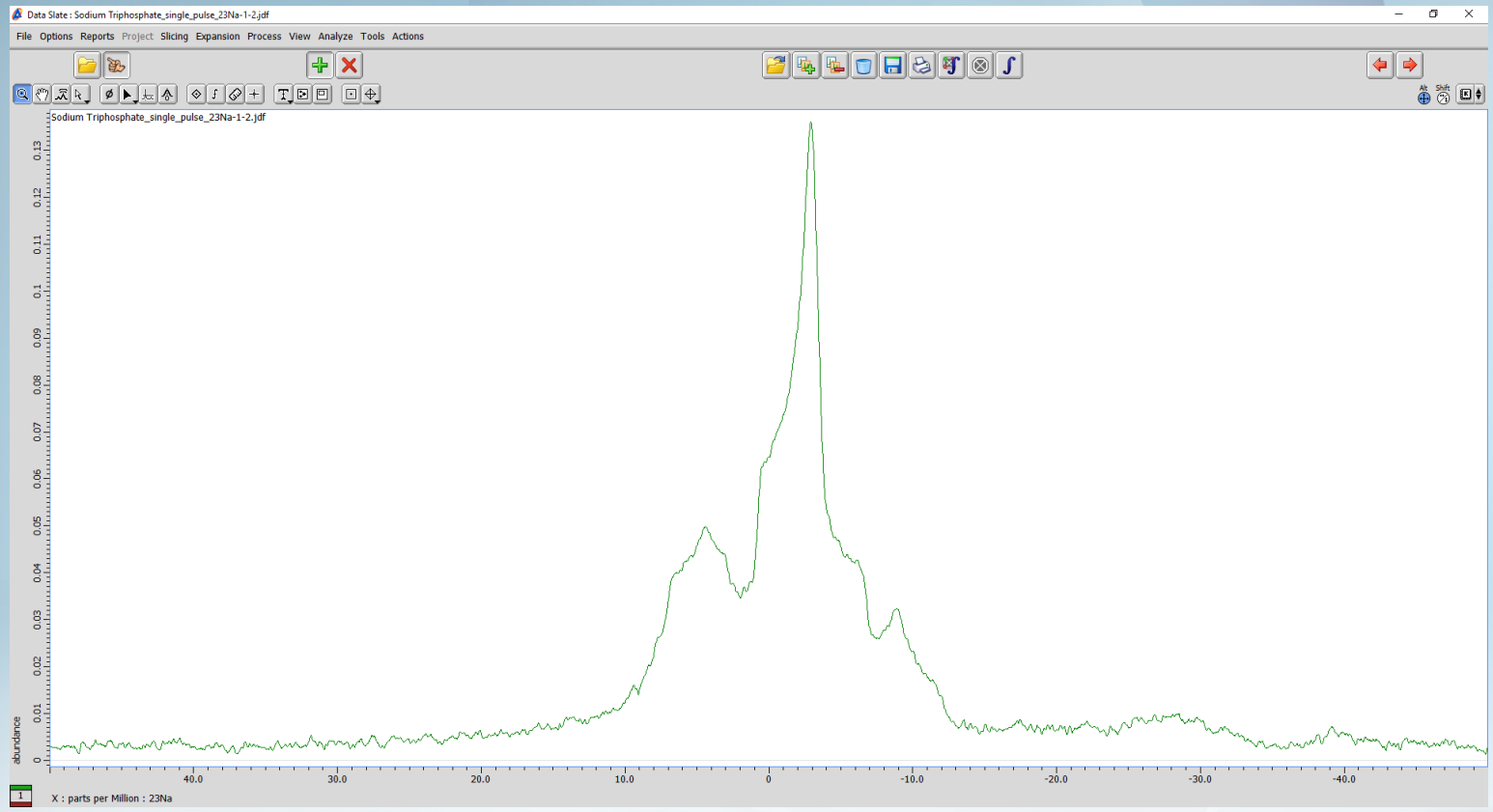




Resulting ^{27}Al 3Q MQMAS of AlAcAc



^{23}Na NMR of Sodium Triphosphate example, $Na_5P_3O_{10}$



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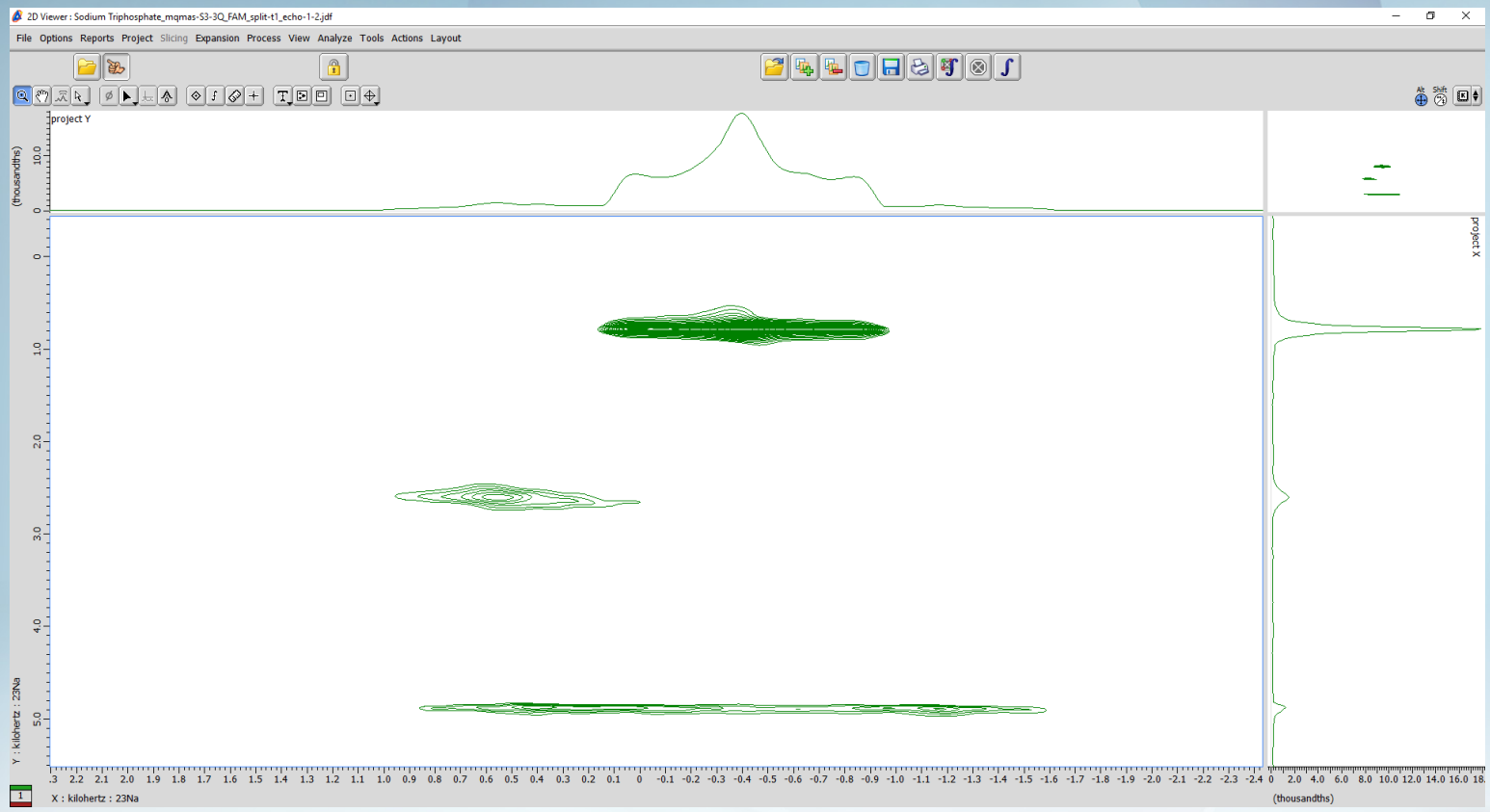

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  - **What is the proposed structure?**
    - **Can greatly affect NMR parameters**
    - **Molecular weight?**
  - **What is the density?**
    - **Can destroy the probe!**
  - **What nuclei do you want to observe?**
    - **Is the machine capable and will the probe tune?**

- **If you do not spend the time setting up properly you will get exactly what you deserve NOISE!!**

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