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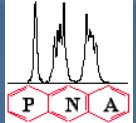
# **On-Line Applications of 60 MHz High-Resolution NMR Systems in Industry: Direct Measurements, Chemometric Correlations and Multiple Spectroscopy Data Fusion**

**Presented By**

**John Edwards, Ph.D.**

**Process NMR Associates, LLC  
Danbury, Connecticut**

**October 16, 2012  
PANIC 2012, Schaumburg IL**



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250+ Analytical NMR Customers

**cosa+xentaur**

**MODCON**

**ACTIVE SPECTRUM**

**QUALION**  
NMR ANALYZERS

**Swagelok**

Process NMR Associates LLC  
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N.M.R.  
Process Systems LLC  
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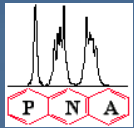
**TTC Labs, Inc.**  
*Process Engineering Excellence*

Analytical Services And Consulting

**cosa+xentaur**

**ASPECT**

**TopNIR Systems**



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## High Resolution FT-NMR – Online / in Process



**First Generation NMR – 1998**  
**Elbit-ATI/Foxboro NMR**



**Second Generation NMR – 2003**  
**Qualion**

## Third Generation NMR – Aspect AI NMR System

### New magnet design – 30mm bore size

- The amount of magnetic pieces that assemble the magnet reduced from 34 to 10. Reduction in Mechanical Complexity
- Bore size of the magnet was increased to 30 mm - improved temperature susceptibility
- Improved temperature and shim stability.

**New Digital Spectrometer Design** - reduces footprint, improves signal processing capabilities

**Probe** - Improved Probe Q for Higher Sensitivity.

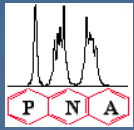
**Software** – Windows 7 – Improved Chemometric Capabilities



Lab version



On-Line version



# New Magnet System

## New magnet design solves the problem of:

- Long term and short term Stability
- Temperature sensitivity

## State of the Art electronics:

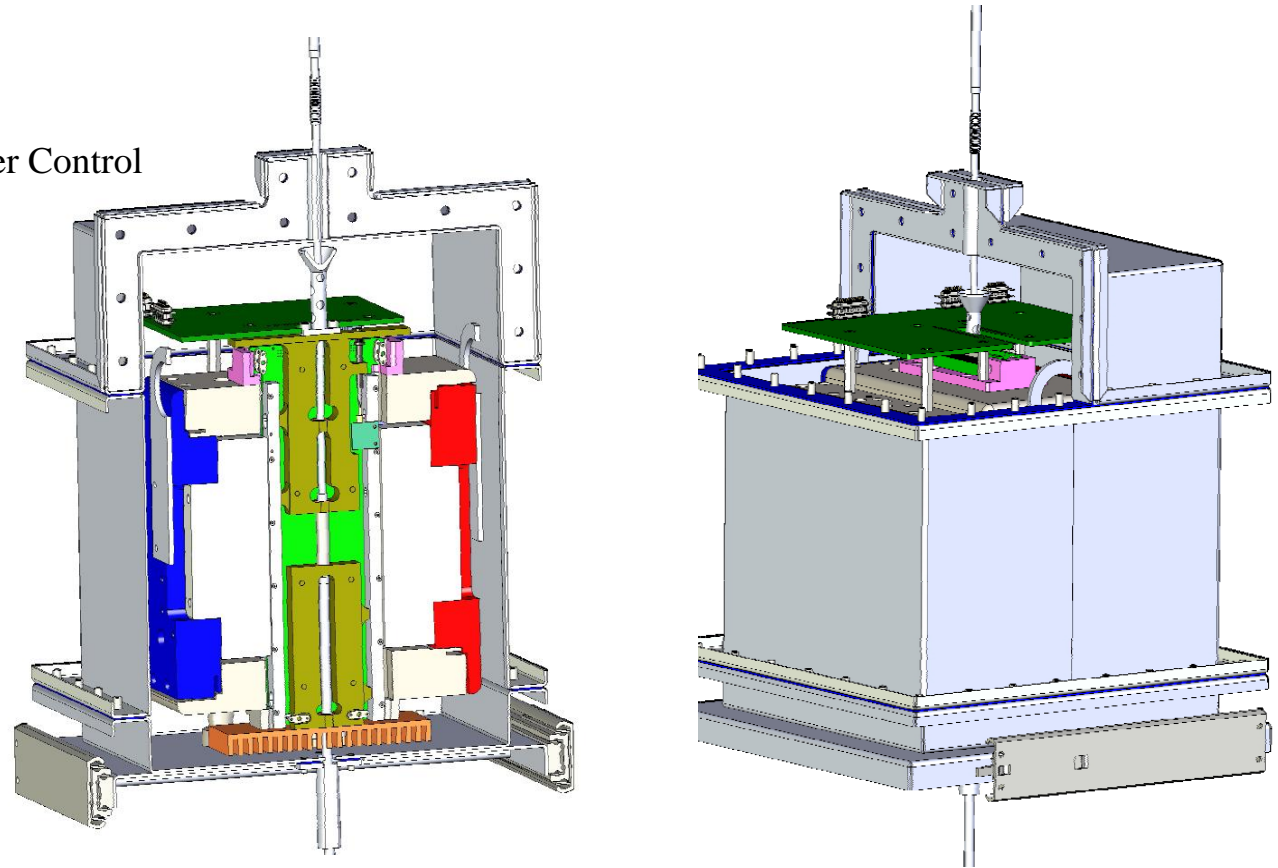
- Smaller foot-print
- 40 Shim coils on 2 single PCB
- Integrated PCB for Shim & Heater Control
- Digital RF & Acquisition – improve SNR

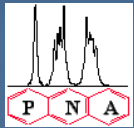
## New concept of Process Probe:

- Entire sample pipe through without contact with the system
- Much better temperature insulation
- Higher Q (better sensitivity)

## New Software:

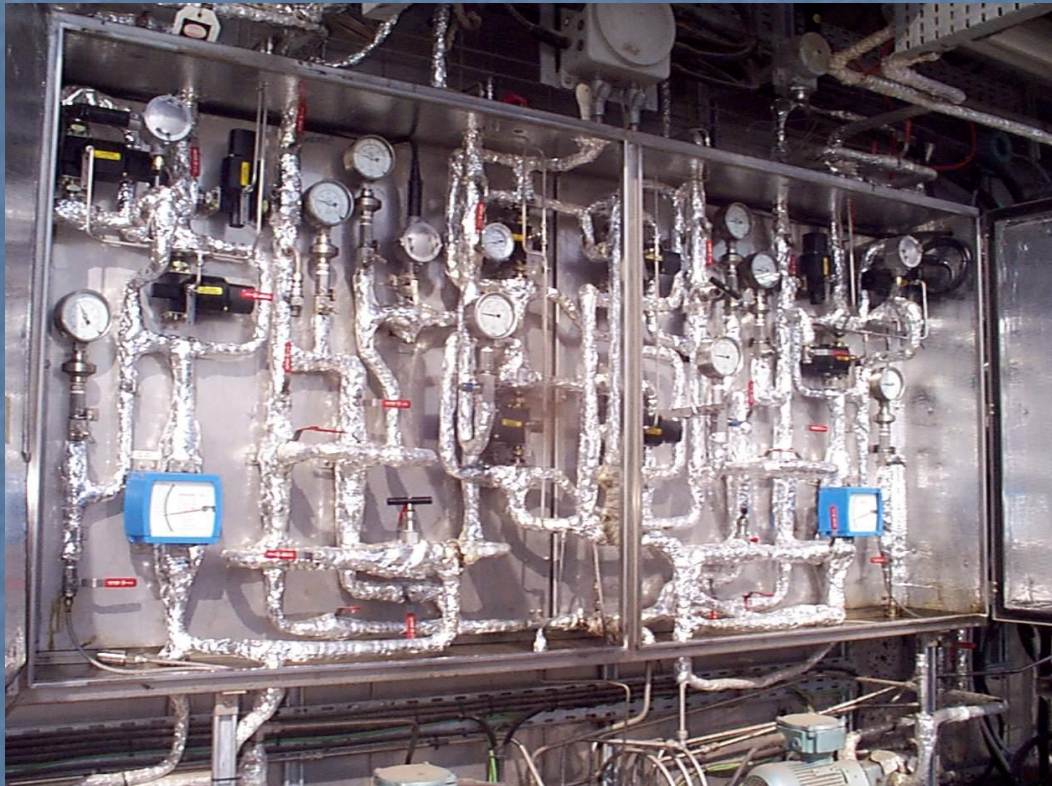
- Includes new algorithm for standard and global Models
- Fully automated process capacity
- Extensive remote diagnostic capabilities

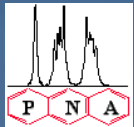




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## NMR Sample System and Placement



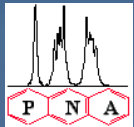


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NMR Lock - External  $^7\text{Li}$  Lock @ 22.5 MHz Shim DACs Built into the Magnet Enclosure

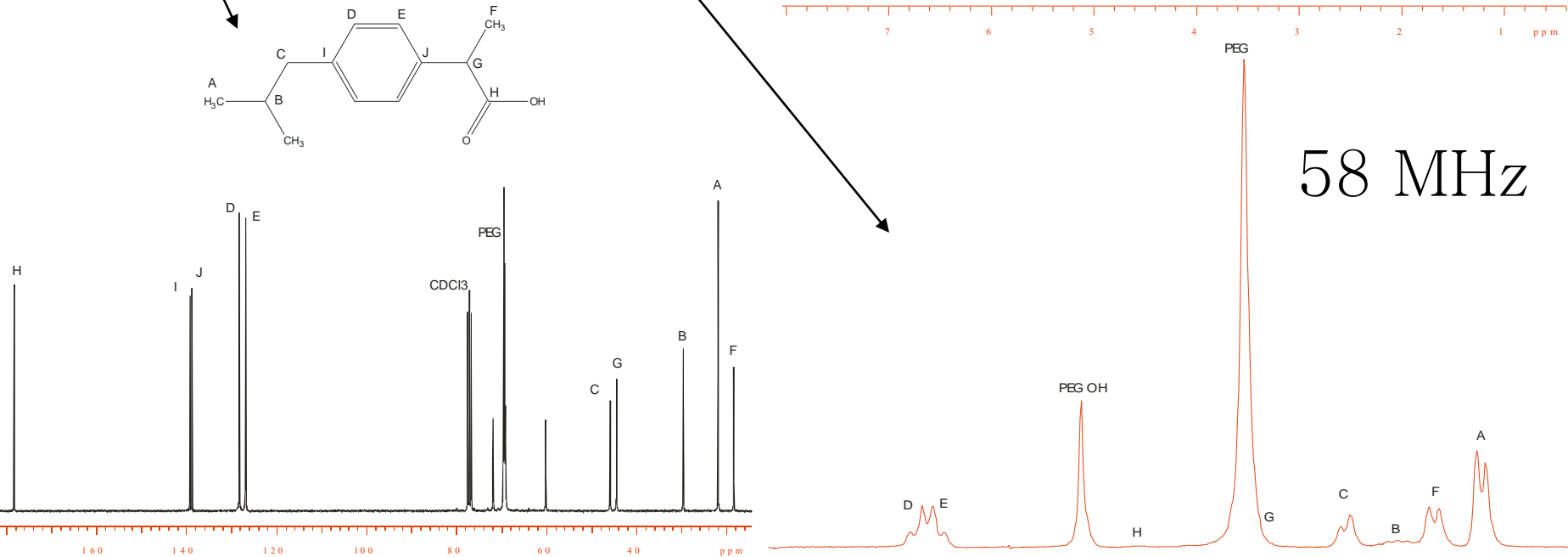
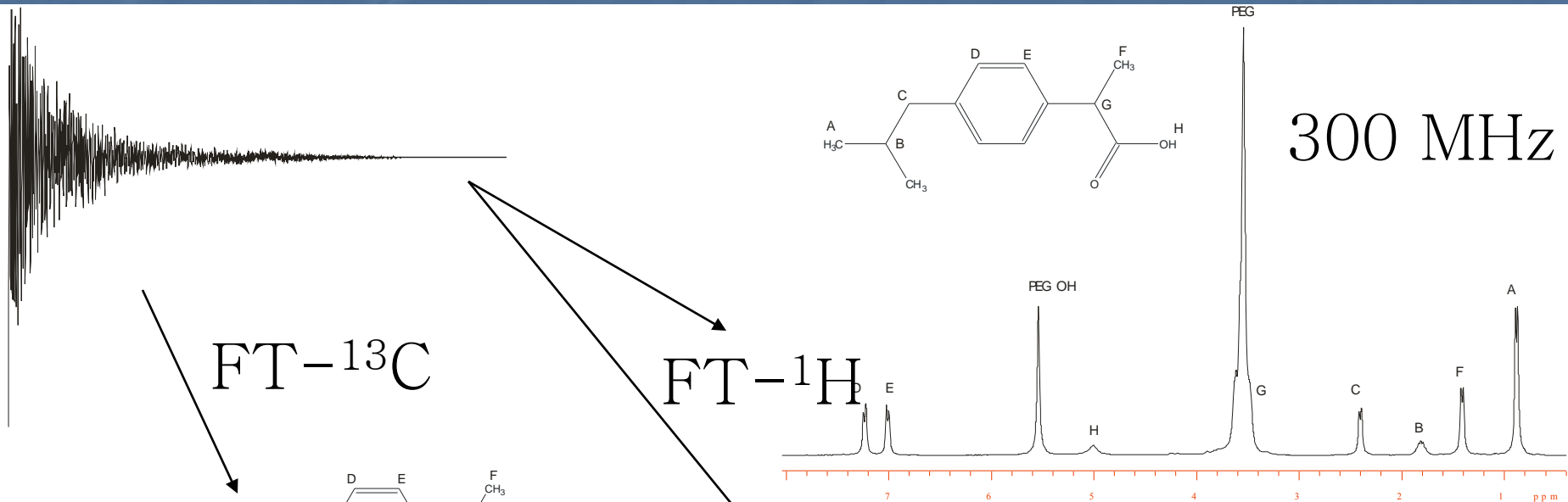
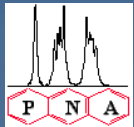


Matrix Shimming Performed  
by Optimizing FID RMS

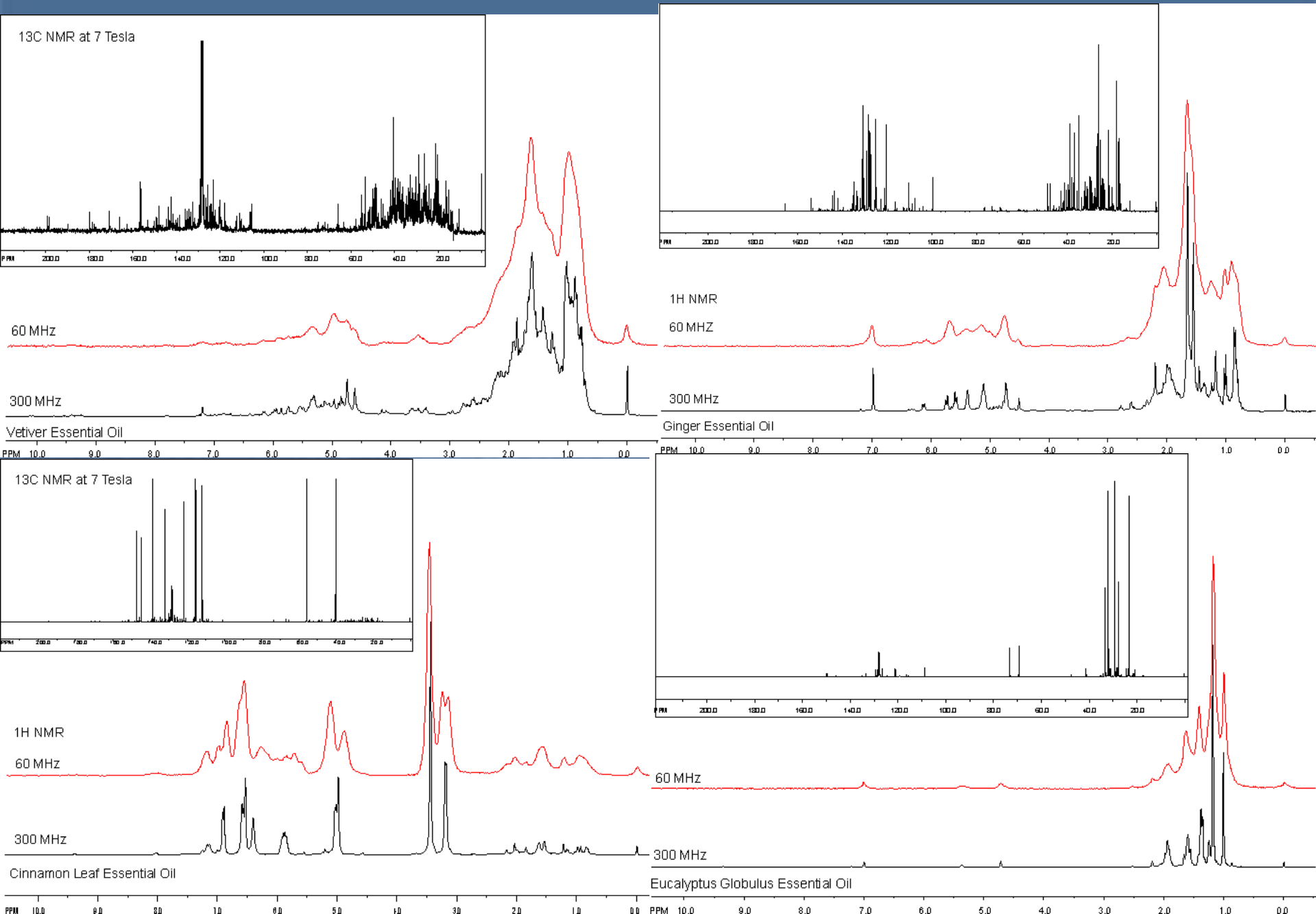


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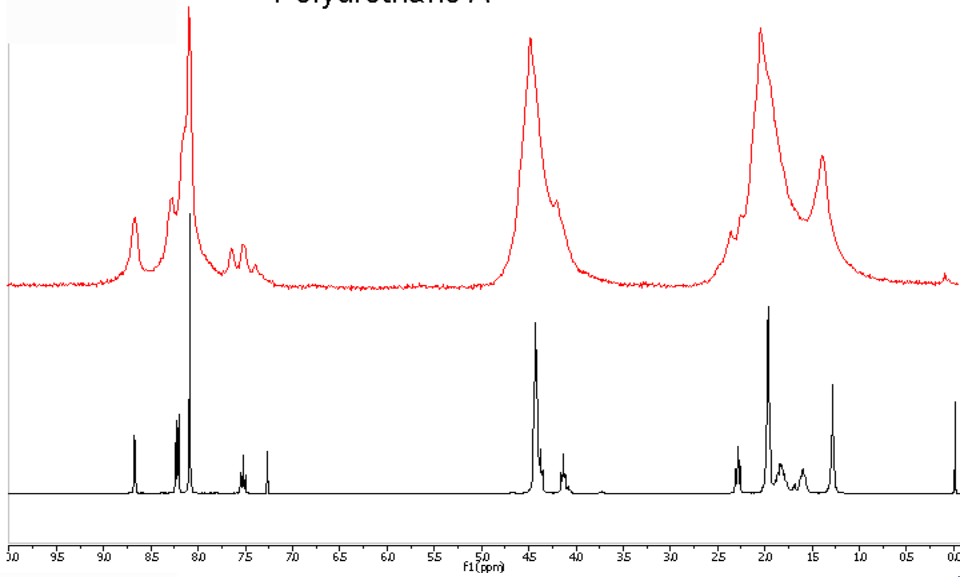


# 60 MHz NMR of Essential Oils

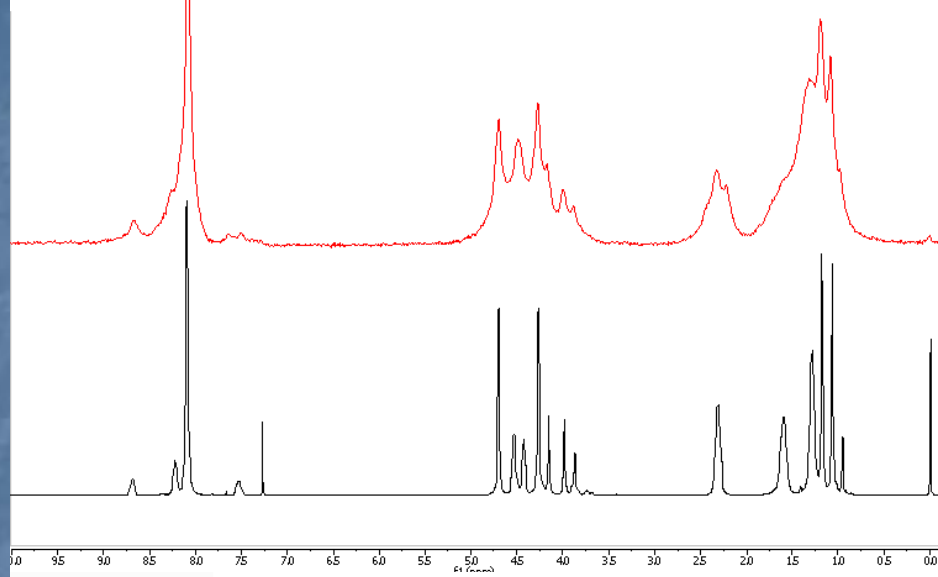


# Adhesive Prepolymers

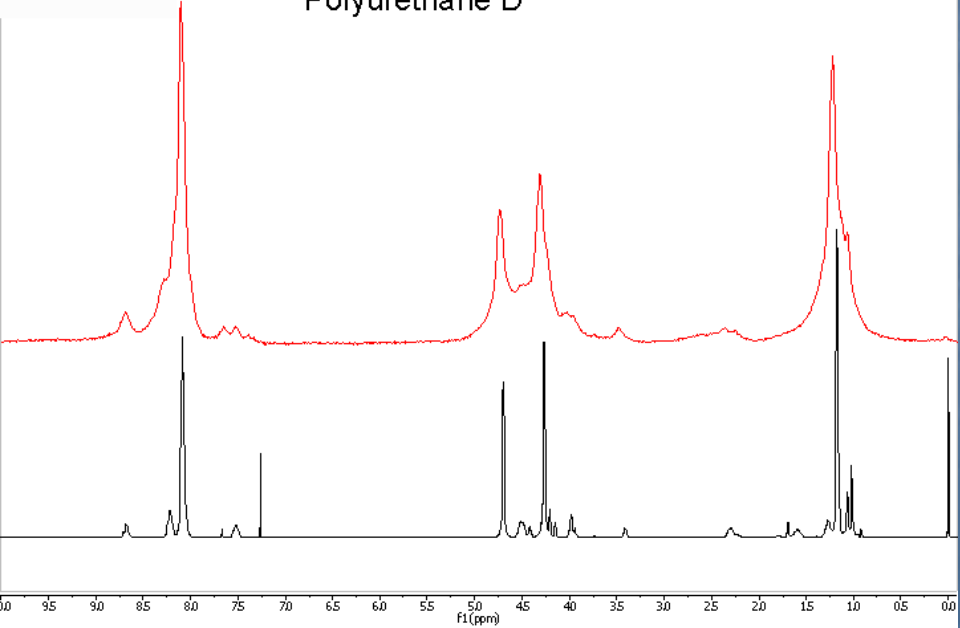
Polyurethane A



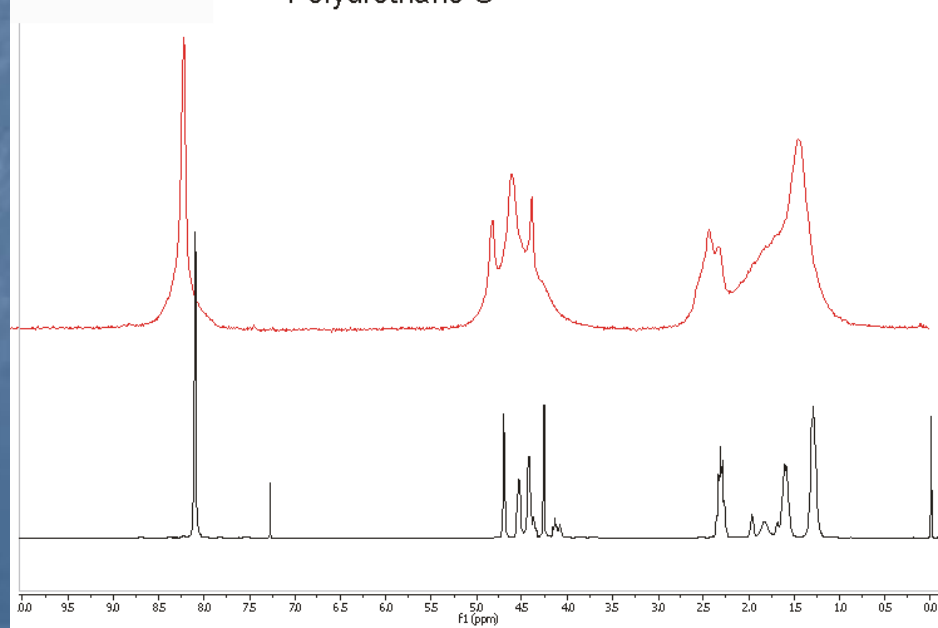
Polyurethane B



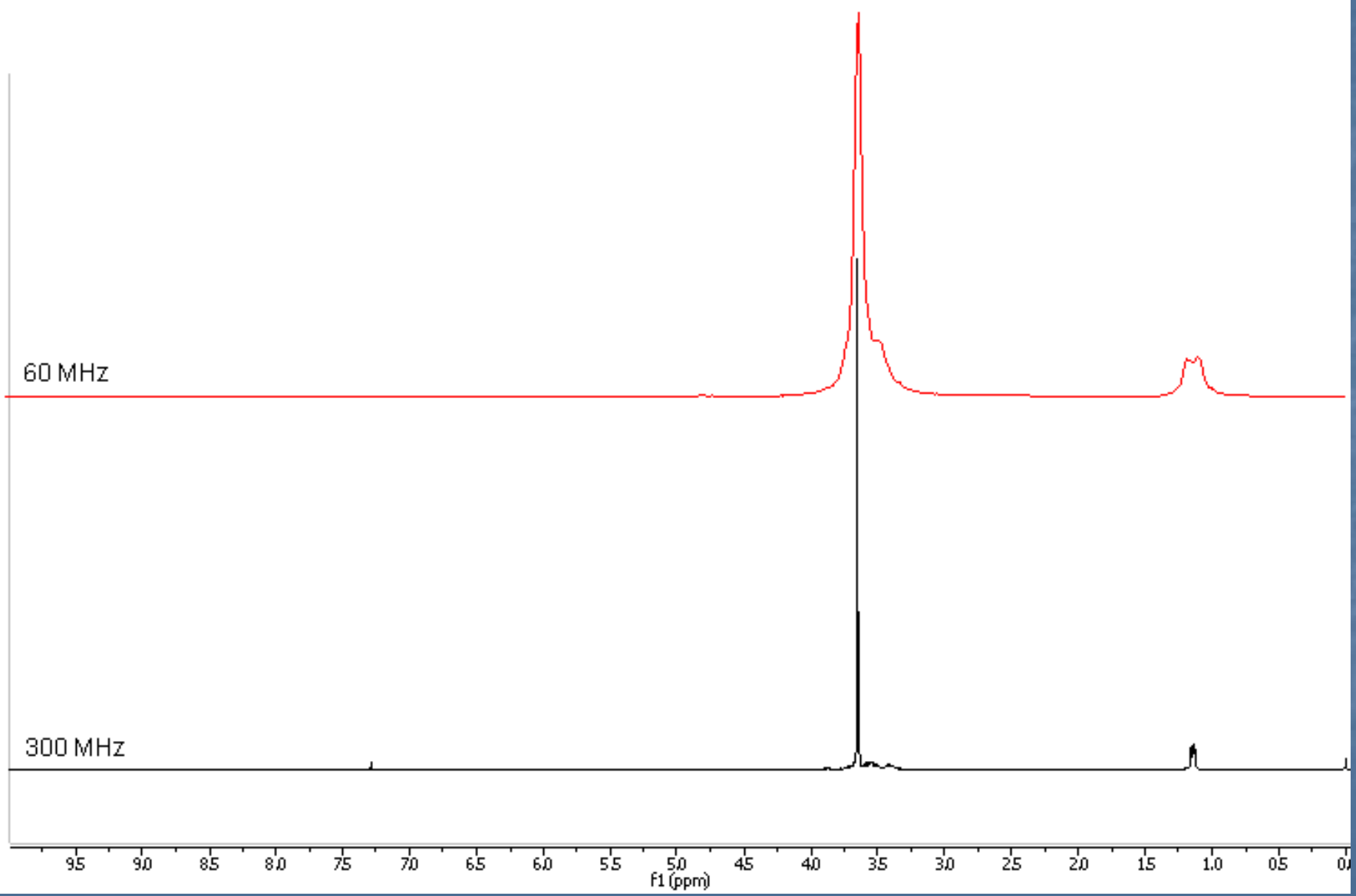
Polyurethane D



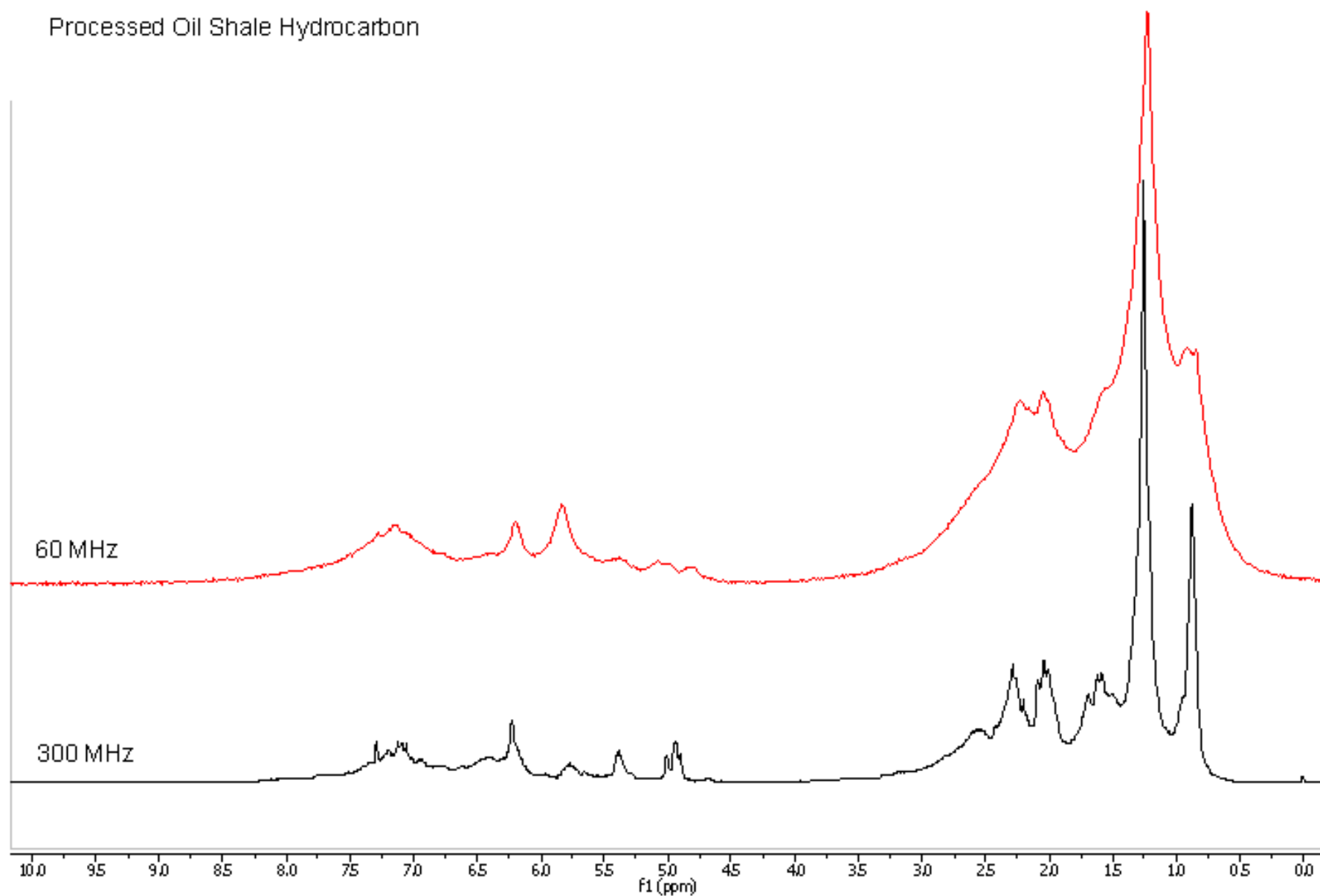
Polyurethane C

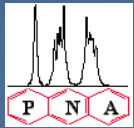


# Poloxamer - Oxyethylene and Oxypropylene Content - USP/NF Method

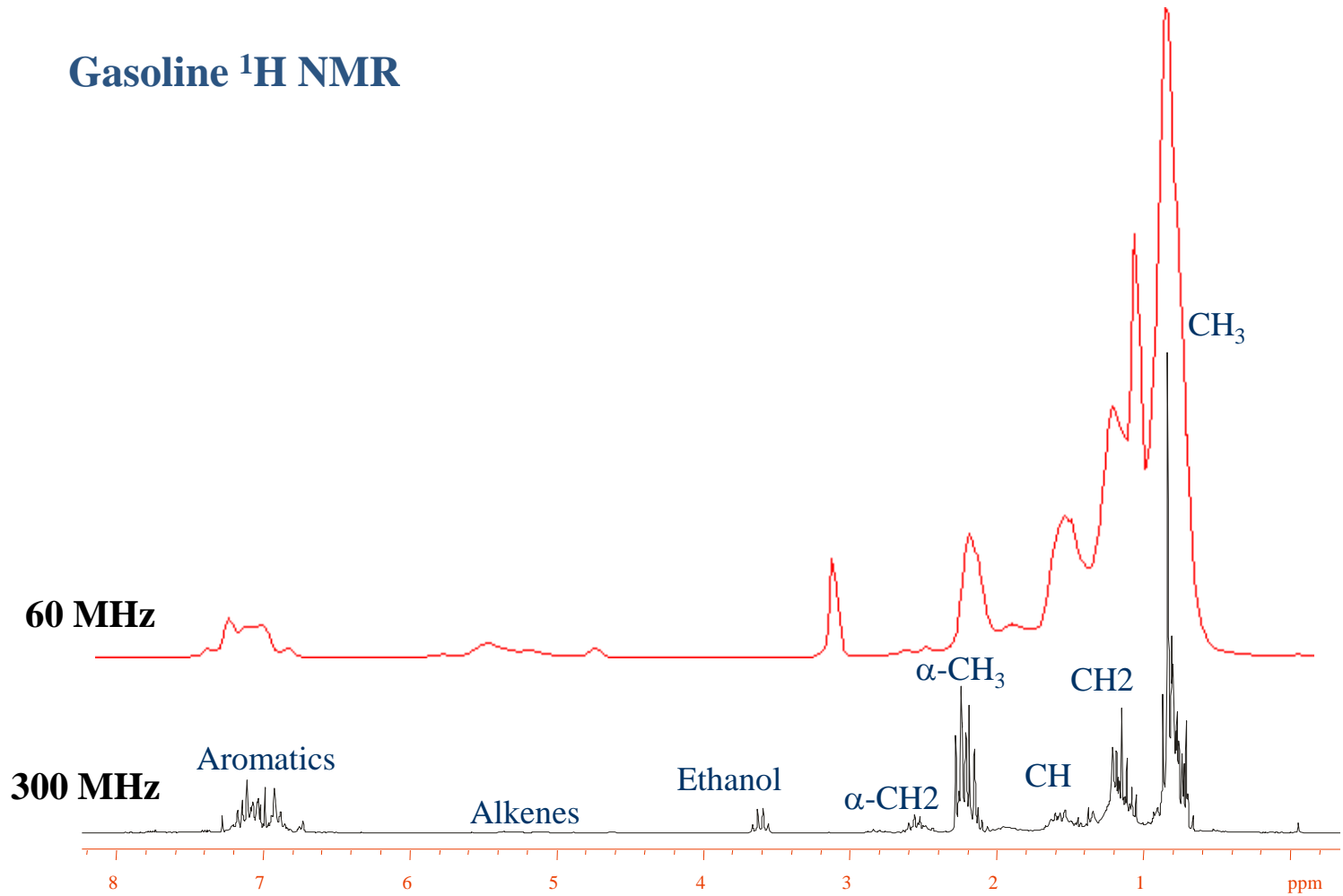


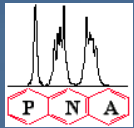
Processed Oil Shale Hydrocarbon



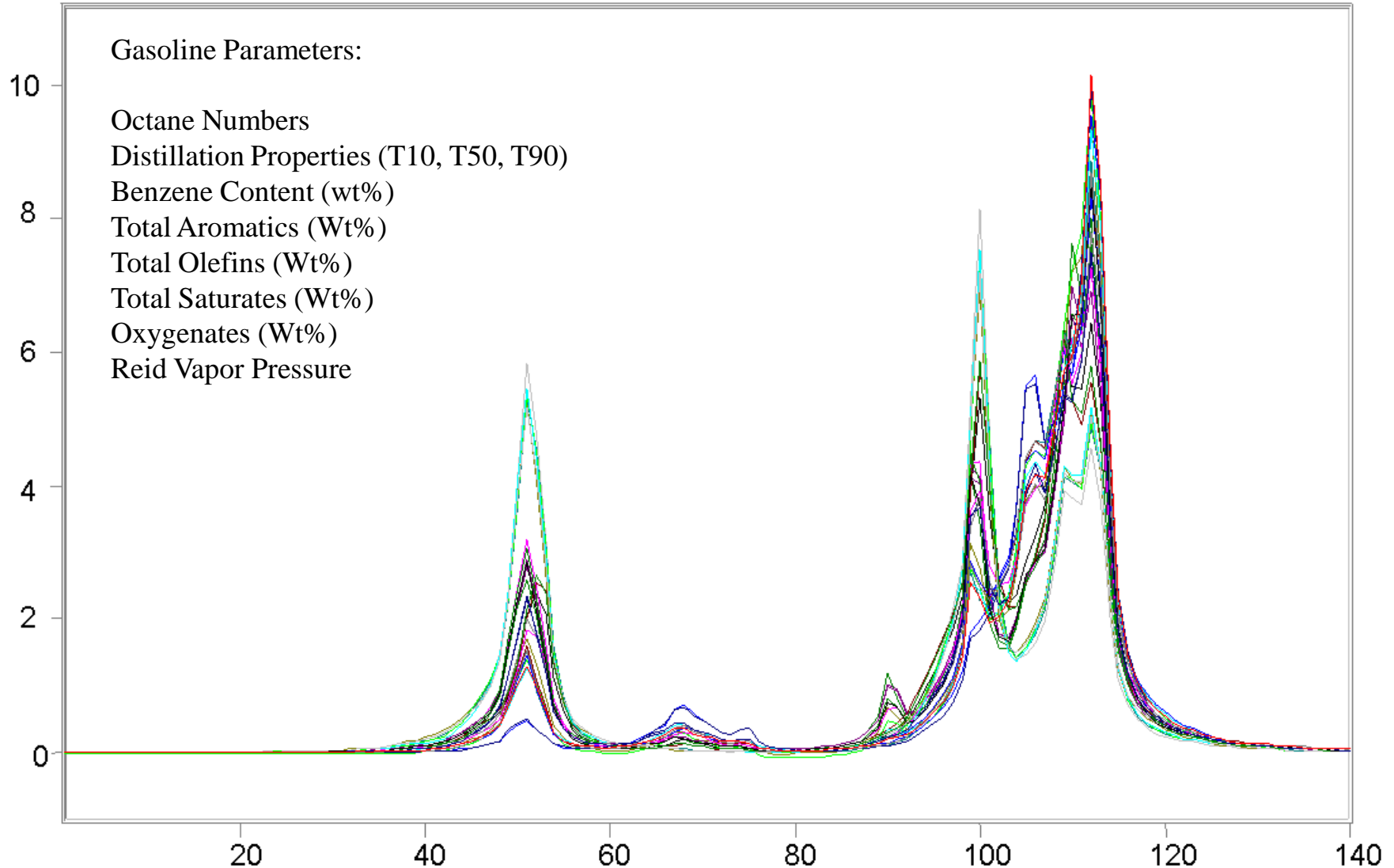


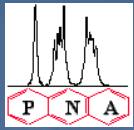
# Gasoline $^1\text{H}$ NMR





## Typical Variability Observed in Gasoline Blending





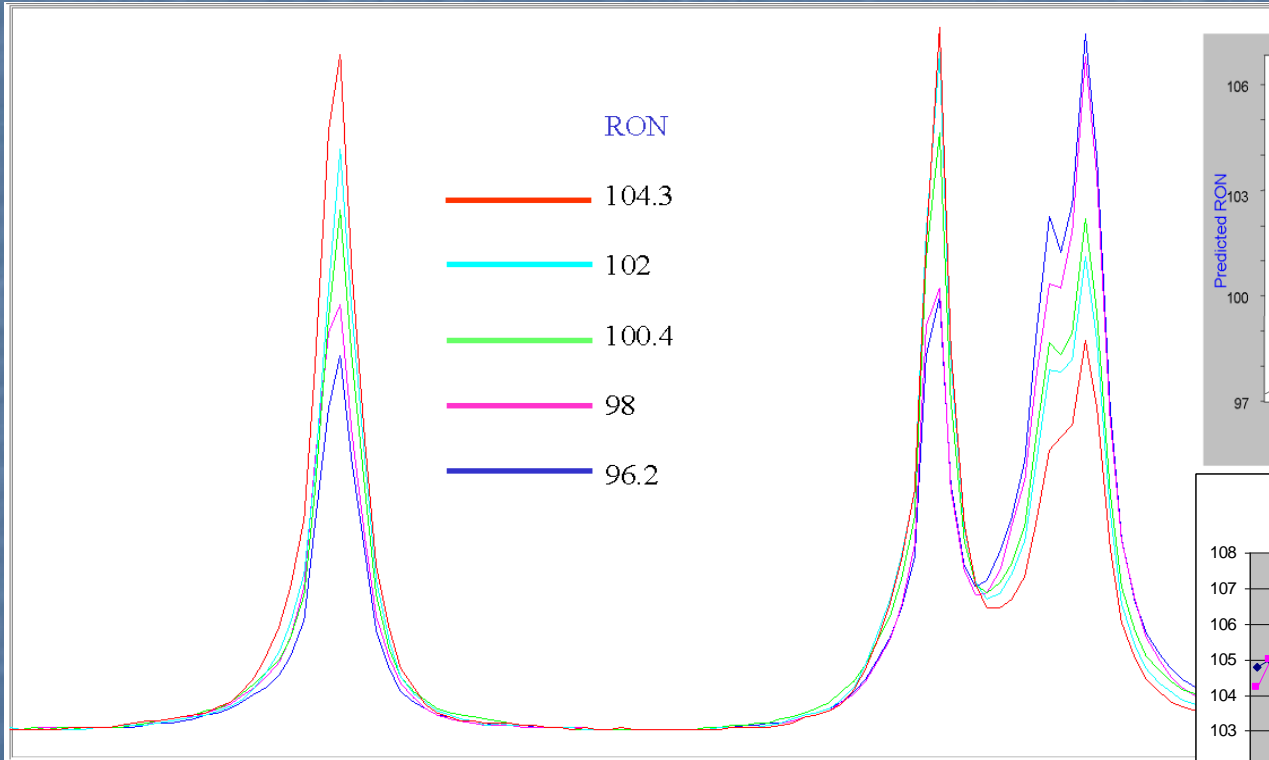
# Application: Closed Loop Reformer Control - Installed 1998

Reformer Capacity: 34,000 Barrels per Day

Control Strategy: Control on MON and Benzene Content

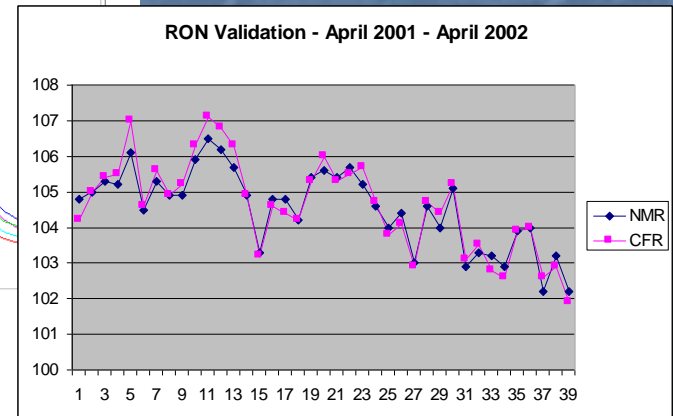
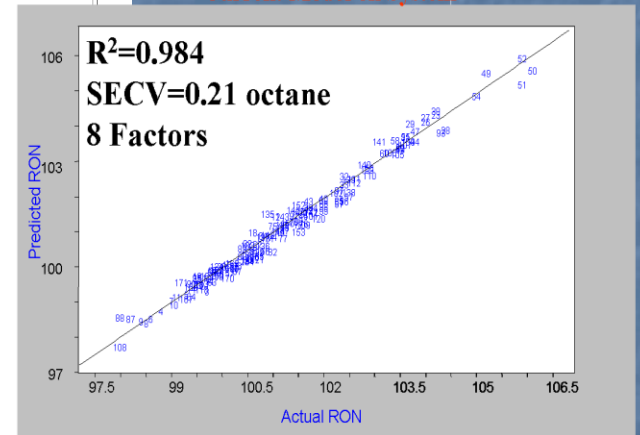
NMR Analysis: 2 Minute Analysis

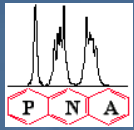
NMR PLS Outputs: RON, MON, Benzene (Wt%) Total Aromatics (Wt%)



Variation of Reformate Processed <sup>1</sup>H NMR Data Observed with Changing Research Octane Number

Current Model on System





## Application: Steam Cracking Optimization Installed 2000

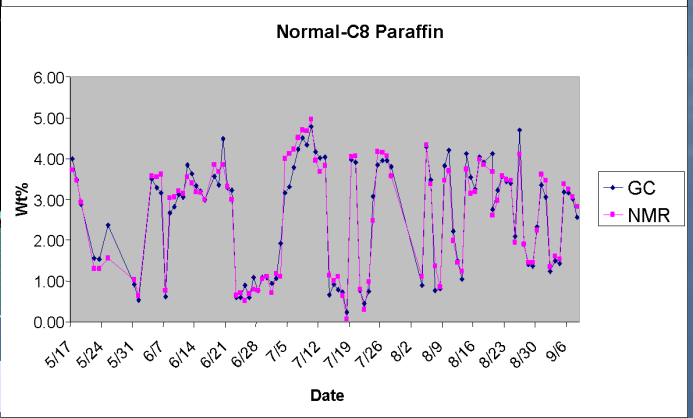
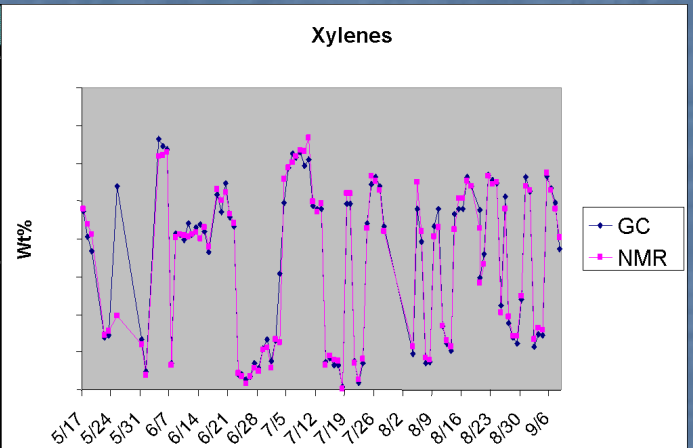
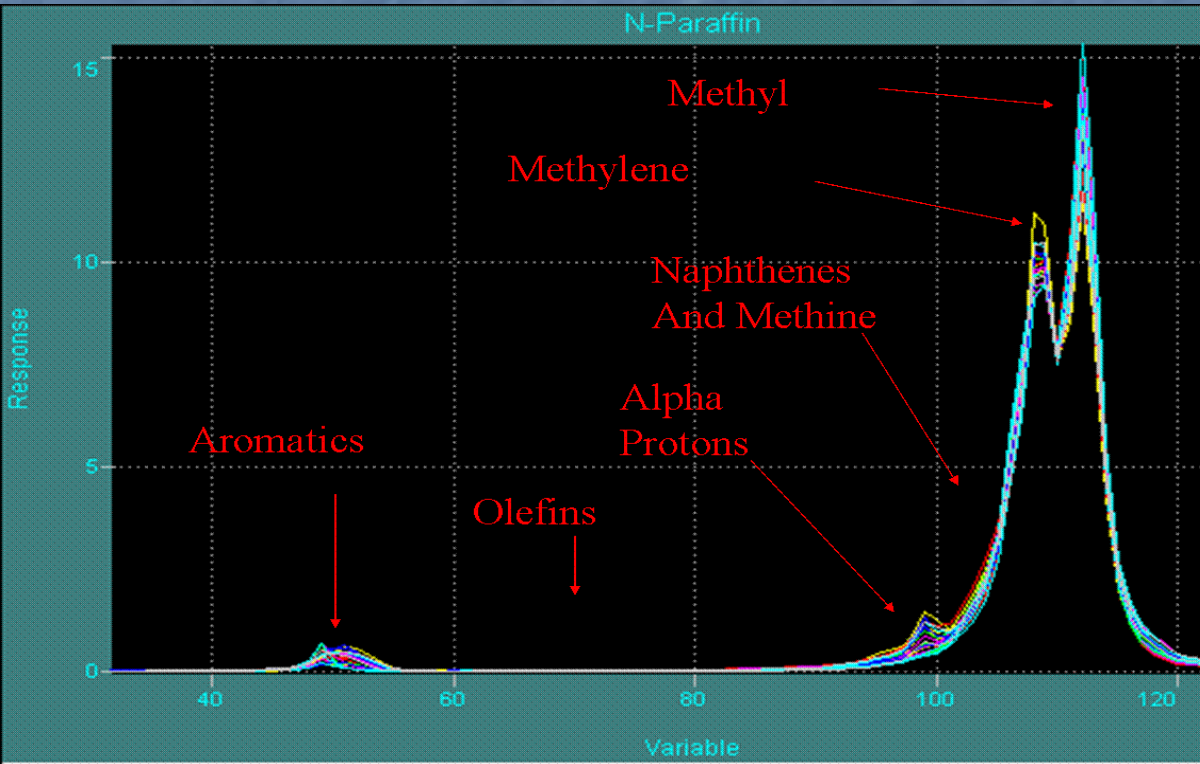
Cracker Facility Capacity: 600,000 Tonnes per Year

Control Strategy: Feed Forward Detailed Hydrocarbon Analysis to SPYRO Optimization

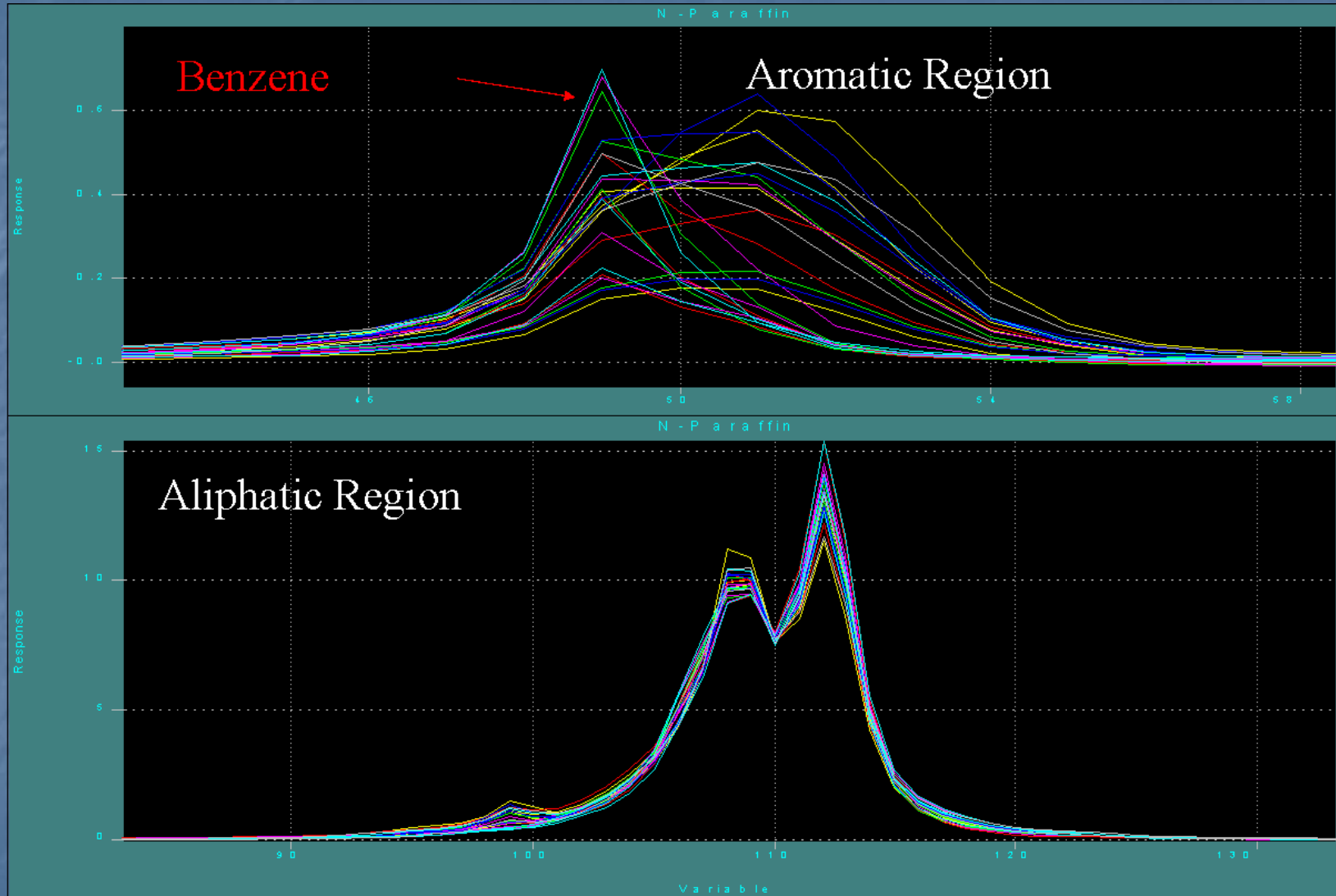
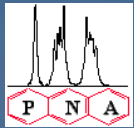
NMR Analysis: 3-4 Minute Cycle (Single Stream)

NMR PLS Outputs: Naptha – Detailed PIONA

C4-C10 normal-paraffin, iso-paraffin, aromatics, naphthenes



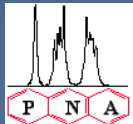
Spectral Variability Observed in Naptha Samples



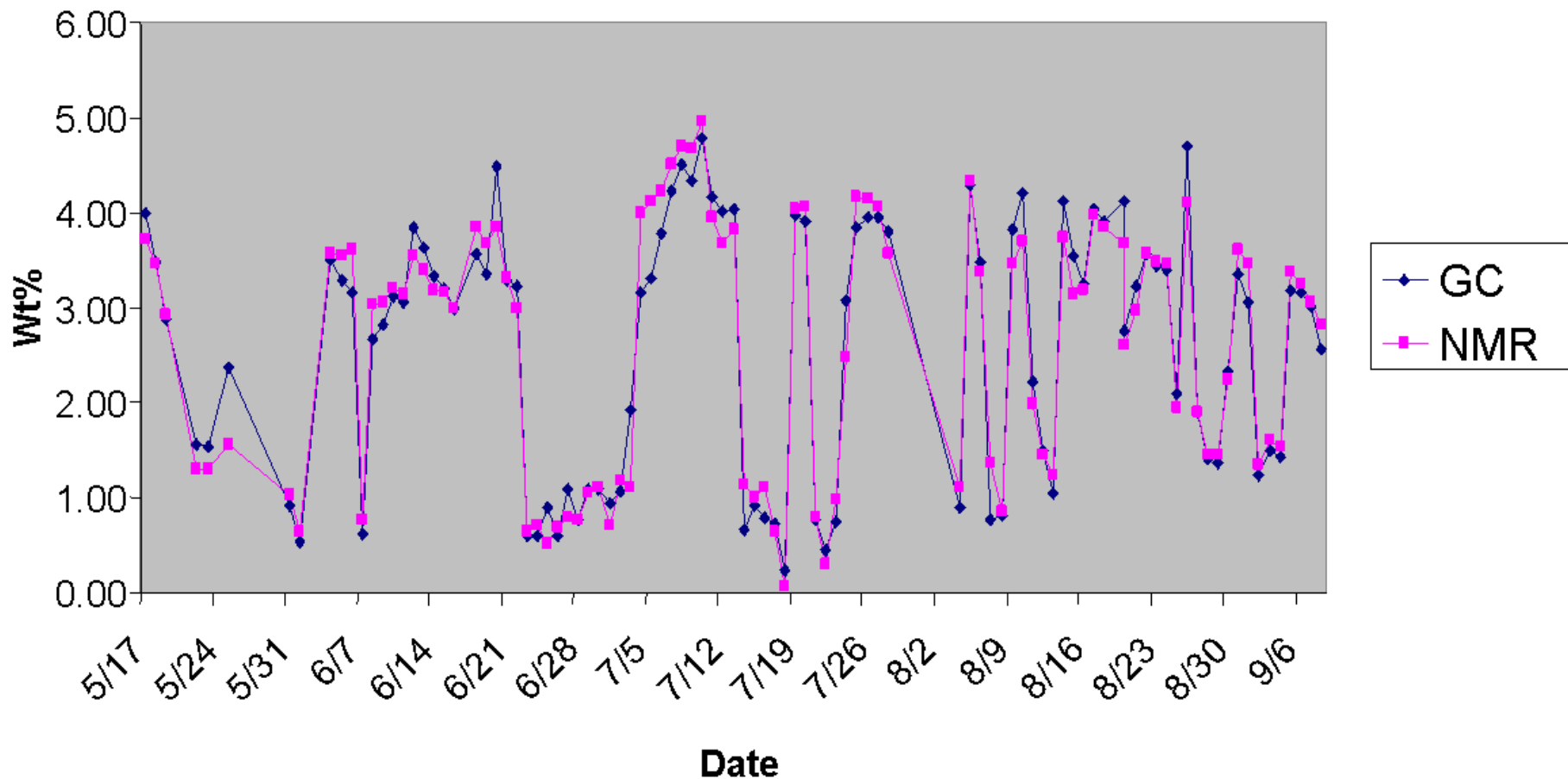
Spectral Variability in Aromatic and Aliphatic Regions

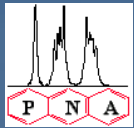




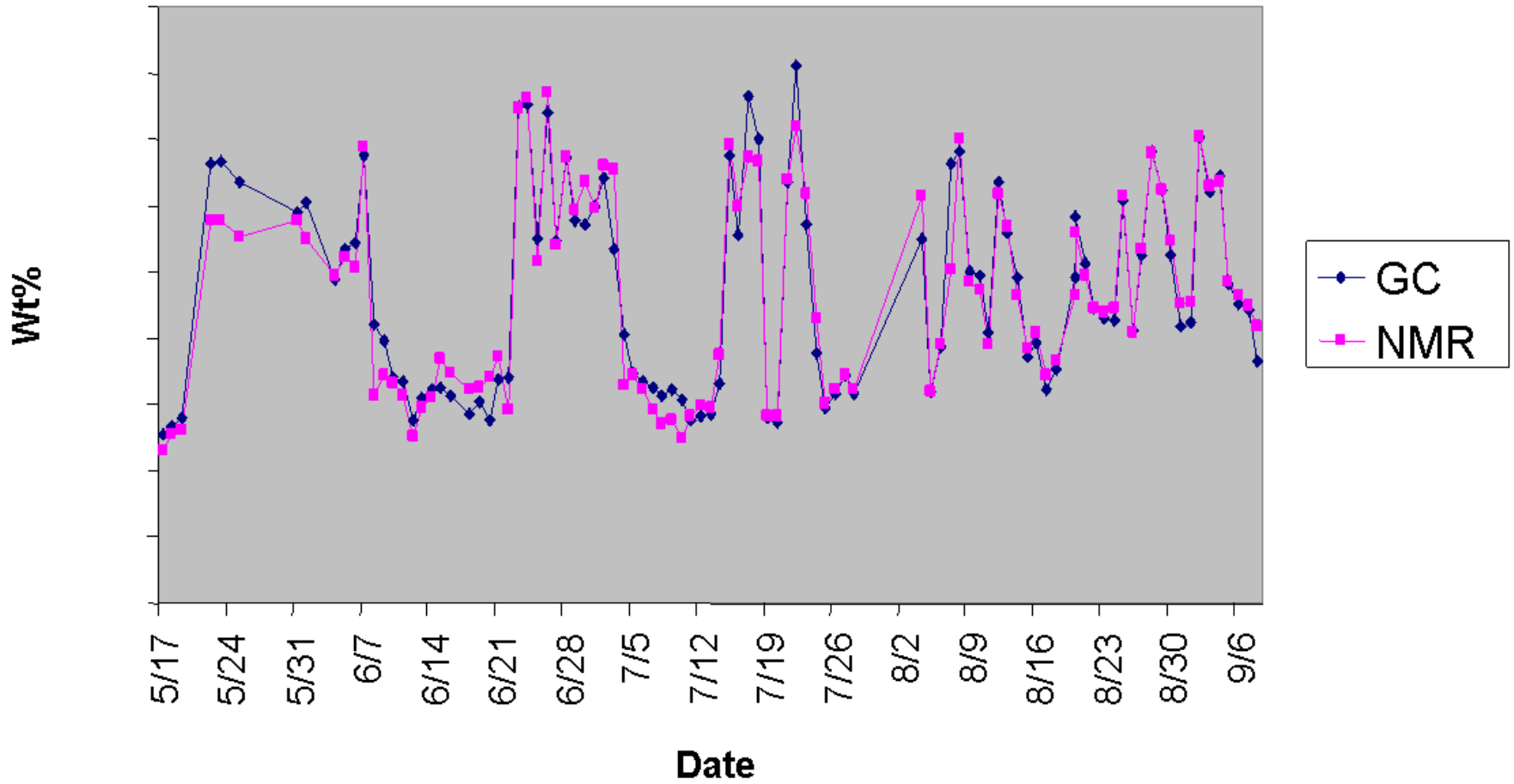


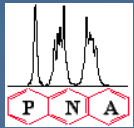
### Normal-C8 Paraffin



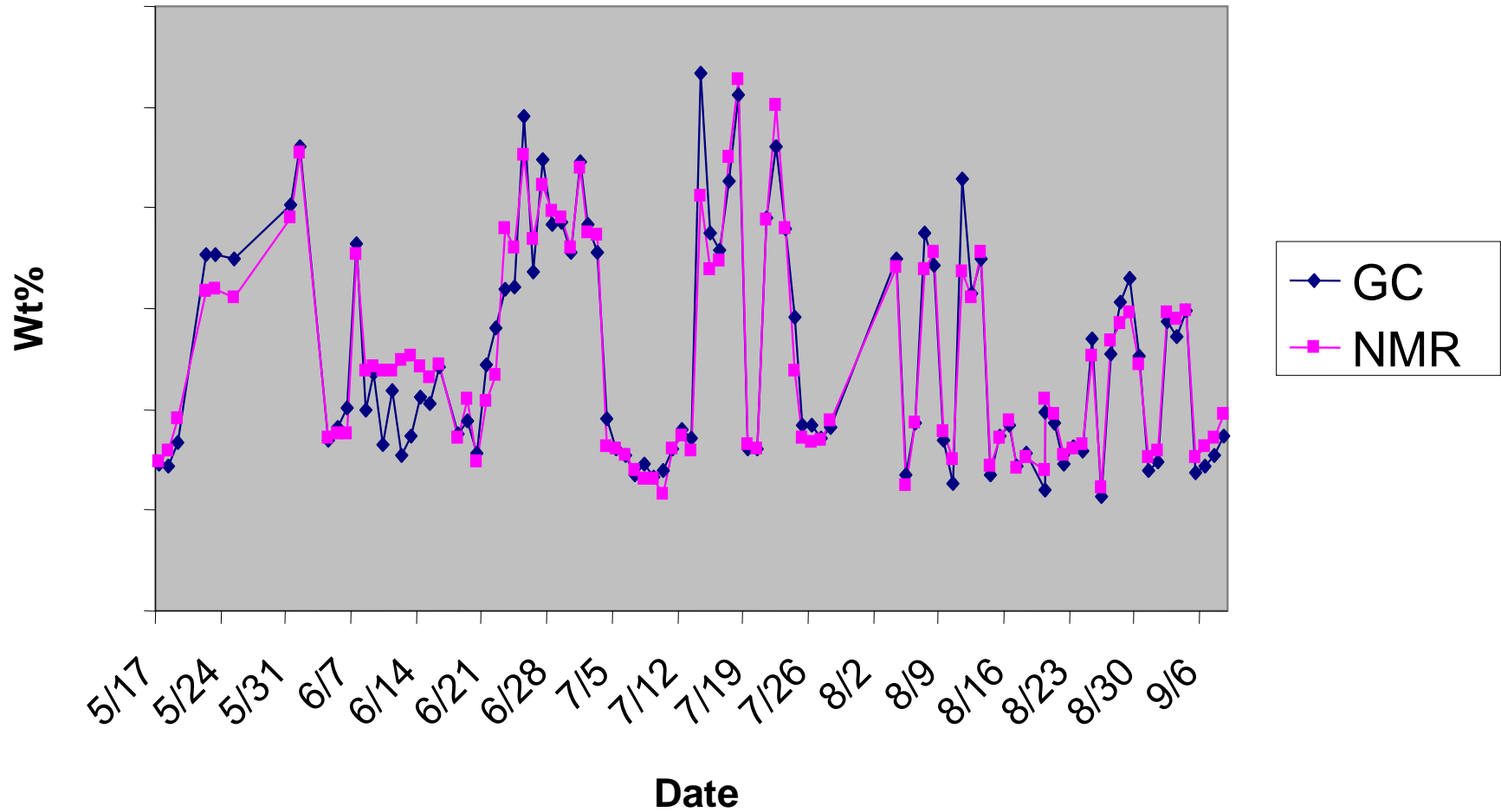


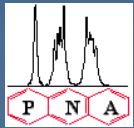
### Iso-C5 Paraffin



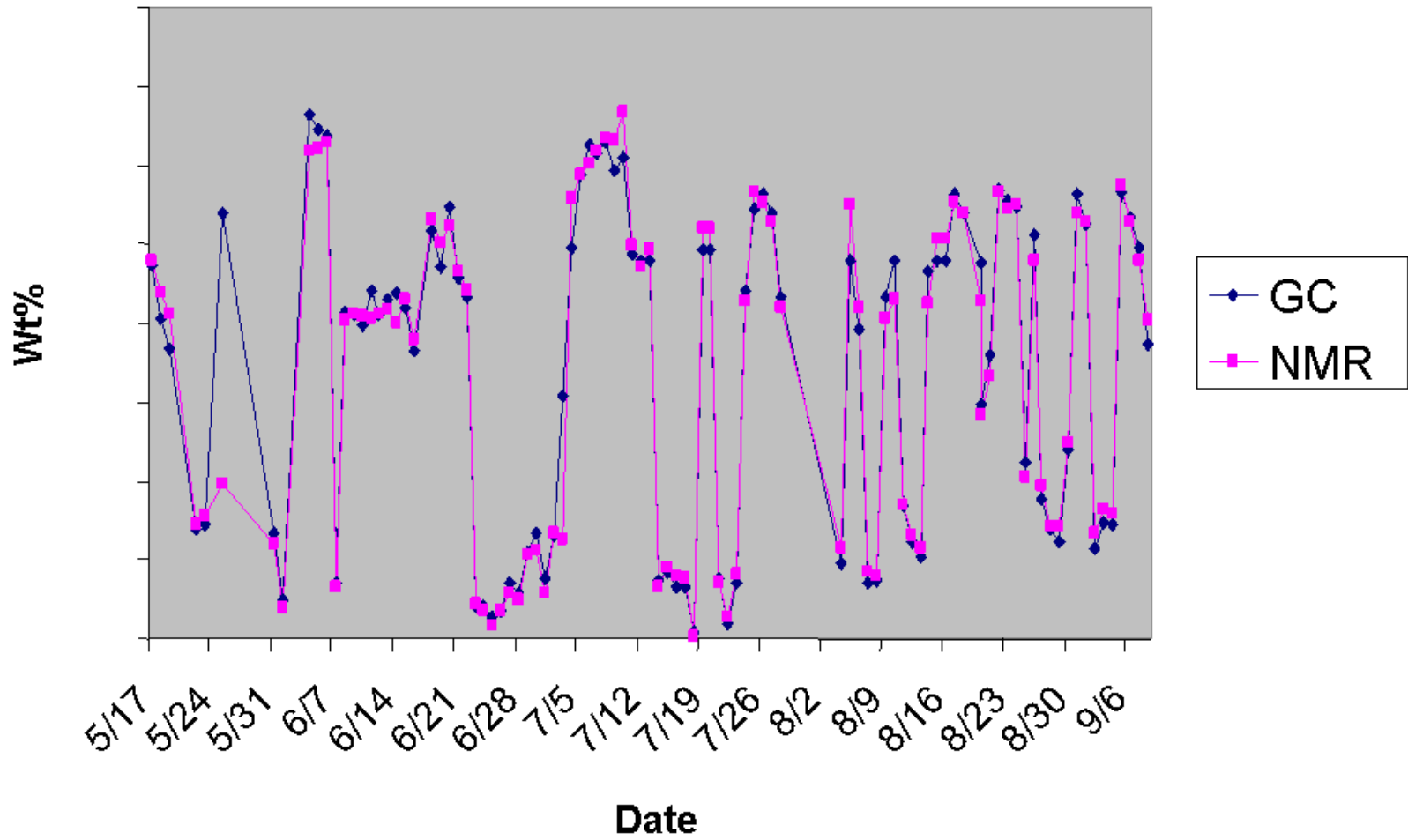


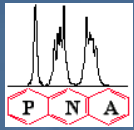
# Cyclopentane



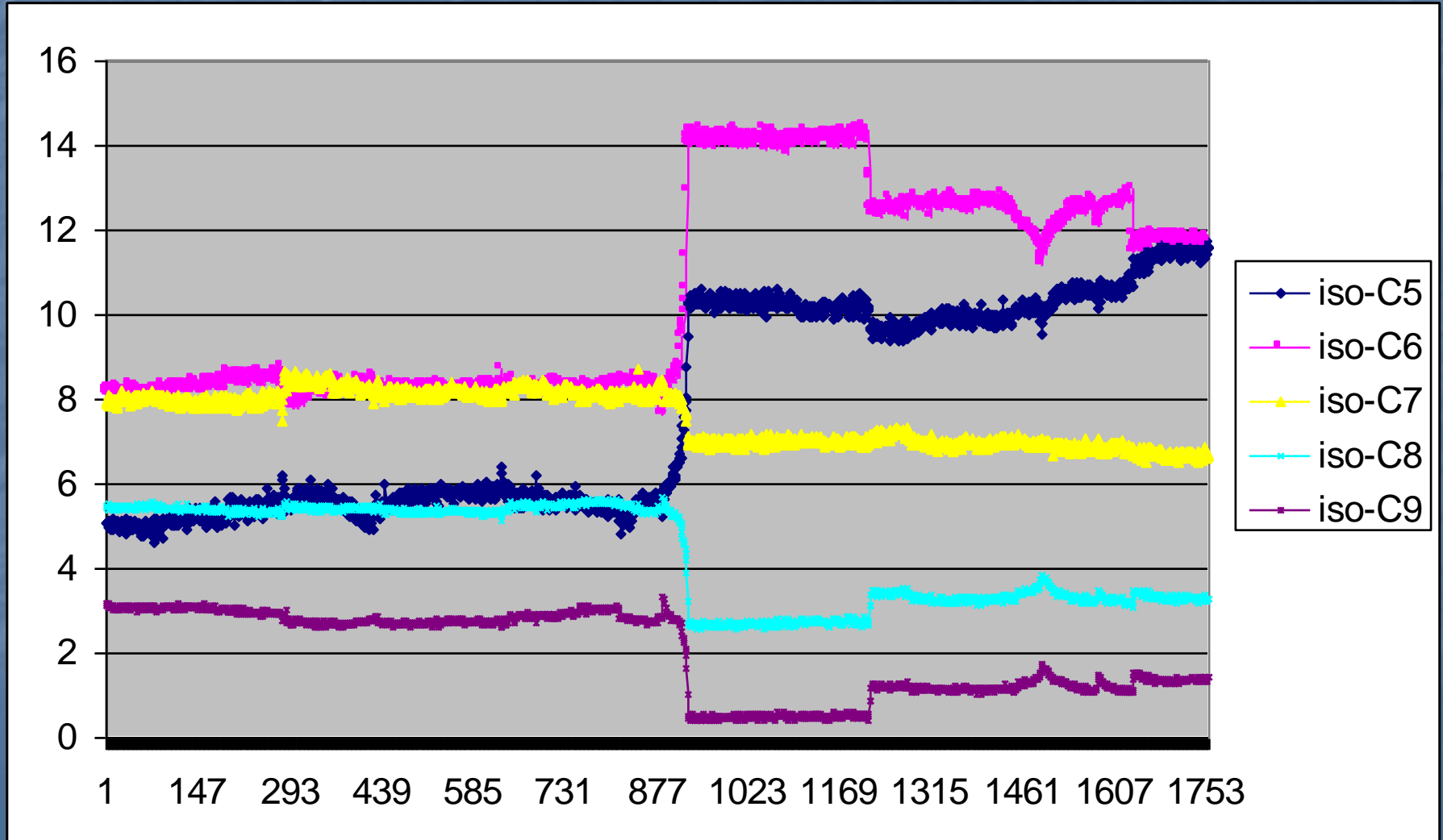


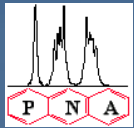
### Xylenes



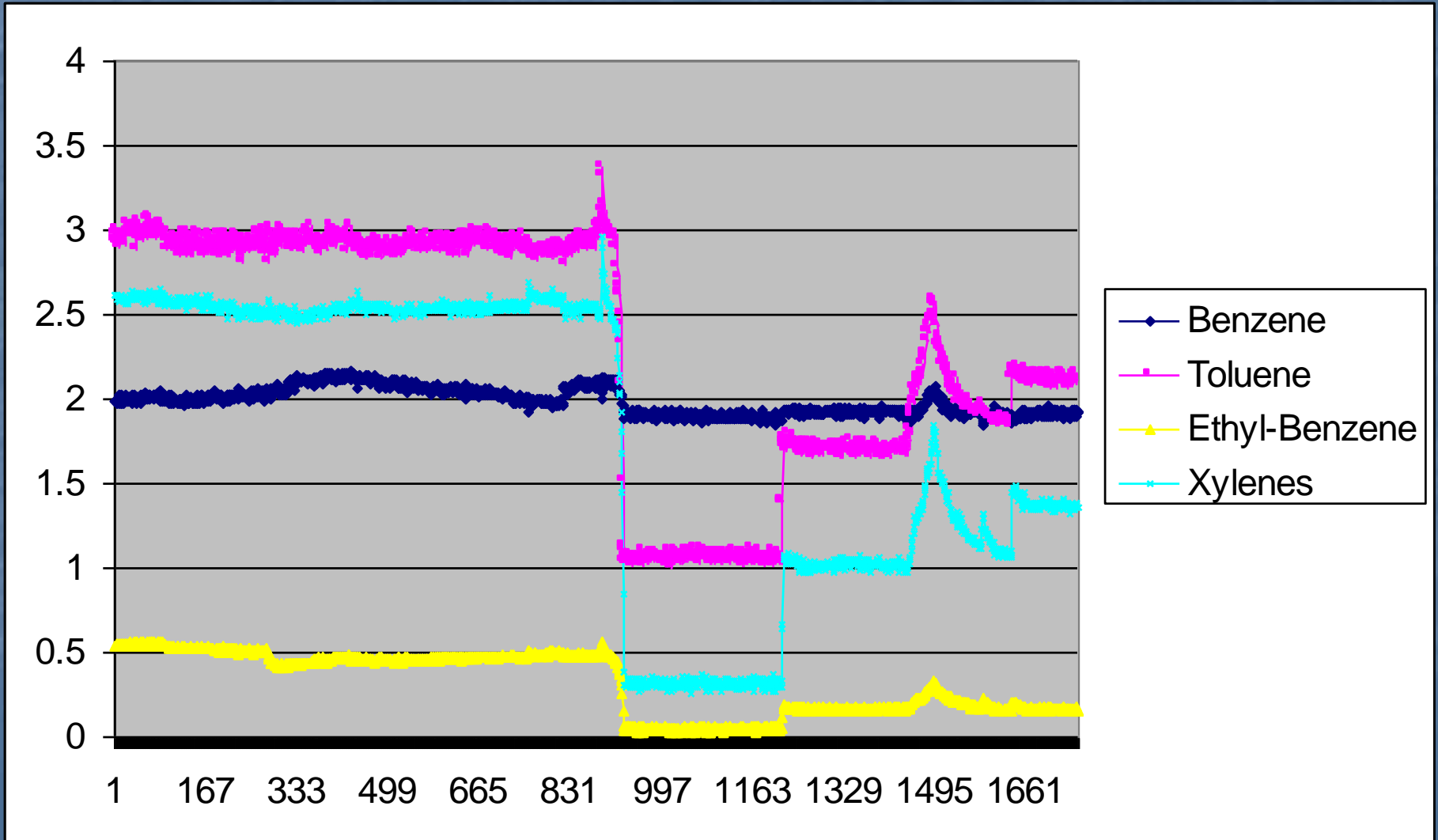


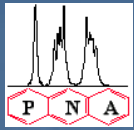
# 96 Hours of NMR Process Output – iso-Paraffin Components





# 96 Hours of NMR Process Output – Aromatic Components

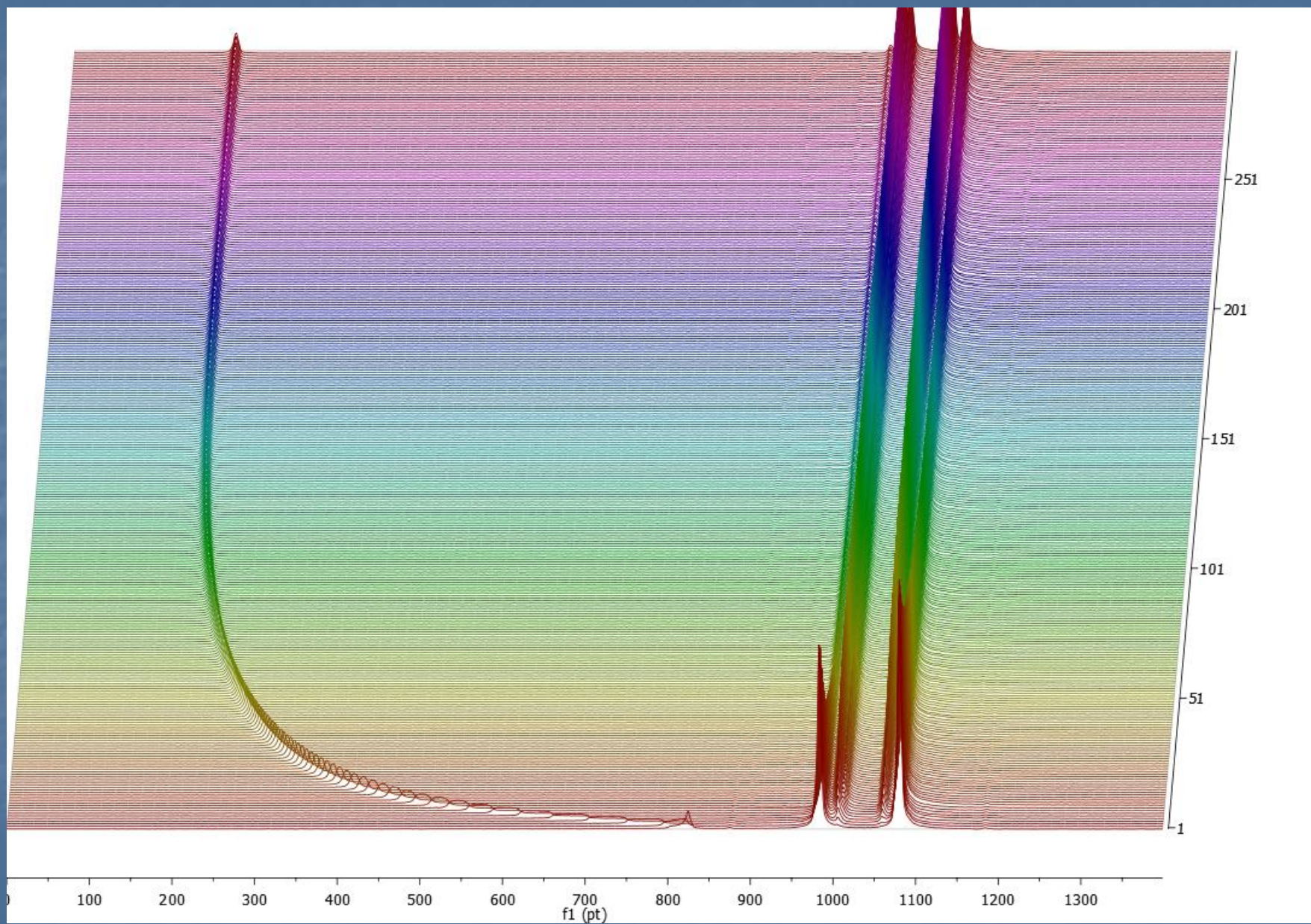


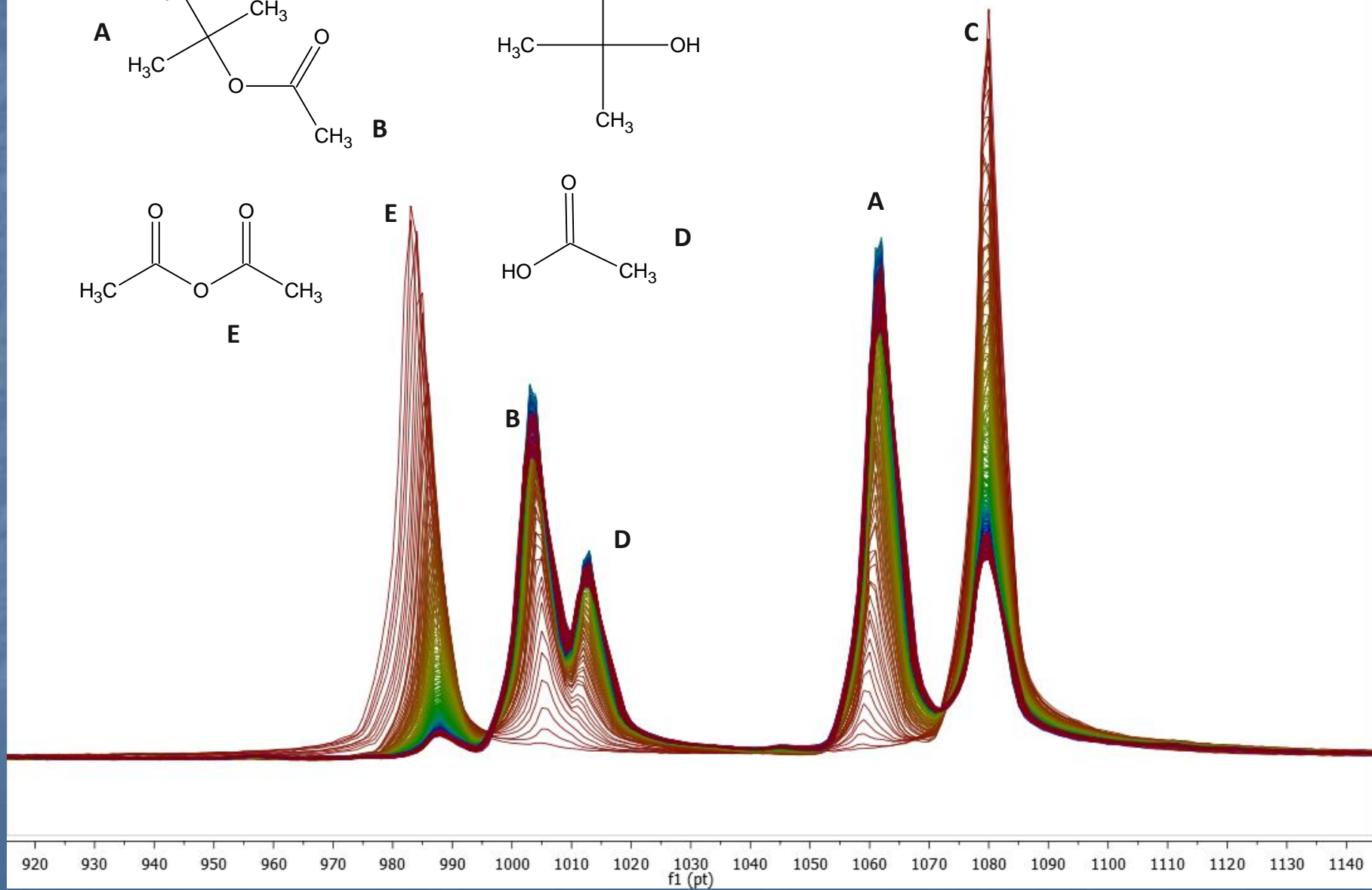
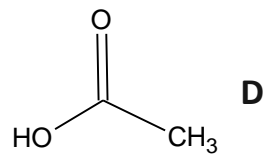
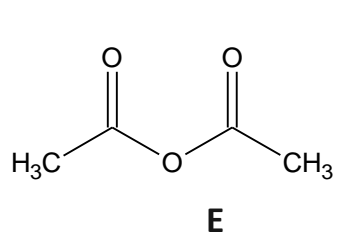
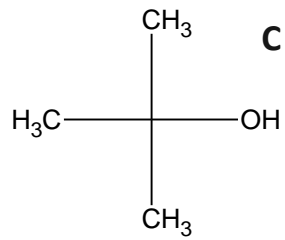
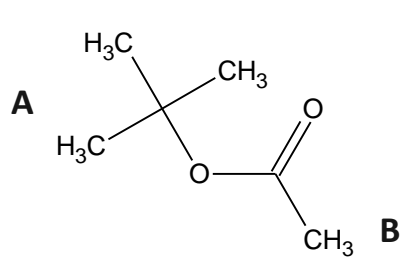


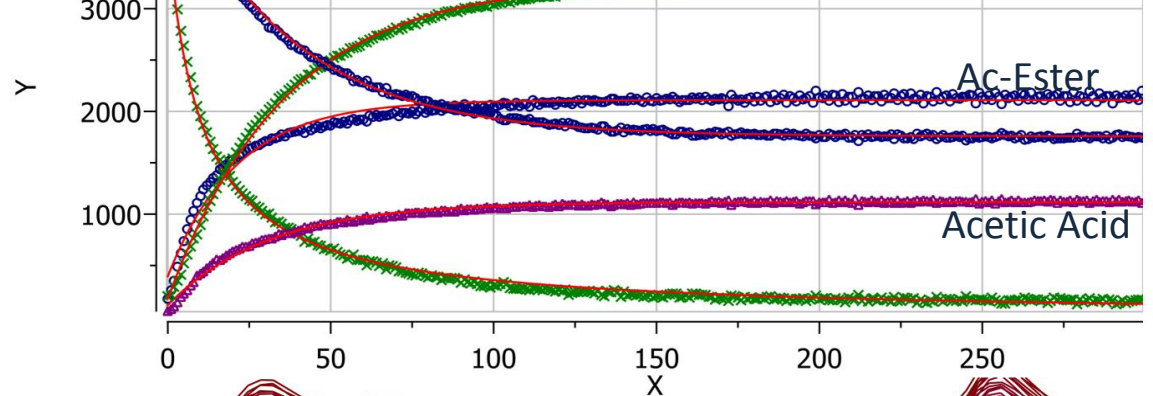
## Online NMR Applications

- 1995 - BTU Analysis of Refinery Fuel Gas - Texaco
- 1995 - Sulfuric Acid Strength in Emulsion Zone of Stratco Acid Alkylation Unit - Texaco
- 1999 - Diesel Blending System - Motiva
- 1999 - Reformer Control System – BP, Pertamina
- 2000 - Naphtha Cracker Feed Analyzer – Full GC PIONA – BASF, Lyondell
- 2000 - Crude Unit Analyzer – PDVSA, BRC, ConocoPhillips
- 2000 - Crude Blending System - Reliance
- 2001 - Gasoline Blending System – Fina, Valero
- 2001 - Base Oil Manufacturing Analyzer - AGIP
- 2002 - FCC Unit Analyzer – BP
- 2002 - At-Line Bitumen and Vacuum Residue Analyzer – ERG

# $^1\text{H}$ NMR Reaction Monitoring – Esterification of t-butanol with acetic anhydride



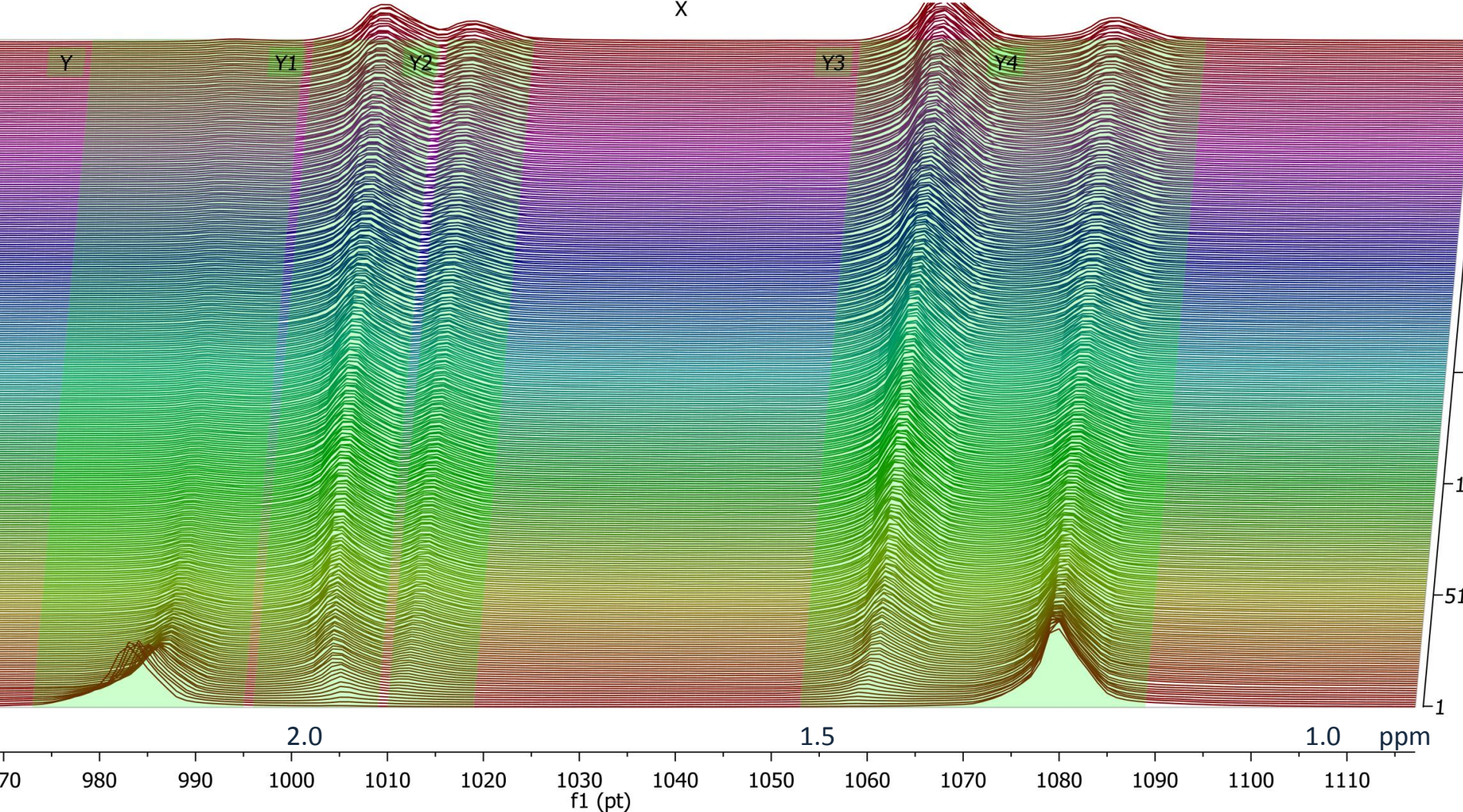




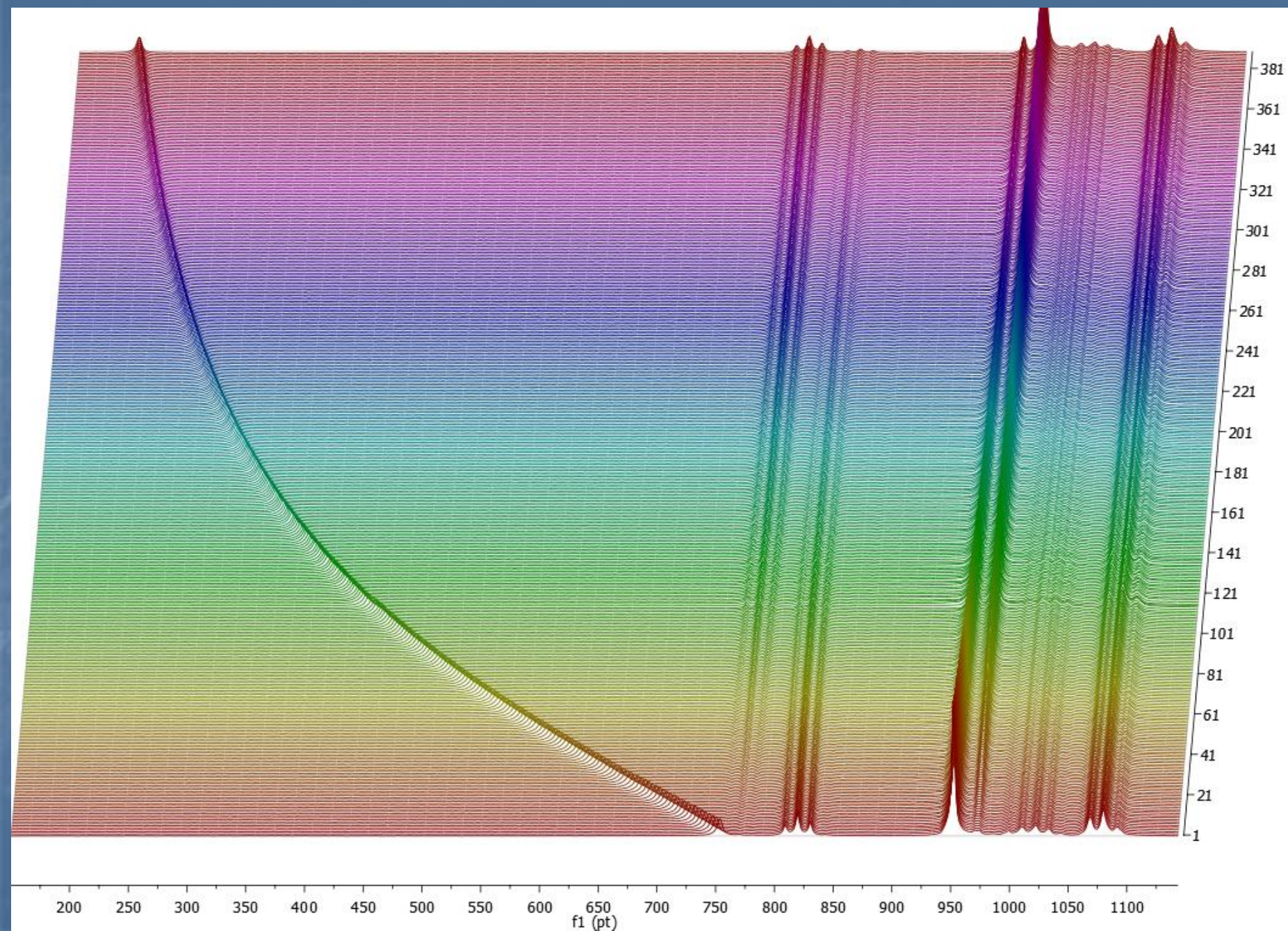
Esterification of t-BuOH

Integral Graph  
And Integration Plot

AcAn

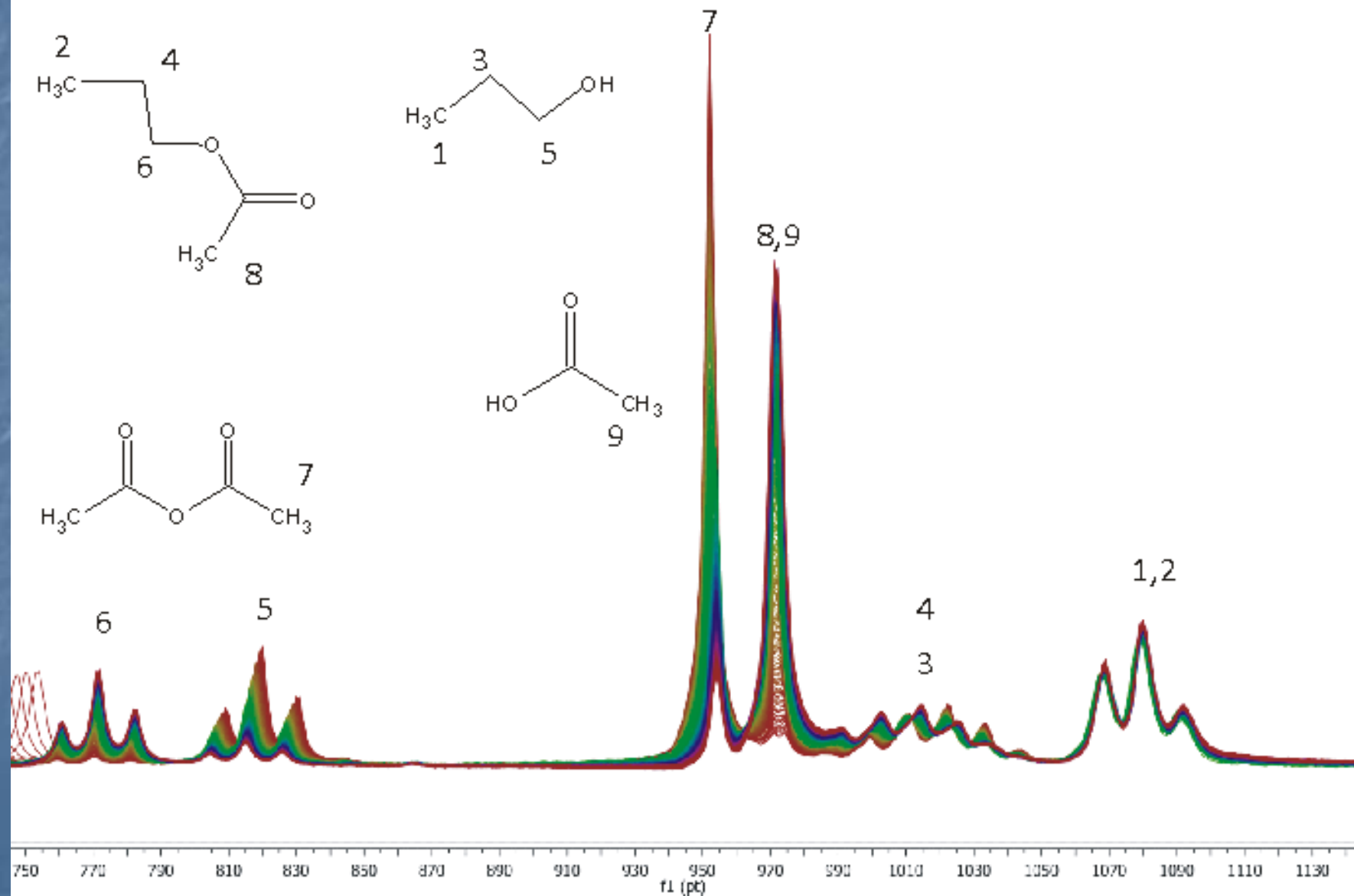


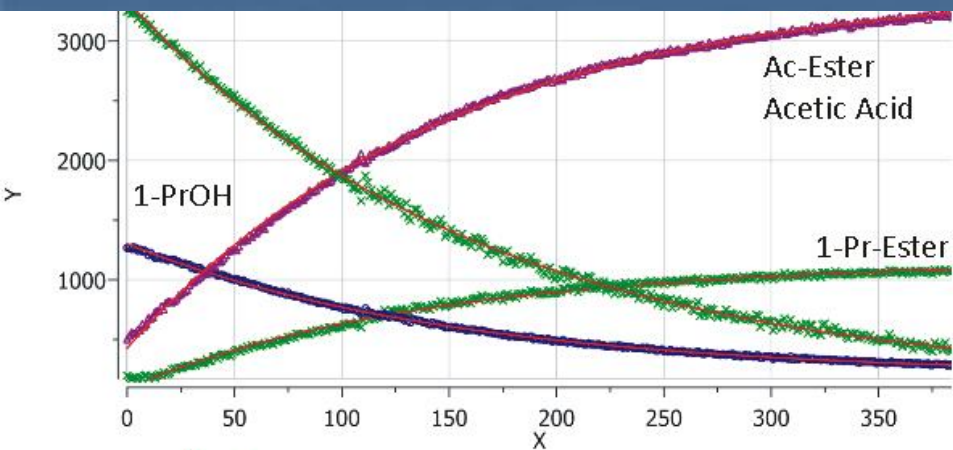
# $^1\text{H}$ NMR Zreaction Monitoring –propanol esterified with acetic anhydride



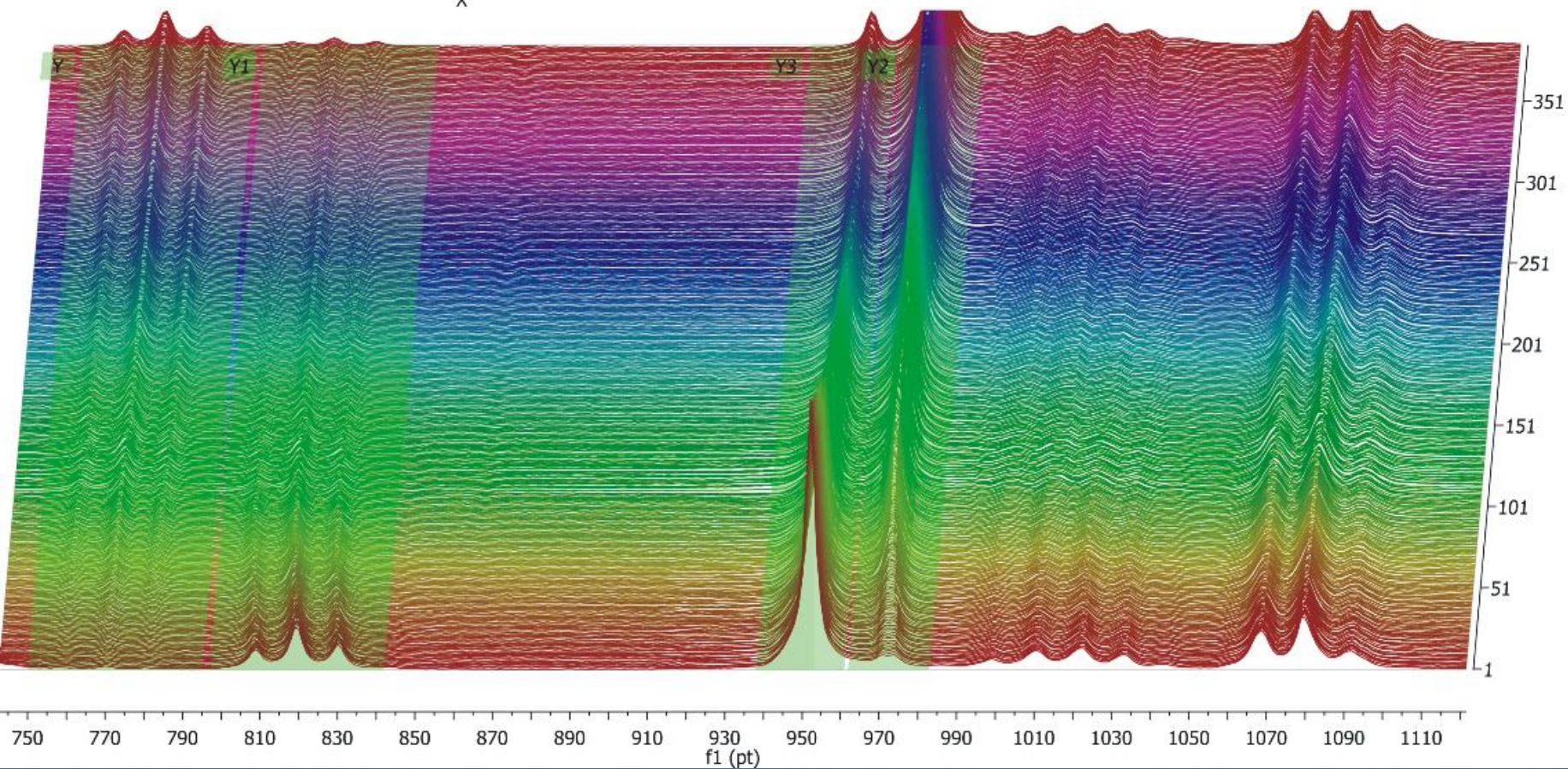
# 1-Propanol Esterification with Acetic Anhydride

Pure Solution – No Solvent – No Acid Catalyst  
8 Hour Reaction Profile

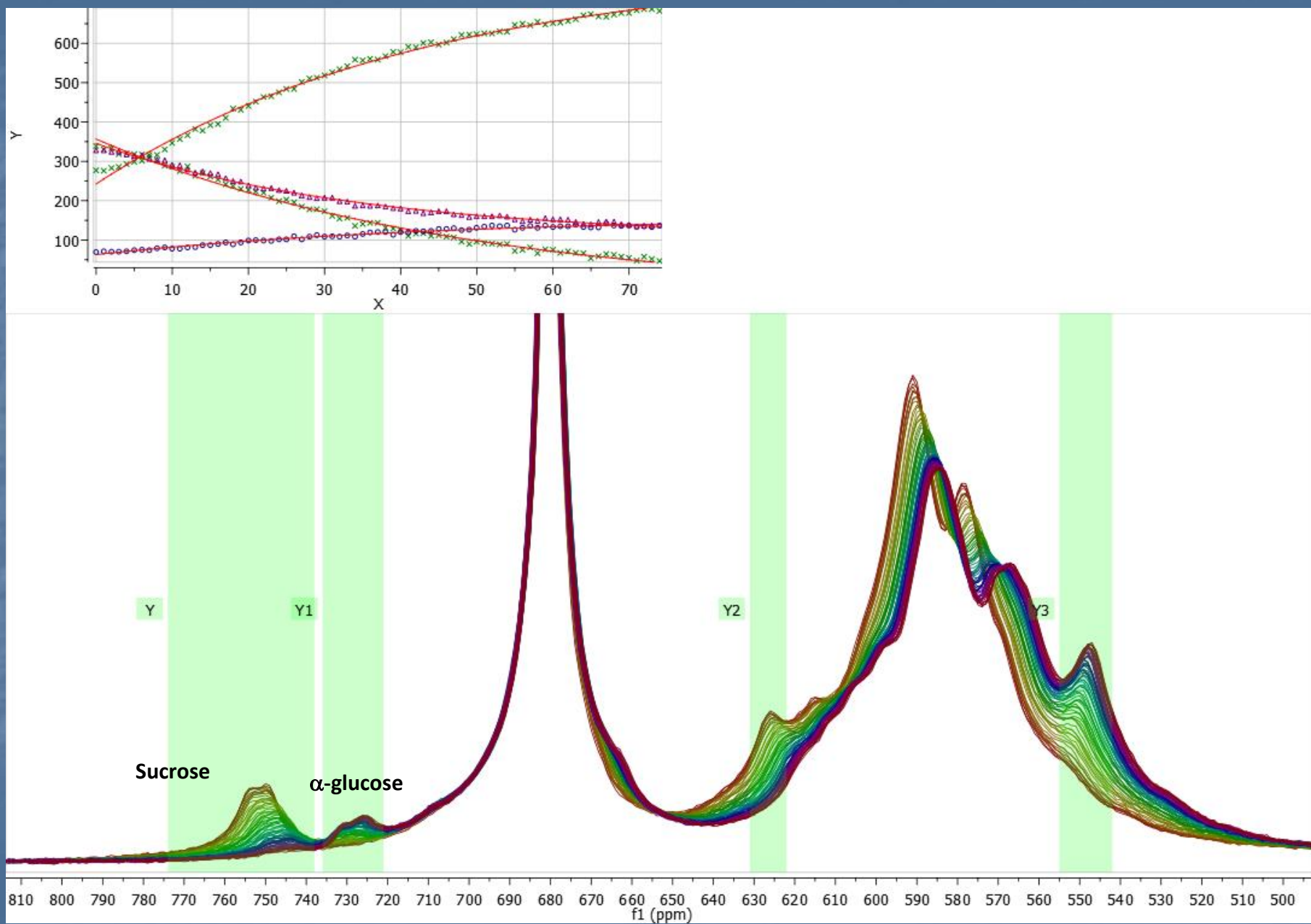




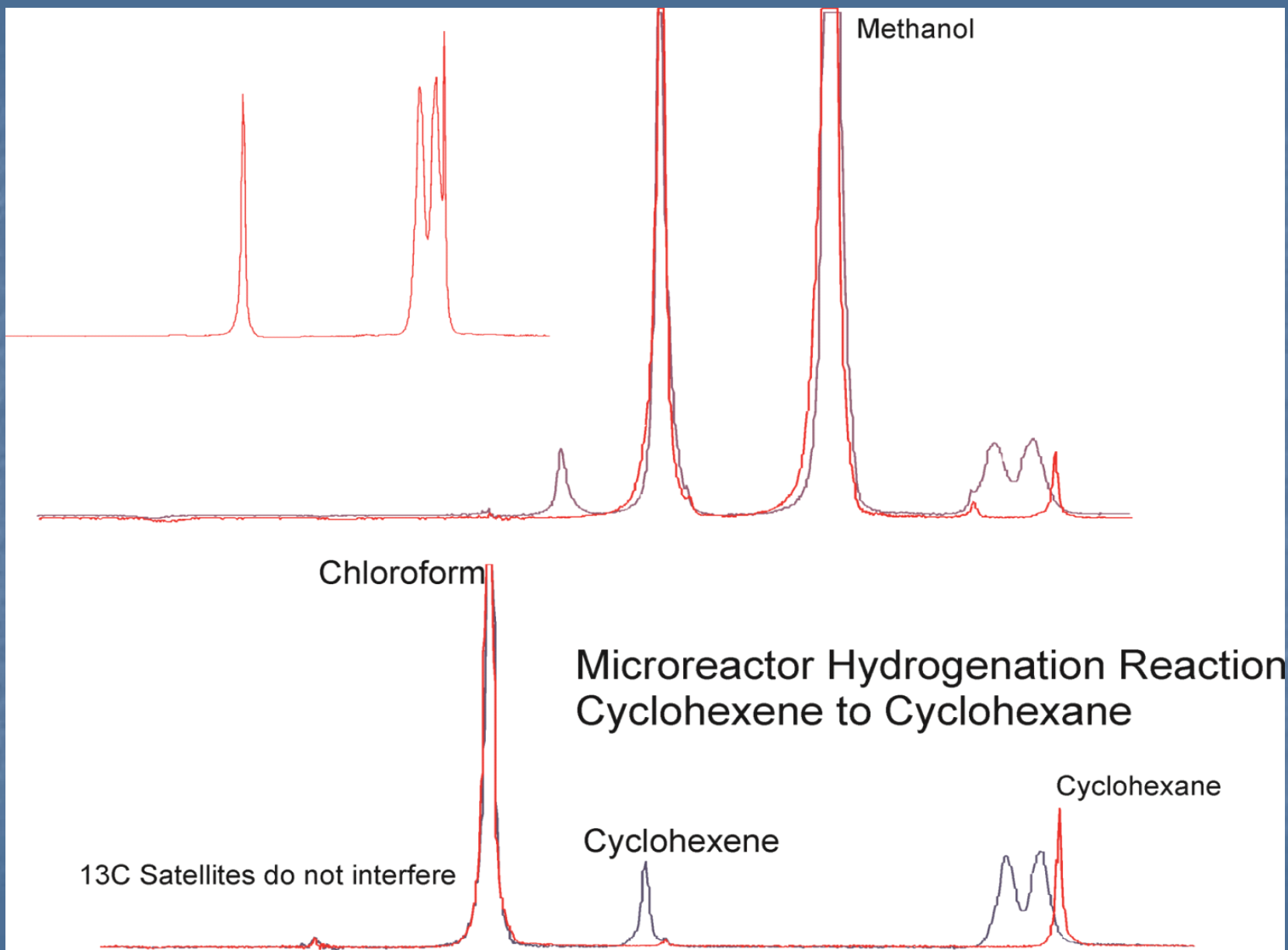
Esterification of 1-Propanol by Acetic Anhydride  
Integral Plots for Reaction Profile

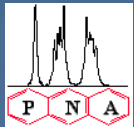


# 1H NMR – Sucrose Hydrolysis



Microreactor Process Monitoring – 1H NMR – Reaction: Cyclohexene --> Cyclohexane

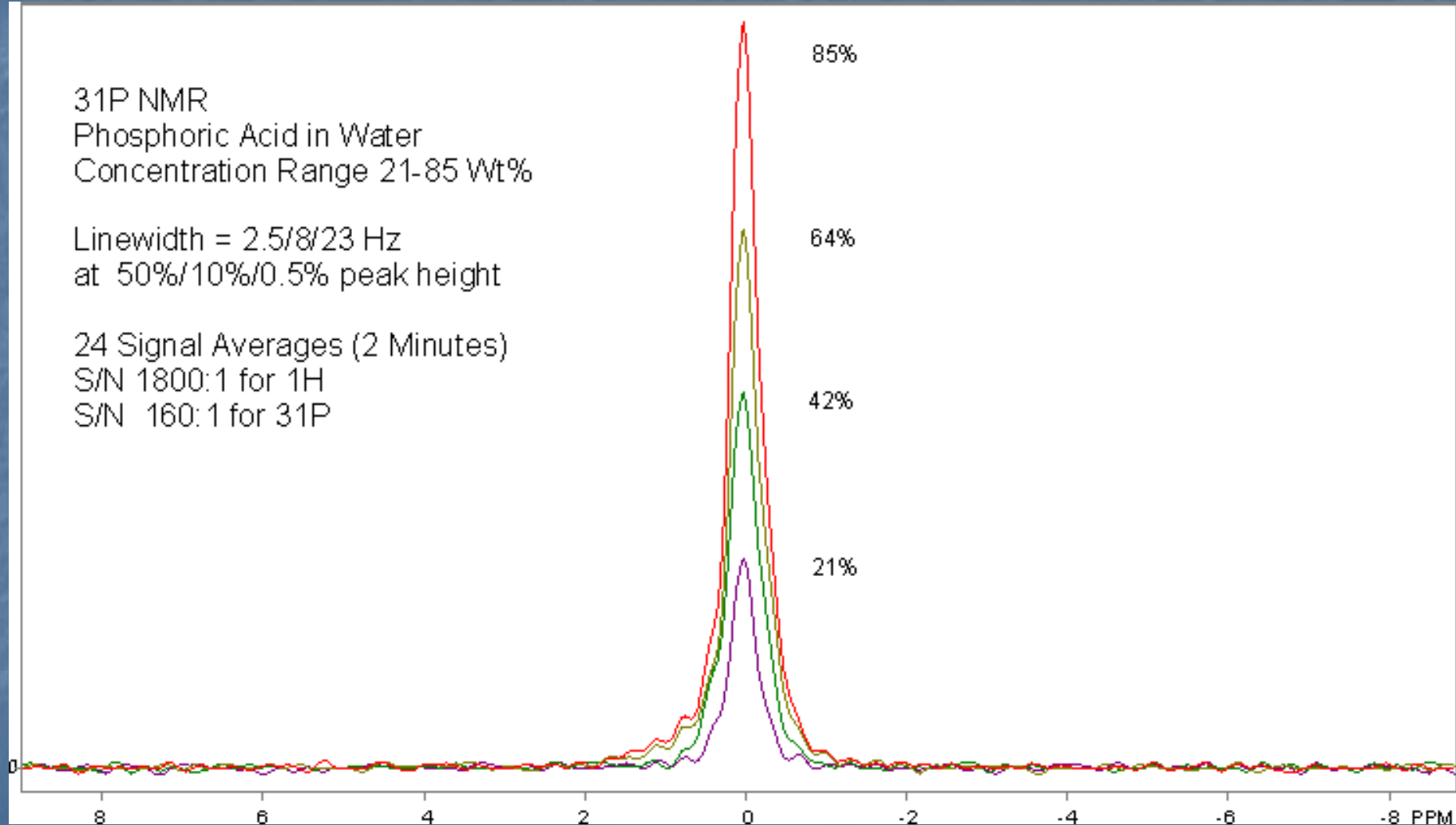


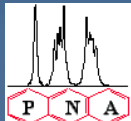


31P NMR  
Phosphoric Acid in Water  
Concentration Range 21-85 Wt%

Linewidth = 2.5/8/23 Hz  
at 50%/10%/0.5% peak height

24 Signal Averages (2 Minutes)  
S/N 1800:1 for 1H  
S/N 160:1 for 31P

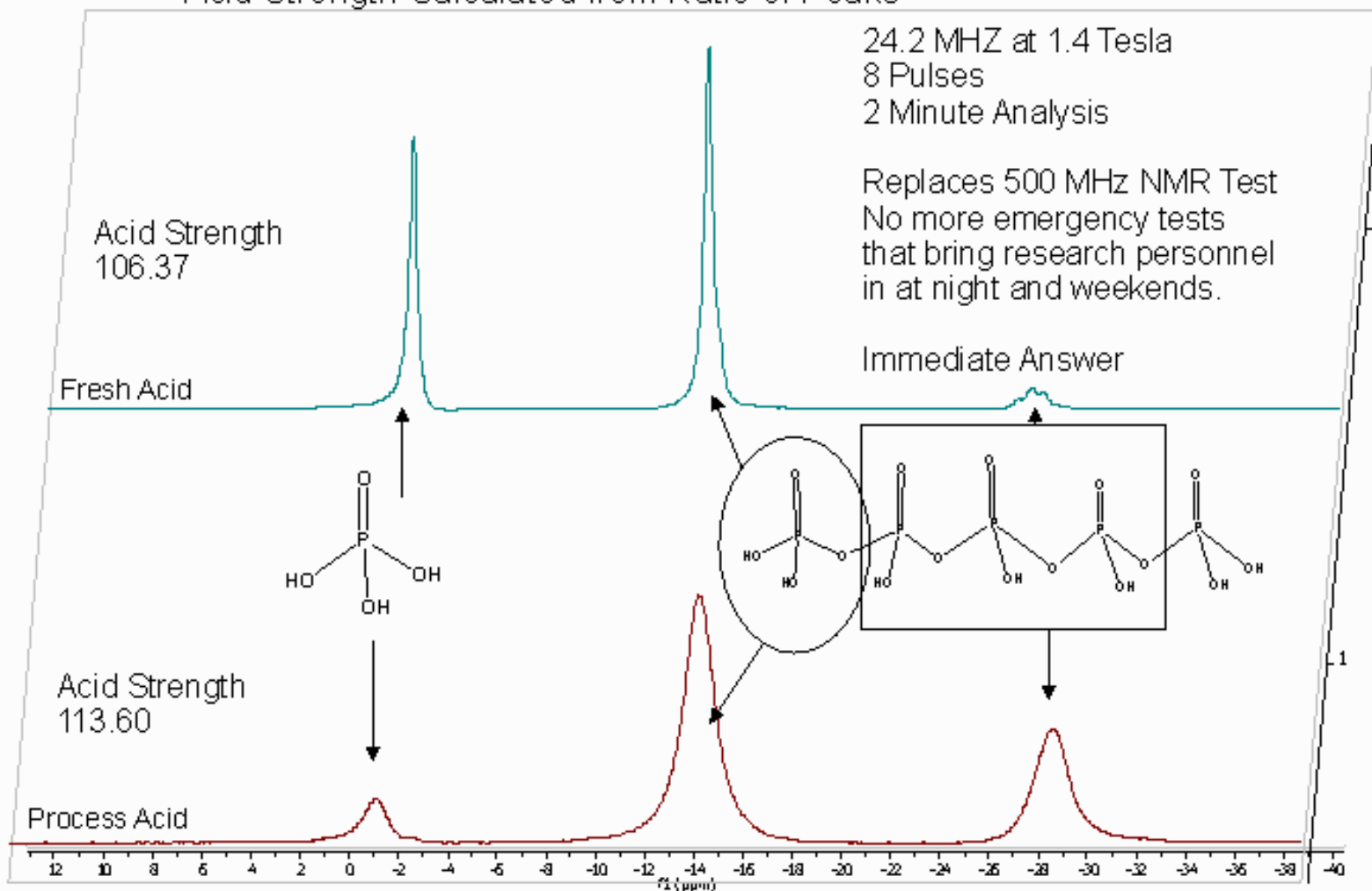


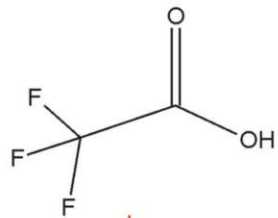
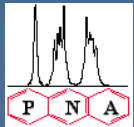


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## 31P NMR - Polyphosphoric Acid - Catalyst for Alkylation Process

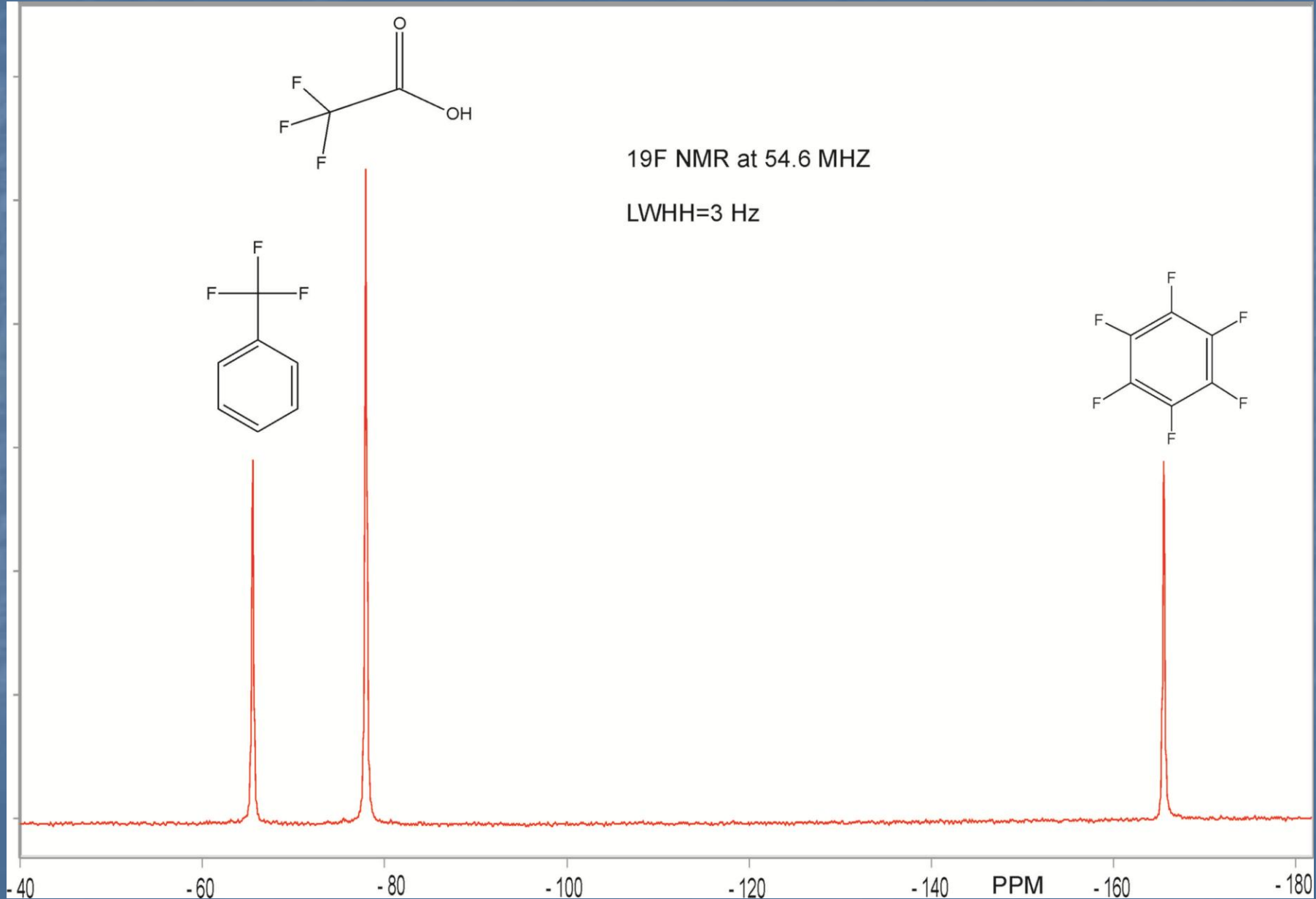
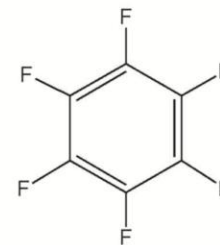
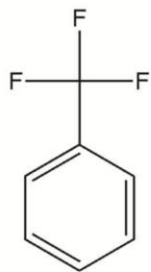
### Acid Strength Calculated from Ratio of Peaks

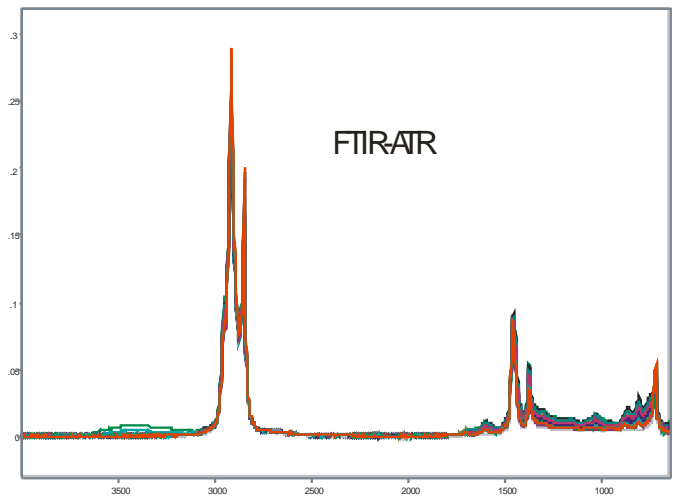




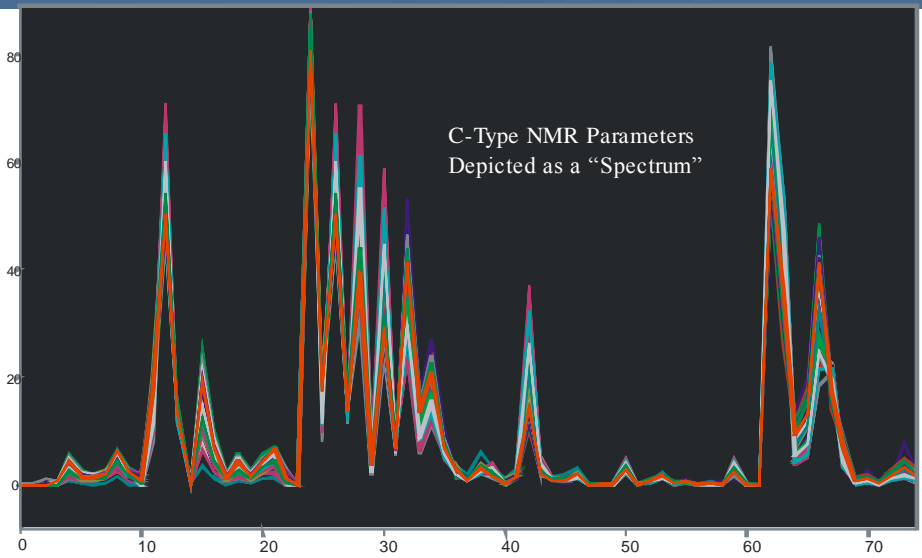
19F NMR at 54.6 MHz

LWHH=3 Hz

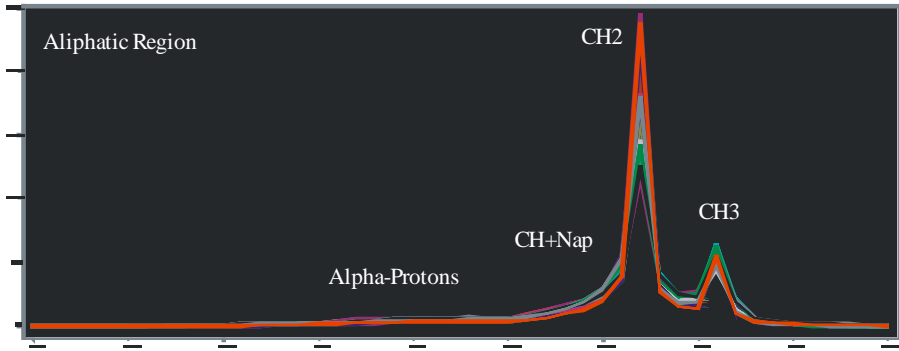
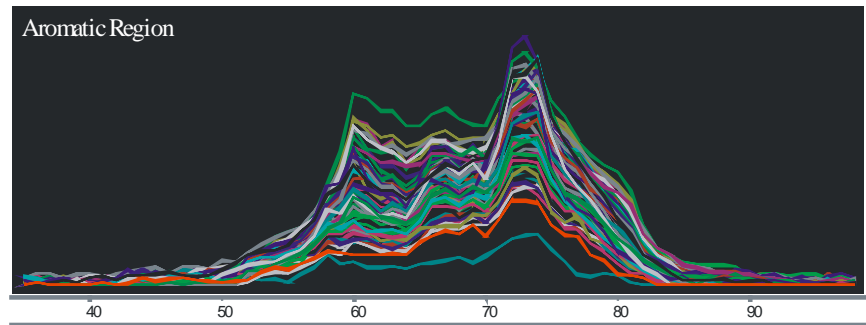
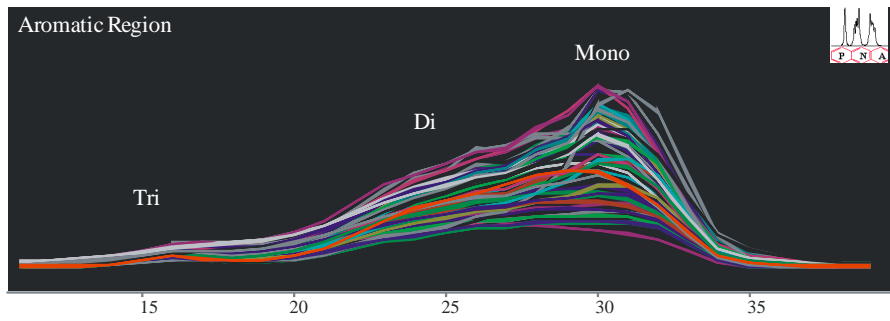




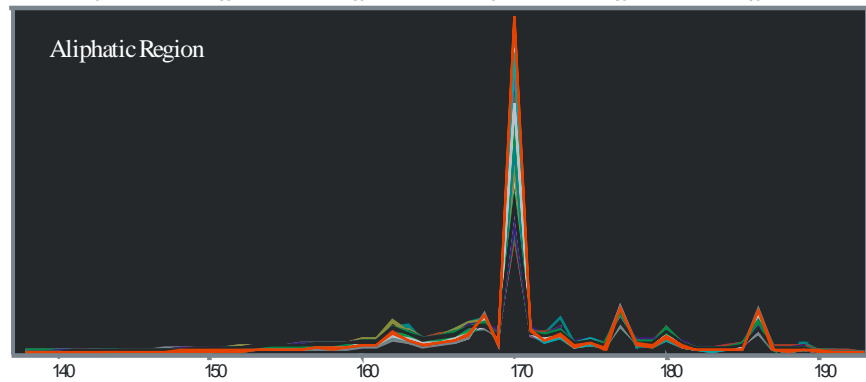
Vacuum Gas Oils - Fluid-Catalytic Cracking Application



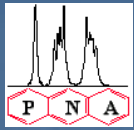
Data Fusion



<sup>1</sup>H NMR



<sup>13</sup>C NMR



PROCESS NMR ASSOCIATES

# Acknowledgements

Paul Giammatteo – PNA

Tal Cohen – ASPECT AI and Modcon