

PROCESS NMR ASSOCIATES

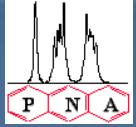
Practical Applications of Compact High-Resolution 60 MHz Permanent Magnet NMR Systems for Reaction Monitoring and On-line Process Control

Presented By

John Edwards, Ph.D.

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

**September 28, 2010
Small Molecule NMR Conference, Portland Oregon**



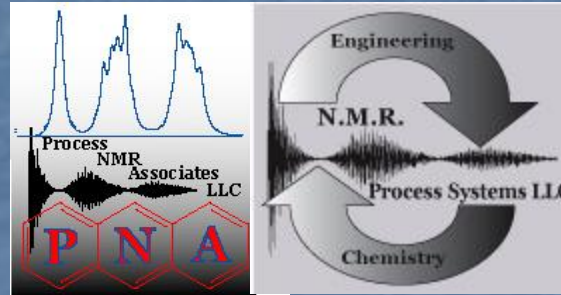
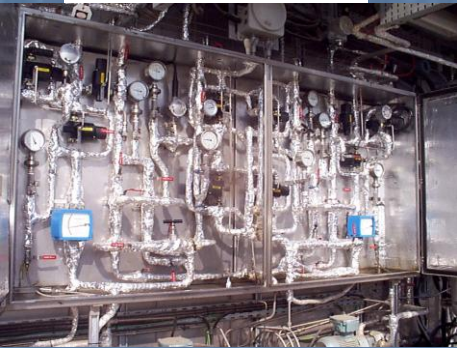
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250+ Analytical NMR Customers

smiths detection
bringing technology to life



Swagelok

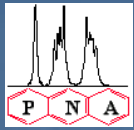


TTC Labs, Inc.
Process Engineering Excellence



TopNIR Systems

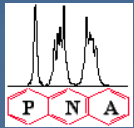




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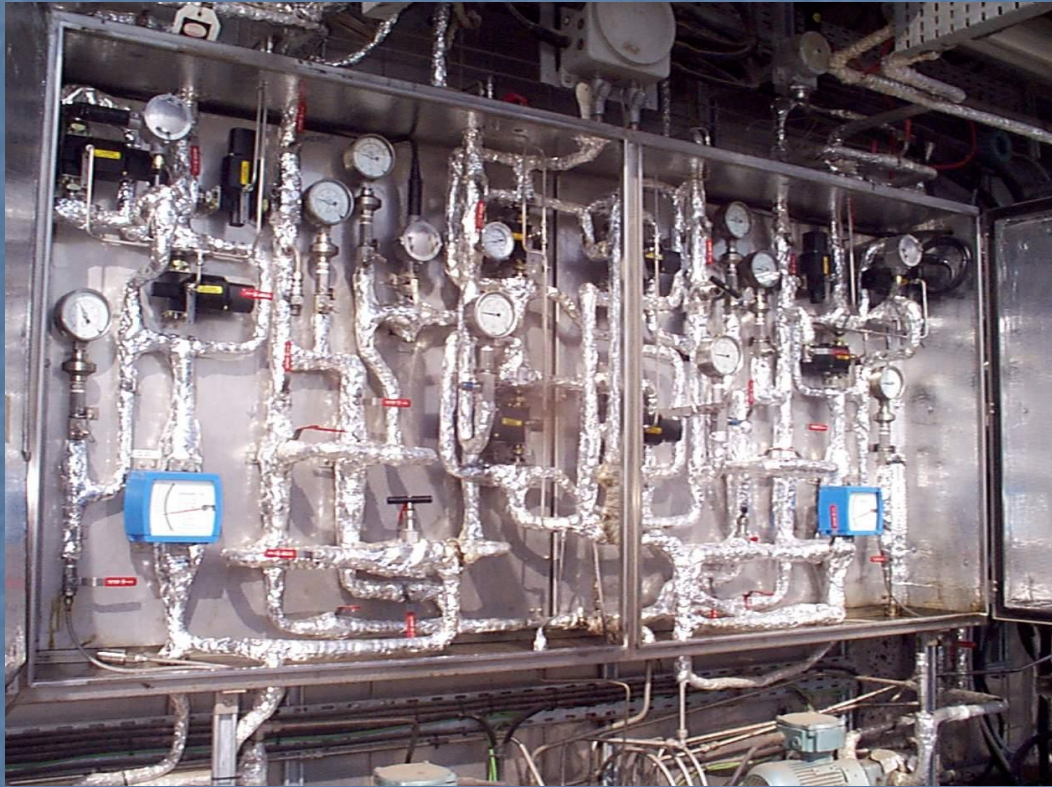
High Resolution FT-NMR – Online / in Process

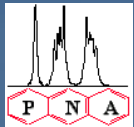




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NMR Sample System and Placement



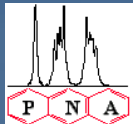


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NMR Lock - External ^7Li Lock @ 22.5 MHz Shim DACs Built into the Magnet Enclosure

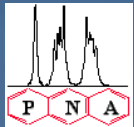


Matrix Shimming Performed
by Optimizing FID RMS



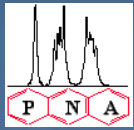
SPECIFICATIONS

Nuclei Observed	H+ (primary)
Operating Frequency	58±1.0 MHz for H+
Sample Tube	Standard laboratory glass tube L: 35.5 cm O.D 8 mm - I.D 7 mm Other size optional
Sample Temperature Heating	Controlled between 30°C – 80°C (86°F to 176°F)
Magnet System	Temperature stabilized, self-condensed field, permanent (neodymium) magnet with integral field gradient (shim) coils and automatic shim control
Field Strength	1.35 Tesla at 45°C
Fringe Field	Less than 1 gauss on external enclosure of magnet
Dimensions	145 cm H x 106 cm W x 65 cm D (57 in H x 42 in W x 26 in D) Add 15 cm (6 in) to height for shipping pallet
Enclosure	Self standing, wheel driven carriage
Weight	400 kg (882 lb) net weight 444 kg (980 lb) gross shipping weight
Power Requirement	220-240 Vac, 3500W maximum 110-120 Vac, 3500W maximum
Other Utilities	Internal Air condition system for higher stability
Operating temperature	Ambient Range: Temperature controlled environment
Relative humidity	Min / Max 30%-50%.
Vibration	Max: 0.3 mm/s ² on the 3 axes
Communication	Local Ethernet Base -10/100. Remote connection via modem.



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New Magnet System

New magnet design solves the problem of:

- Long term and short term Stability
- Temperature sensitivity

State of the Art electronics:

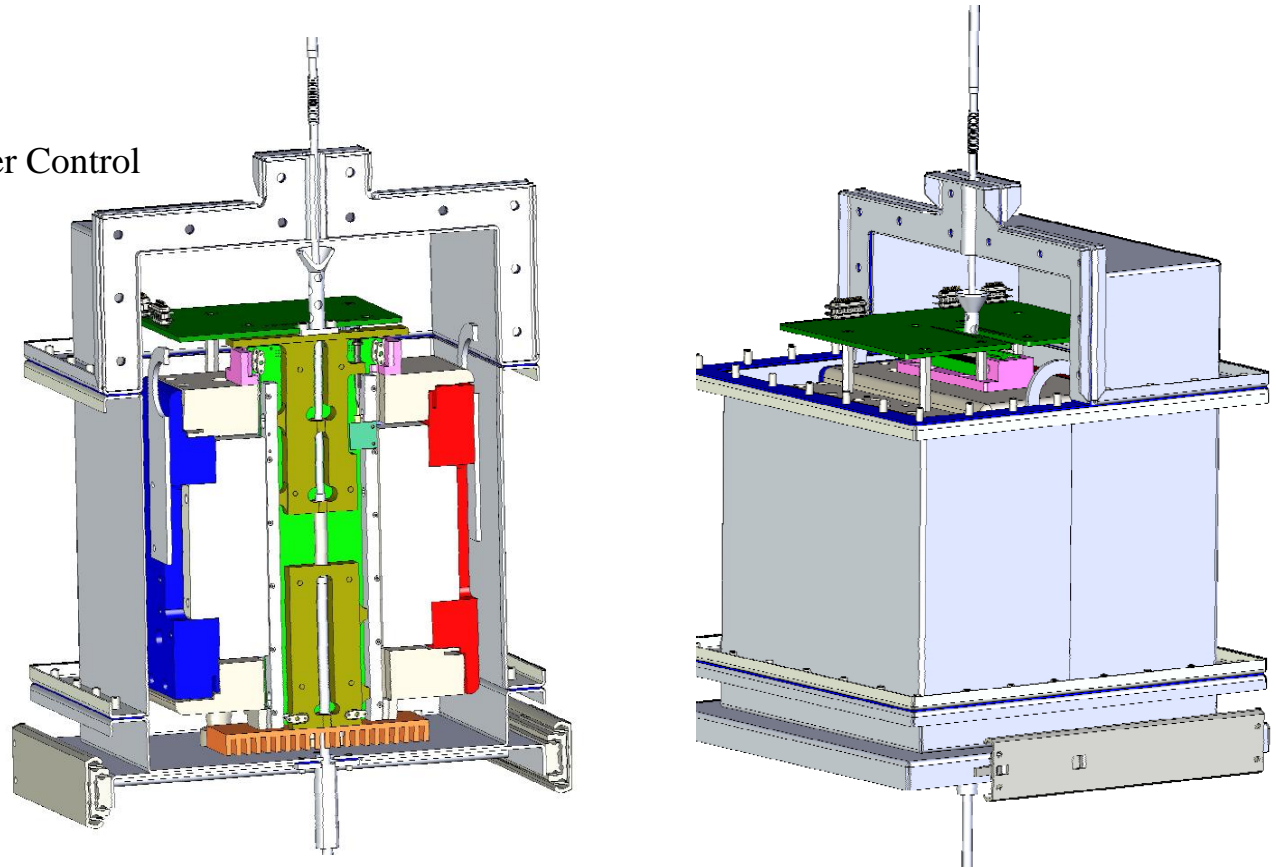
- Smaller foot-print
- 40 Shim coils on 2 single PCB
- Integrated PCB for Shim & Heater Control
- Digital RF & Acquisition – improve SNR

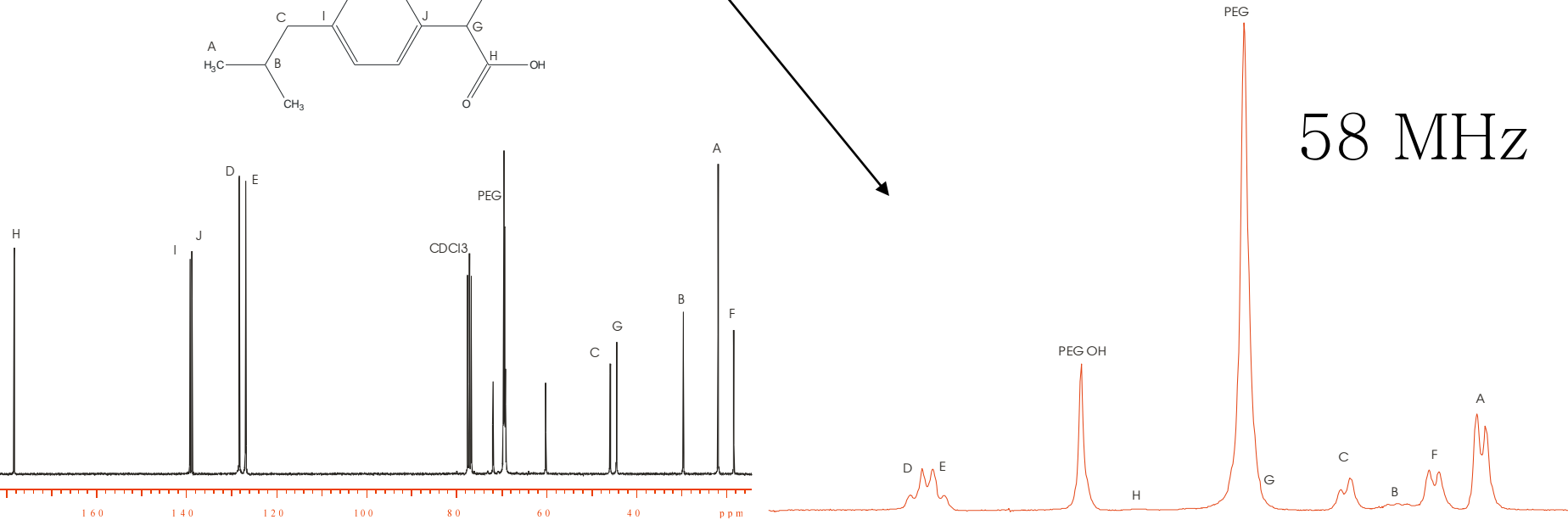
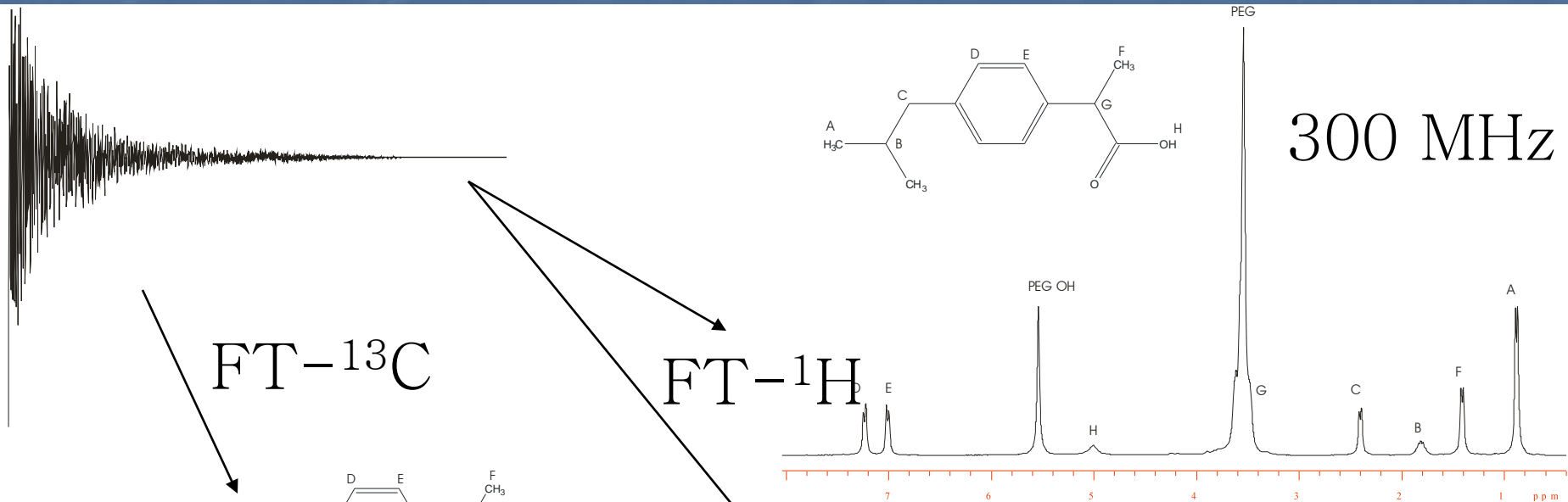
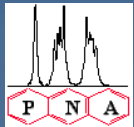
New concept of Process Probe:

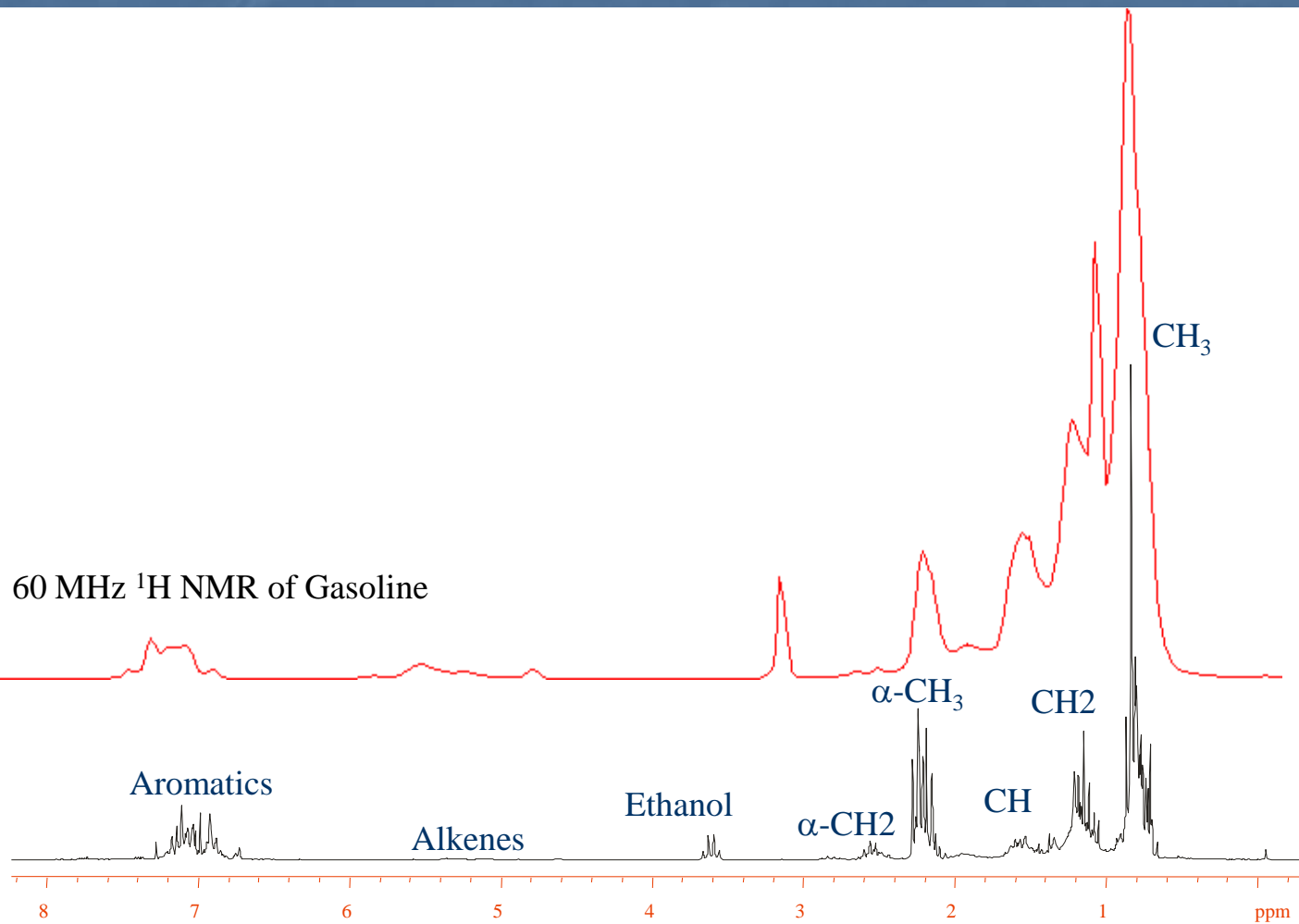
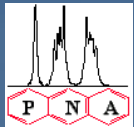
- Entire sample pipe through without contact with the system
- Much better temperature insulation
- Higher Q (better sensitivity)

New Software:

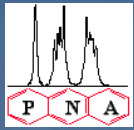
- Includes new algorithm for standard and global Models
- Fully automated process capacity
- Extensive remote diagnostic capabilities



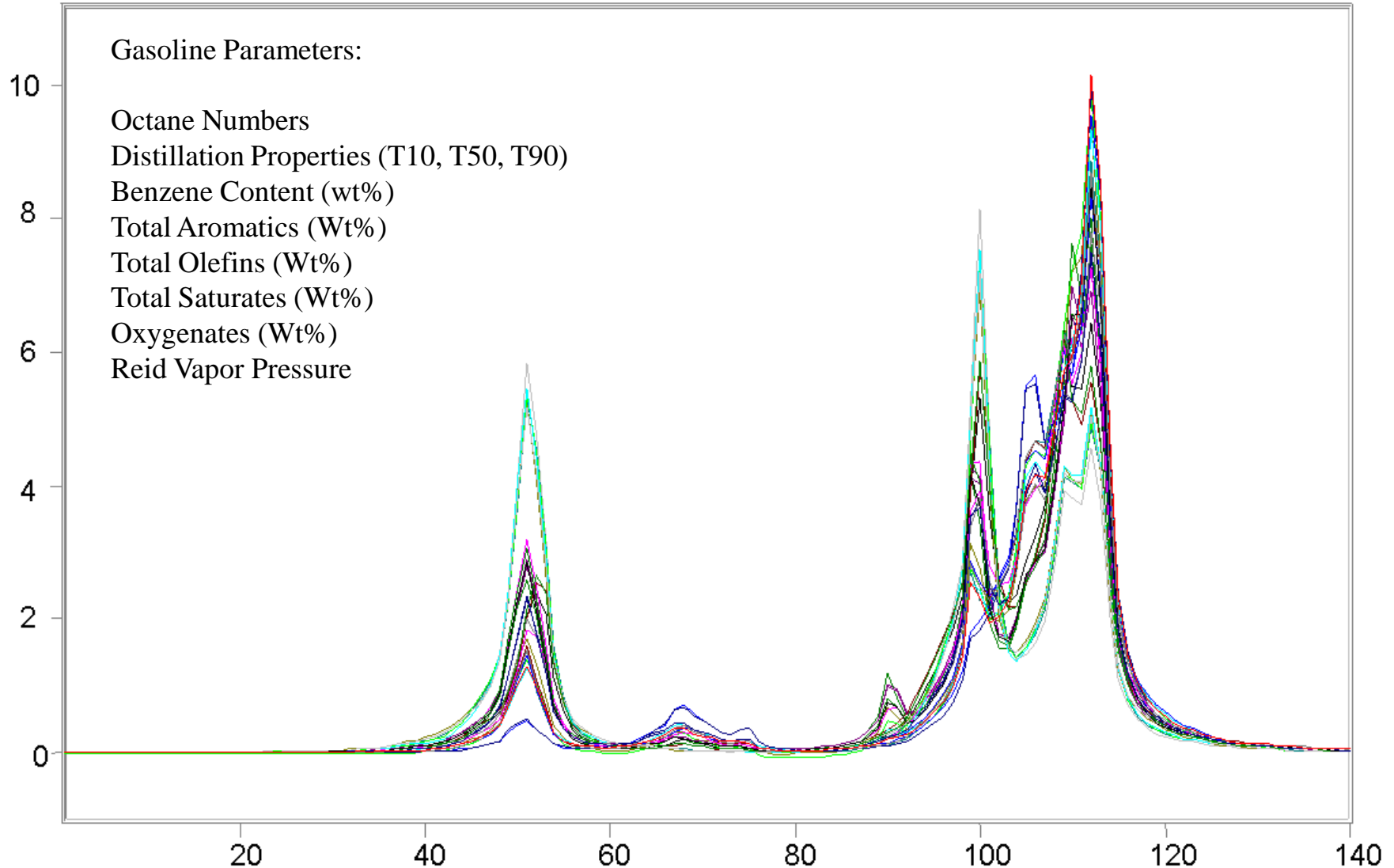


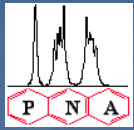


300 MHz ^1H NMR of Gasoline

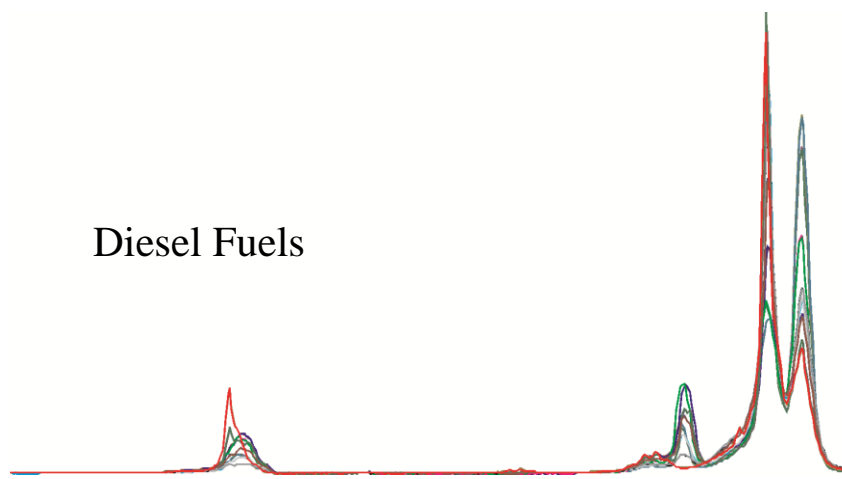


Typical Variability Observed in Gasoline Blending

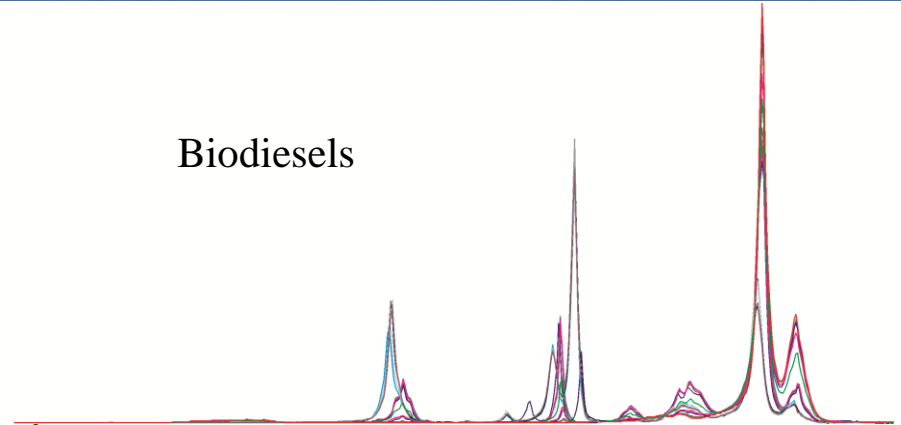




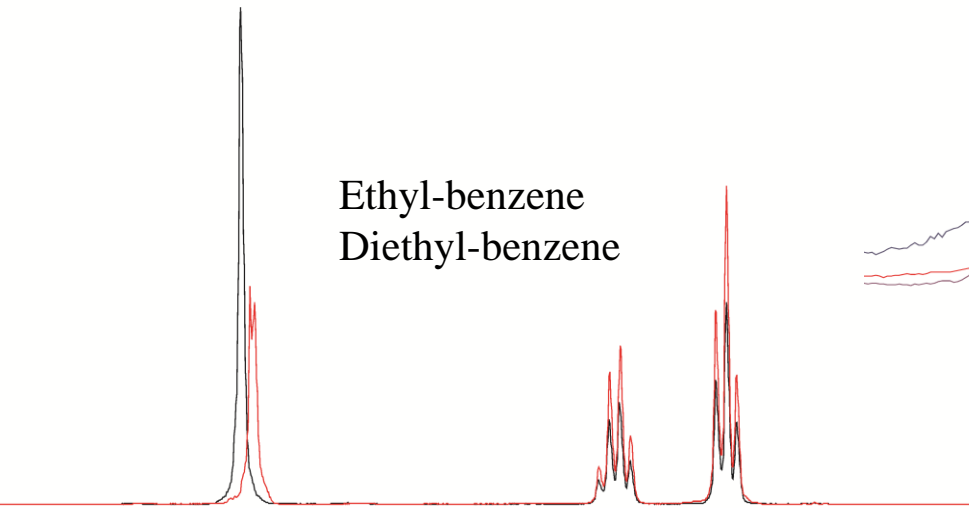
Diesel Fuels



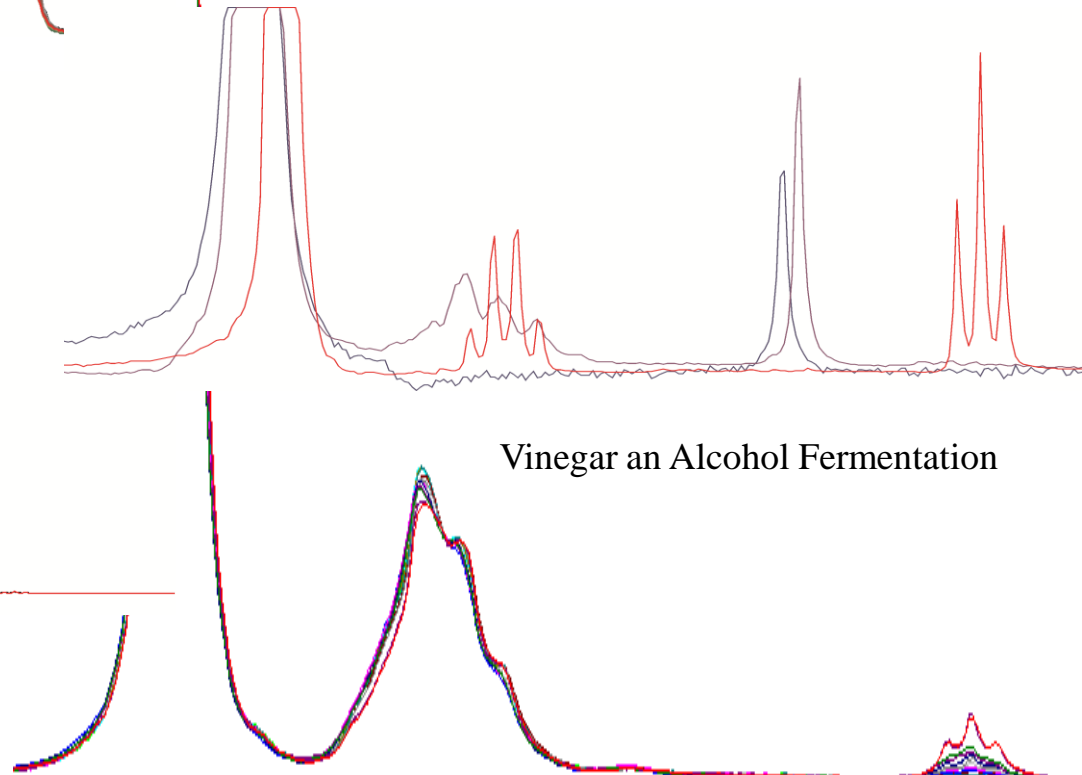
Biodiesels

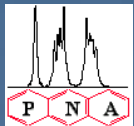


Ethyl-benzene
Diethyl-benzene



Vinegar an Alcohol Fermentation





Advantages and Disadvantages of NMR Applied to Process Control

Advantages:

Non-Optical Spectroscopy

No Spectral Temperature Dependence

Minimal Sampling Requirements

Spectral Response to Sample Chemistry is Linear

Chemical Regions of NMR Spectra are Orthogonal

Entire Volume is Sampled by the RF Experiment

Water is in Distinct Region and can be digitally removed

Detailed Hydrocarbon information is readily observed.

Fundamental Chemical Information Can be Derived Directly from Spectrum.

Colored/Black Samples Readily Observed Without Impact

Disadvantages:

Solids Cannot be Observed in a Liquid Stream

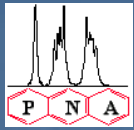
Individual Molecular Component Sensitivity Not Observed Directly in the Spectrum.

Low Sensitivity to Impurities – Quantitative > 500 ppm.

Sensitive to Ferromagnetics.

Sample Viscosity Causes Decrease in Resolution

Non-Hydrogen Containing Species are Not Observed (Exceptions Na, P, F, Al)



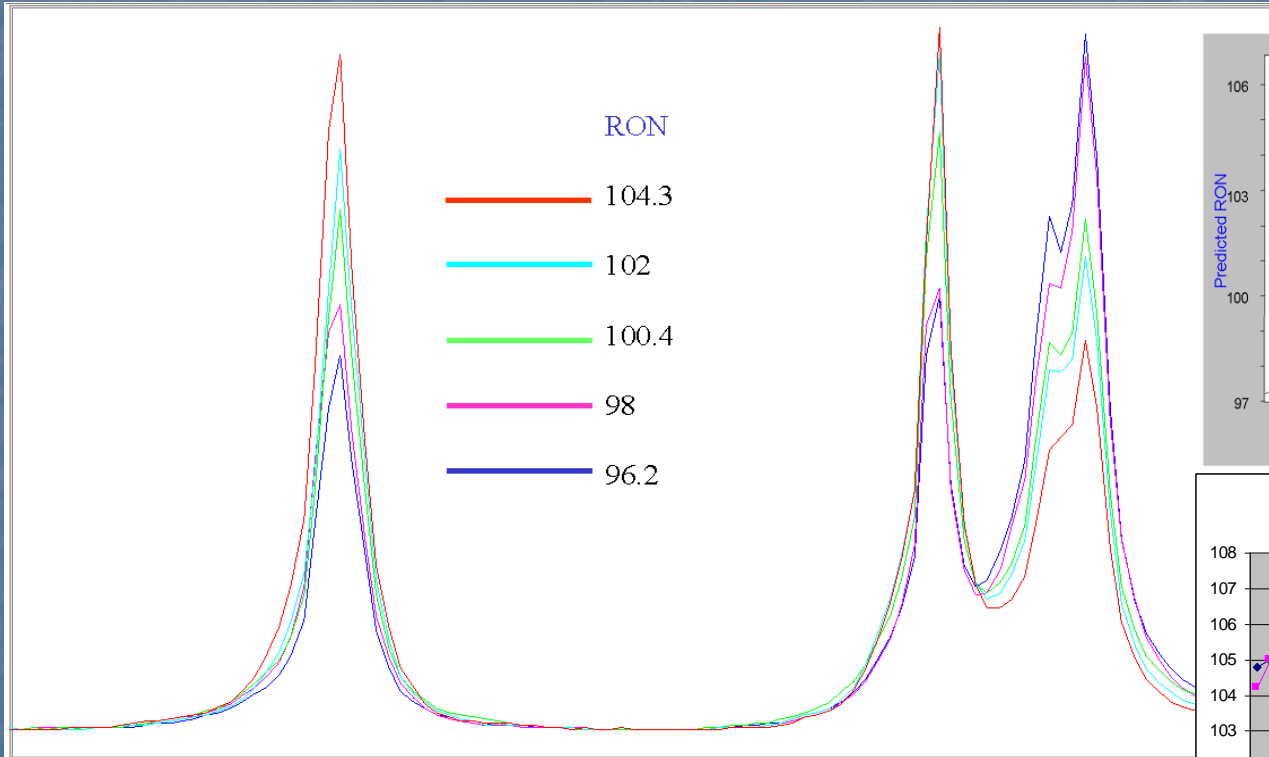
Application: Closed Loop Reformer Control - Installed 1998

Reformer Capacity: 34,000 Barrels per Day

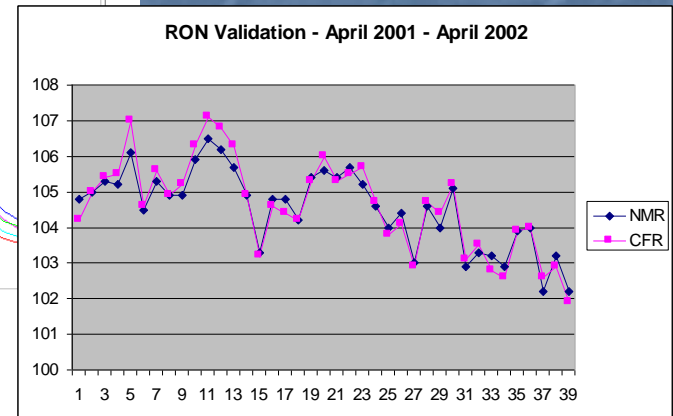
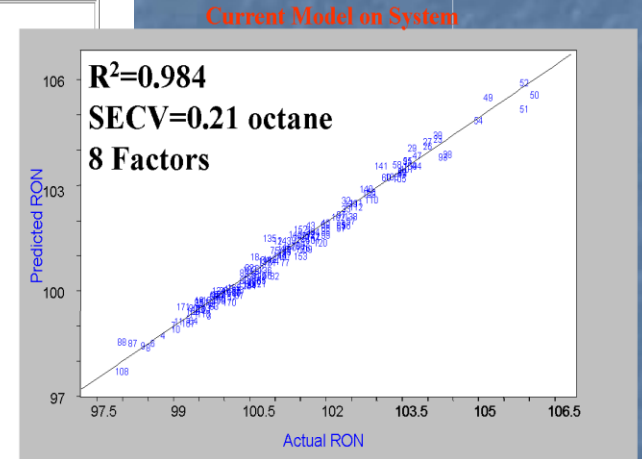
Control Strategy: Control on MON and Benzene Content

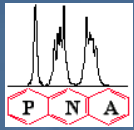
NMR Analysis: 2 Minute Analysis

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



Variation of Reformate Processed ¹H NMR Data Observed with Changing Research Octane Number





Application: Steam Cracking Optimization Installed 2000

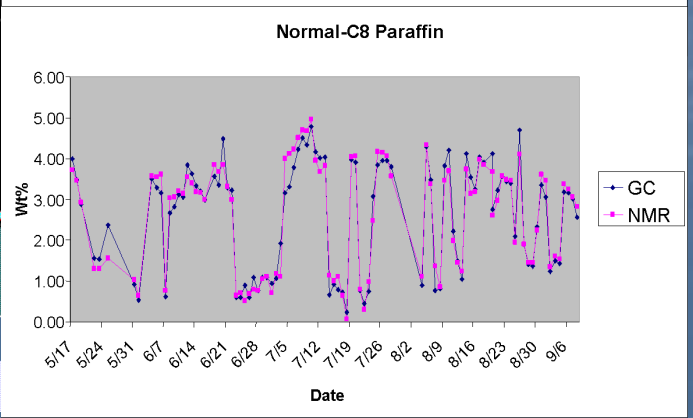
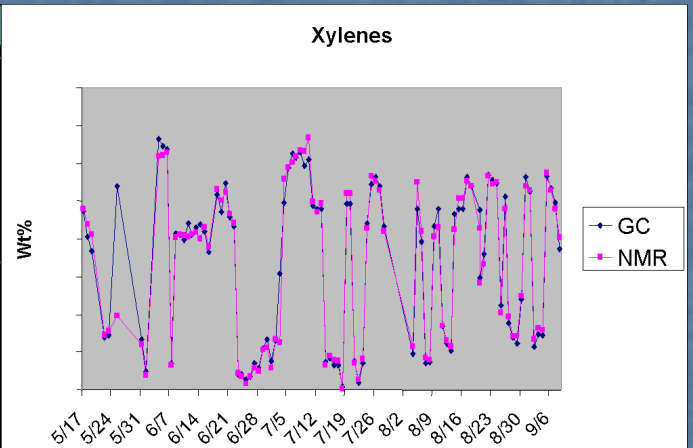
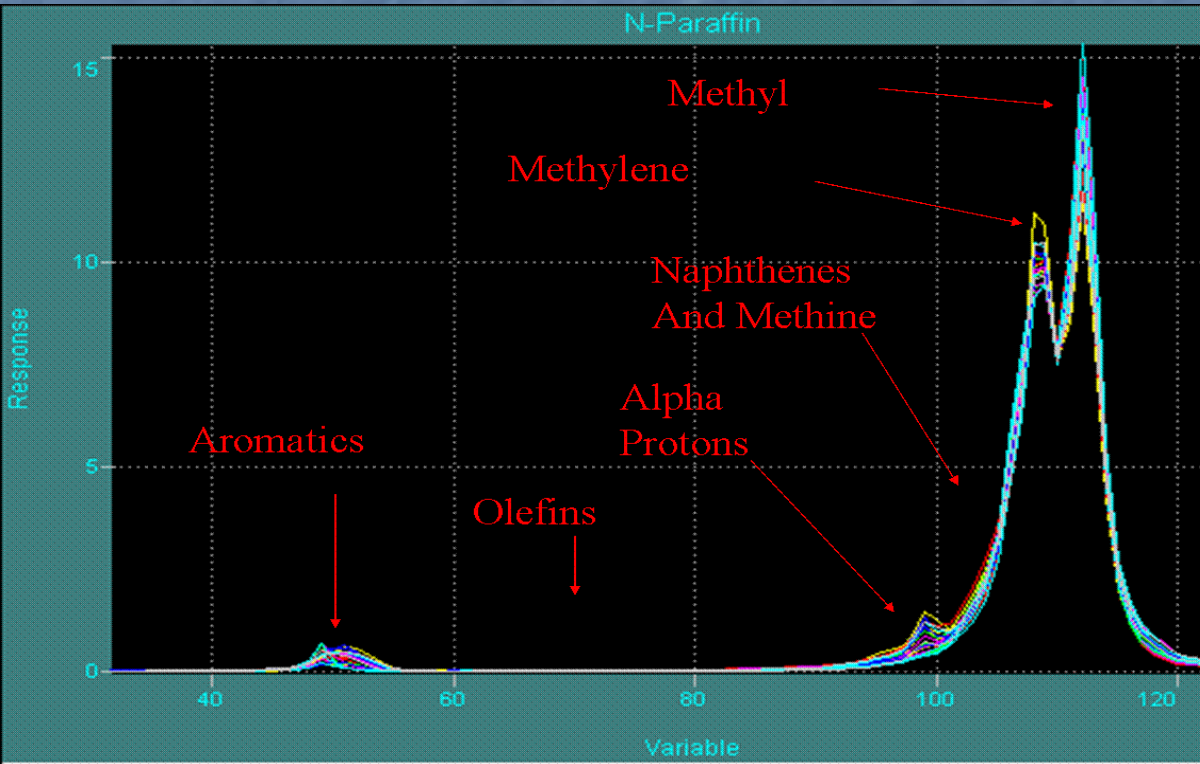
Cracker Facility Capacity: 600,000 Tonnes per Year

Control Strategy: Feed Forward Detailed Hydrocarbon Analysis to SPYRO Optimization

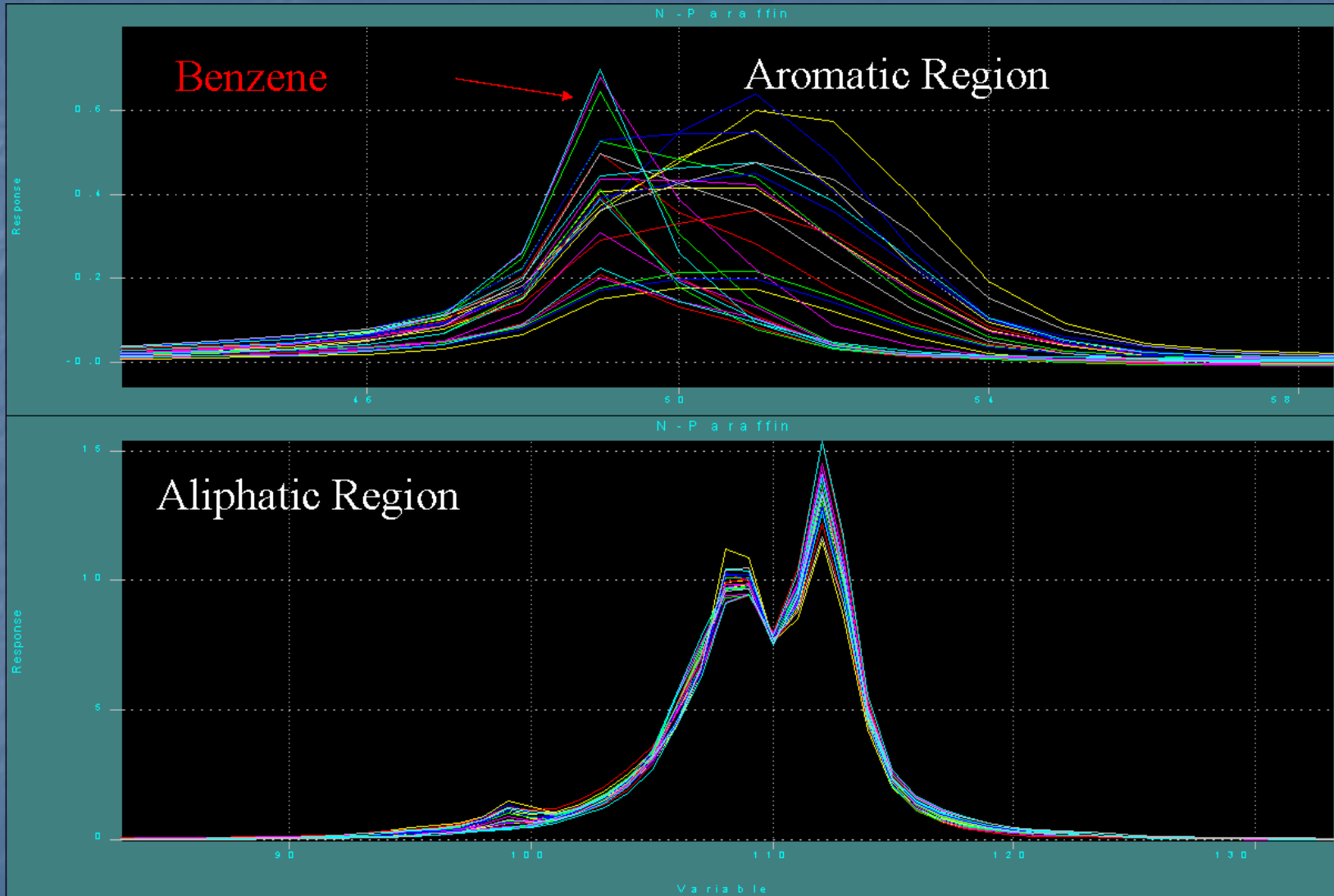
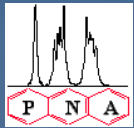
NMR Analysis: 3-4 Minute Cycle (Single Stream)

NMR PLS Outputs: Naptha – Detailed PIONA

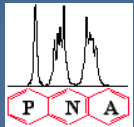
C4-C10 normal-paraffin, iso-paraffin, aromatics, naphthenes



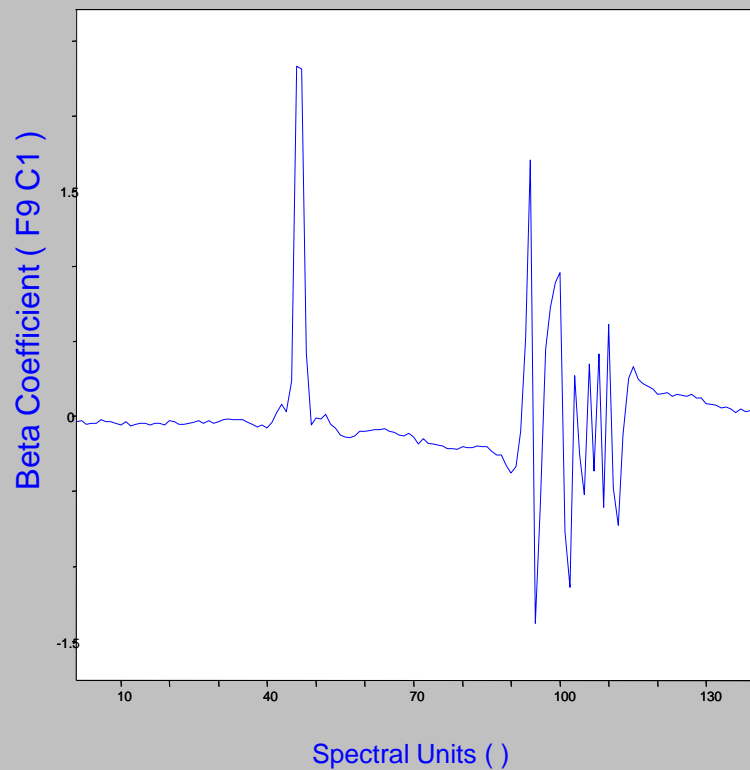
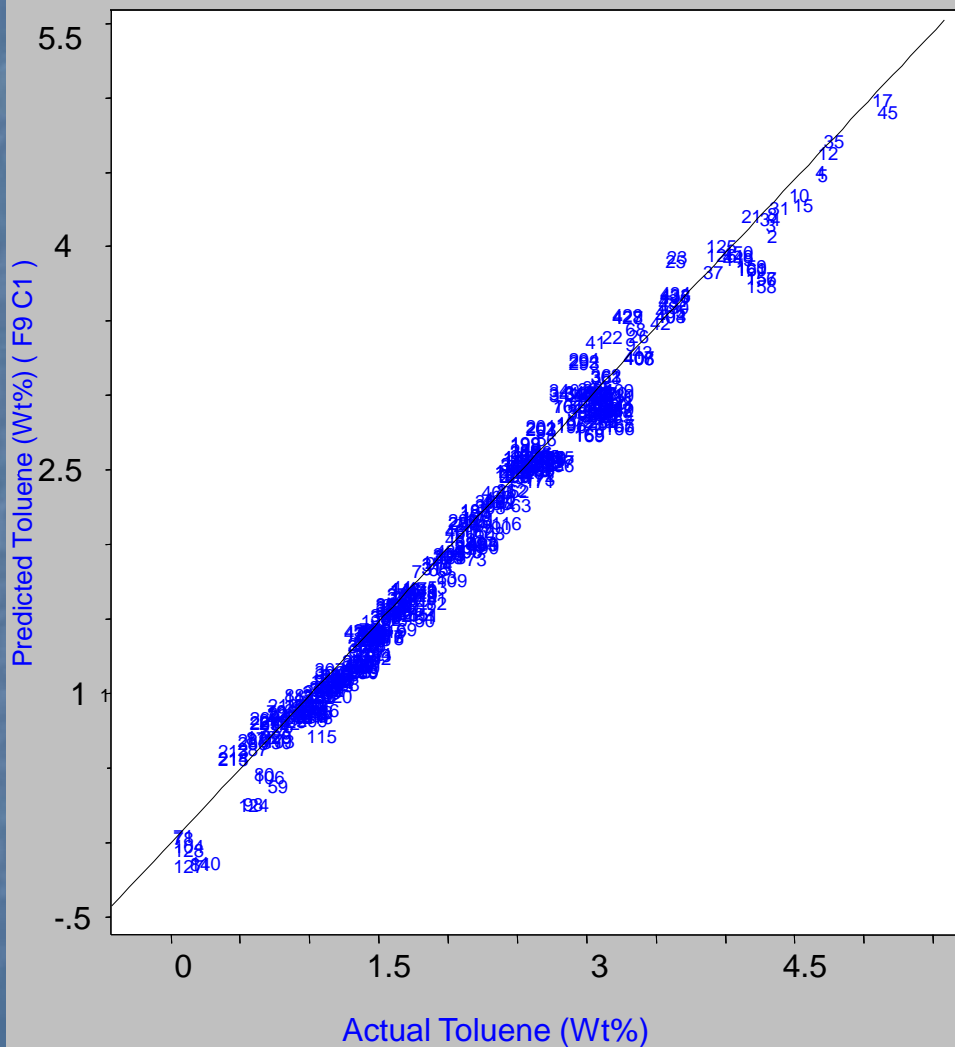
Spectral Variability Observed in Naptha Samples

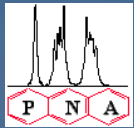


Spectral Variability in Aromatic and Aliphatic Regions

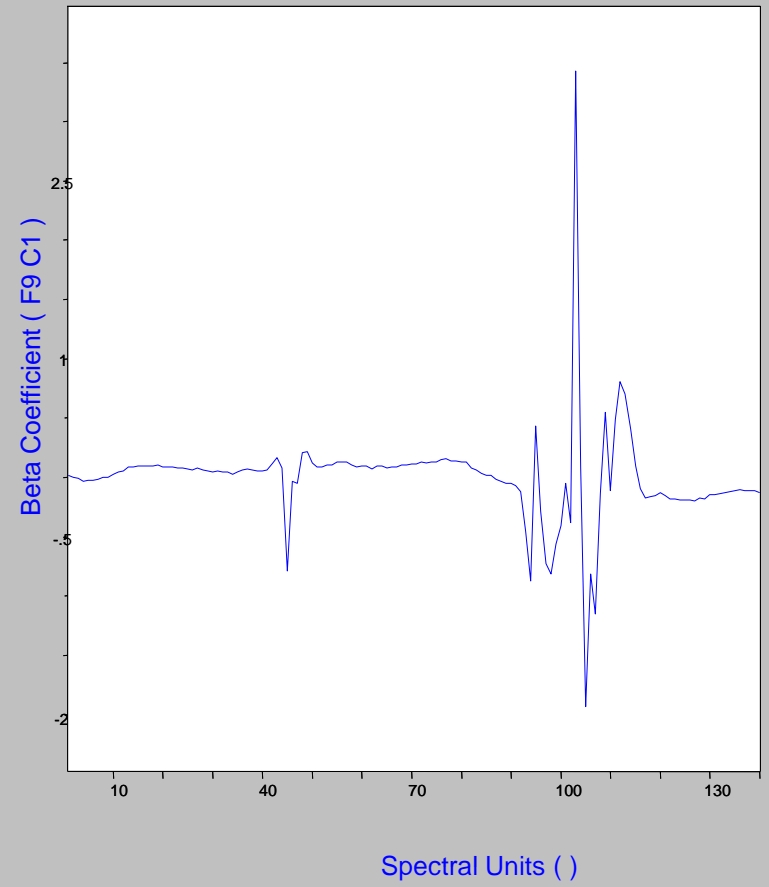
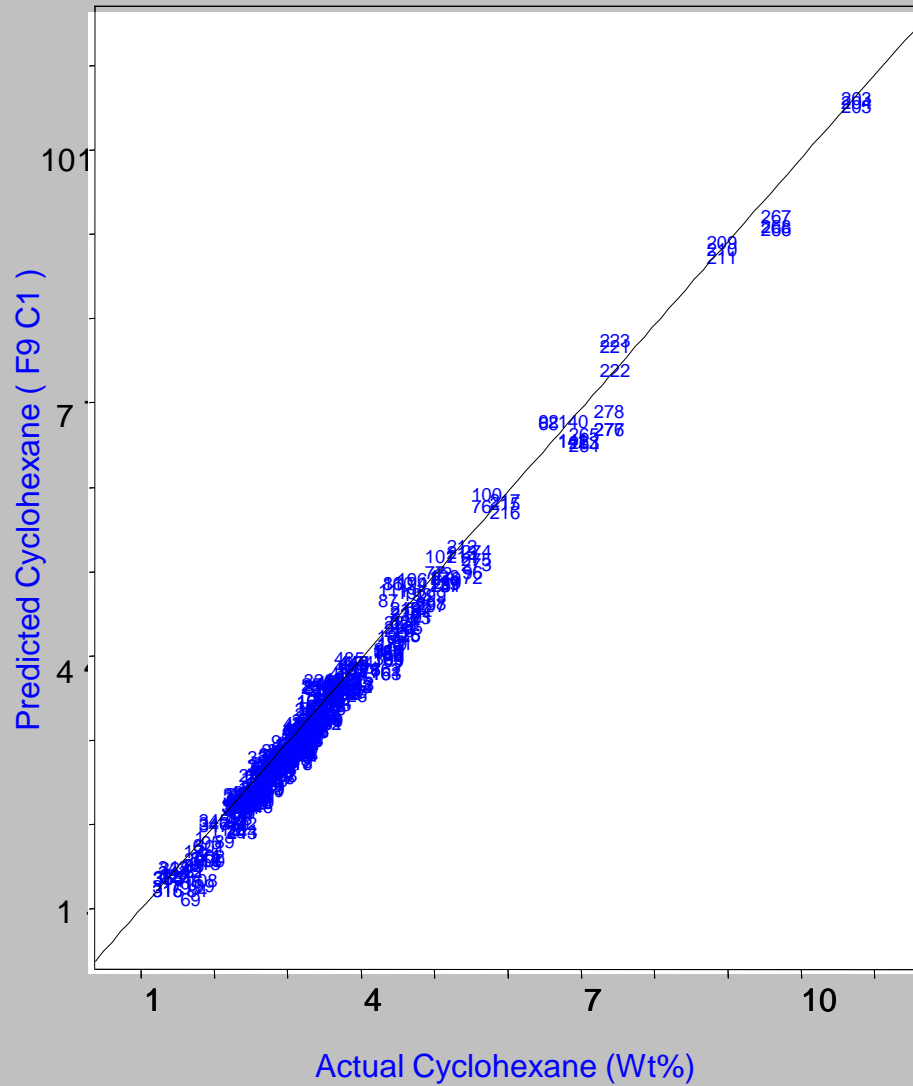


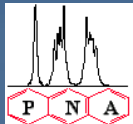
Toluene



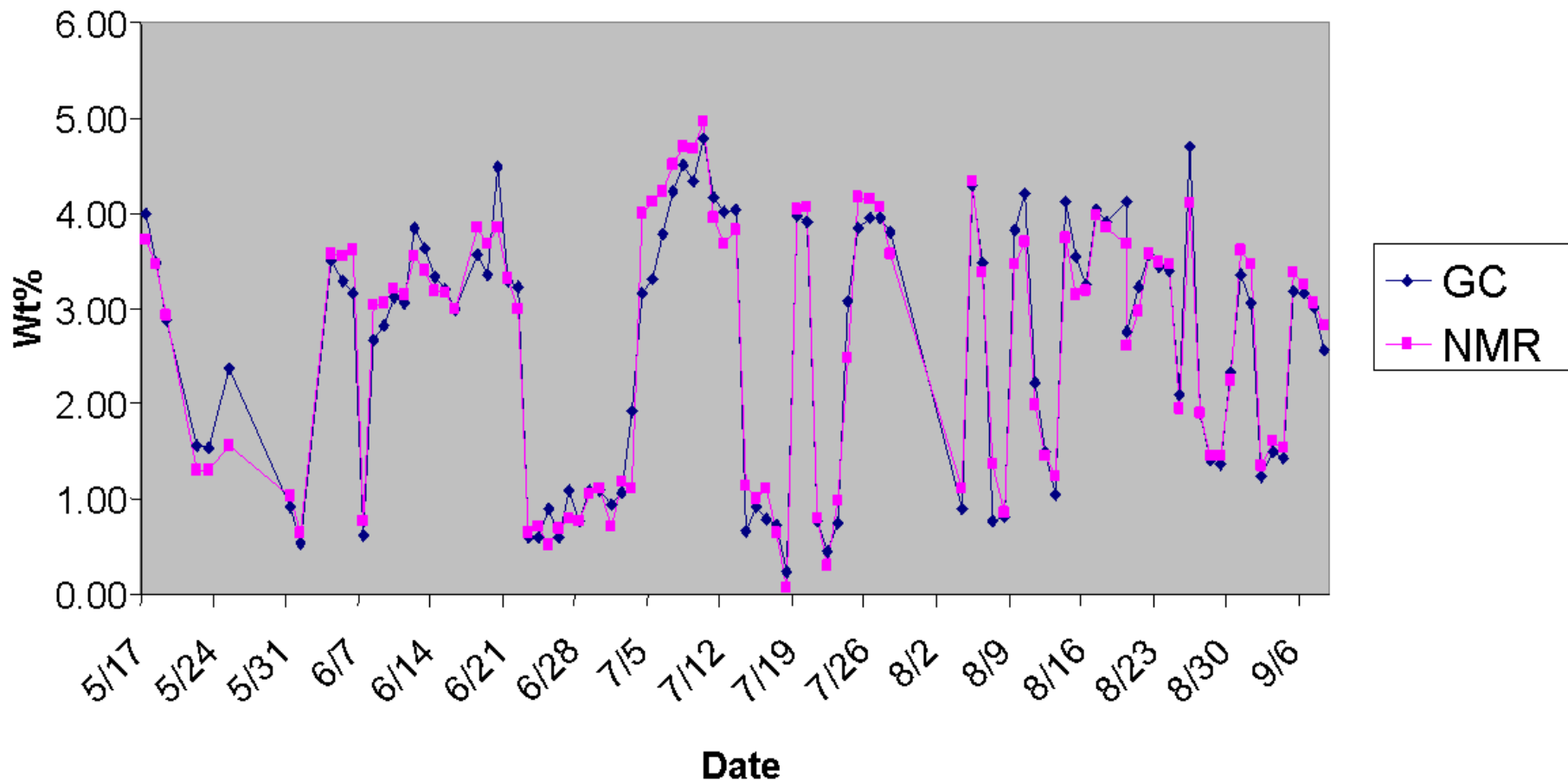


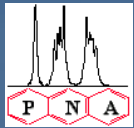
Cyclohexane



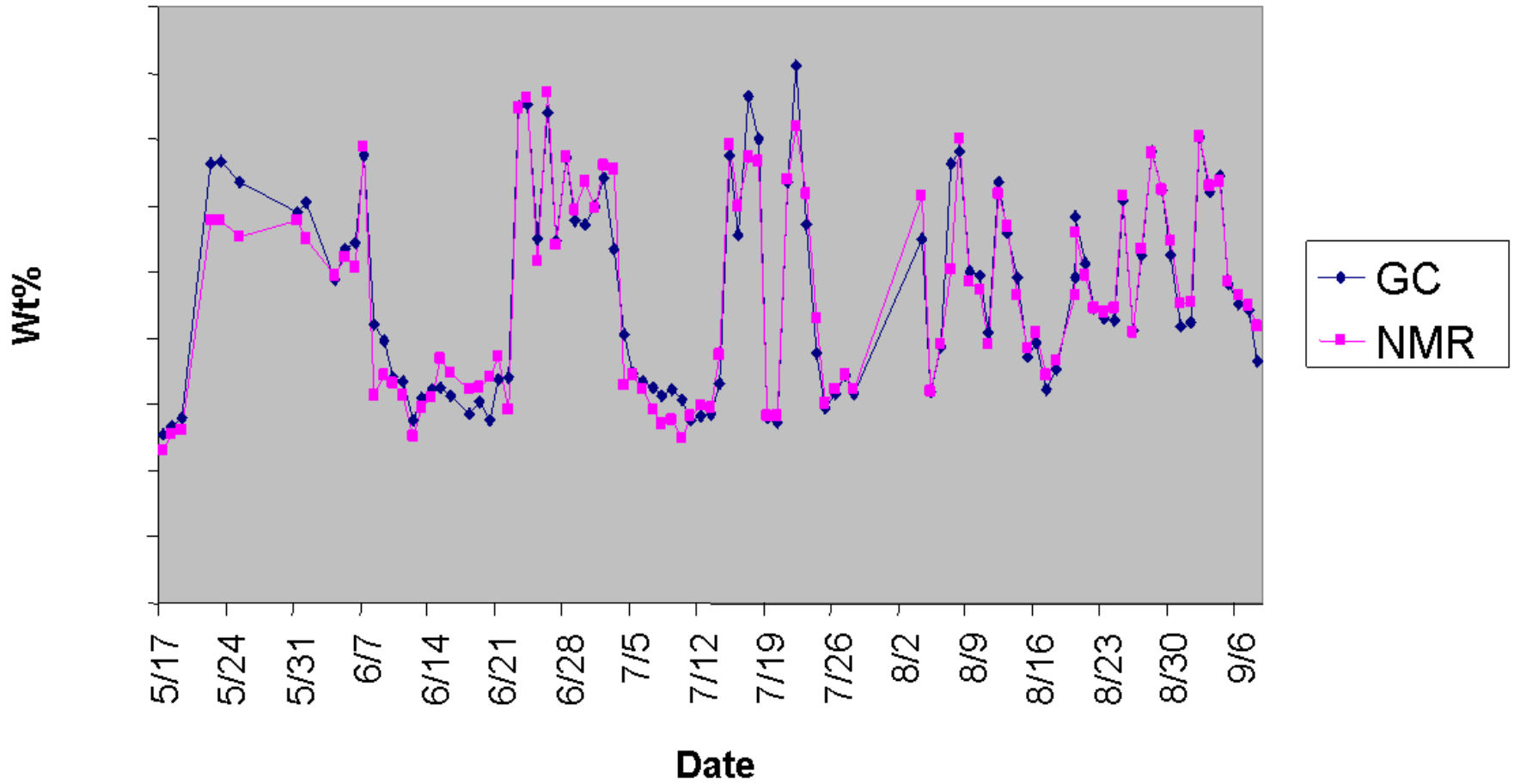


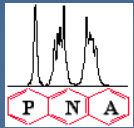
Normal-C8 Paraffin



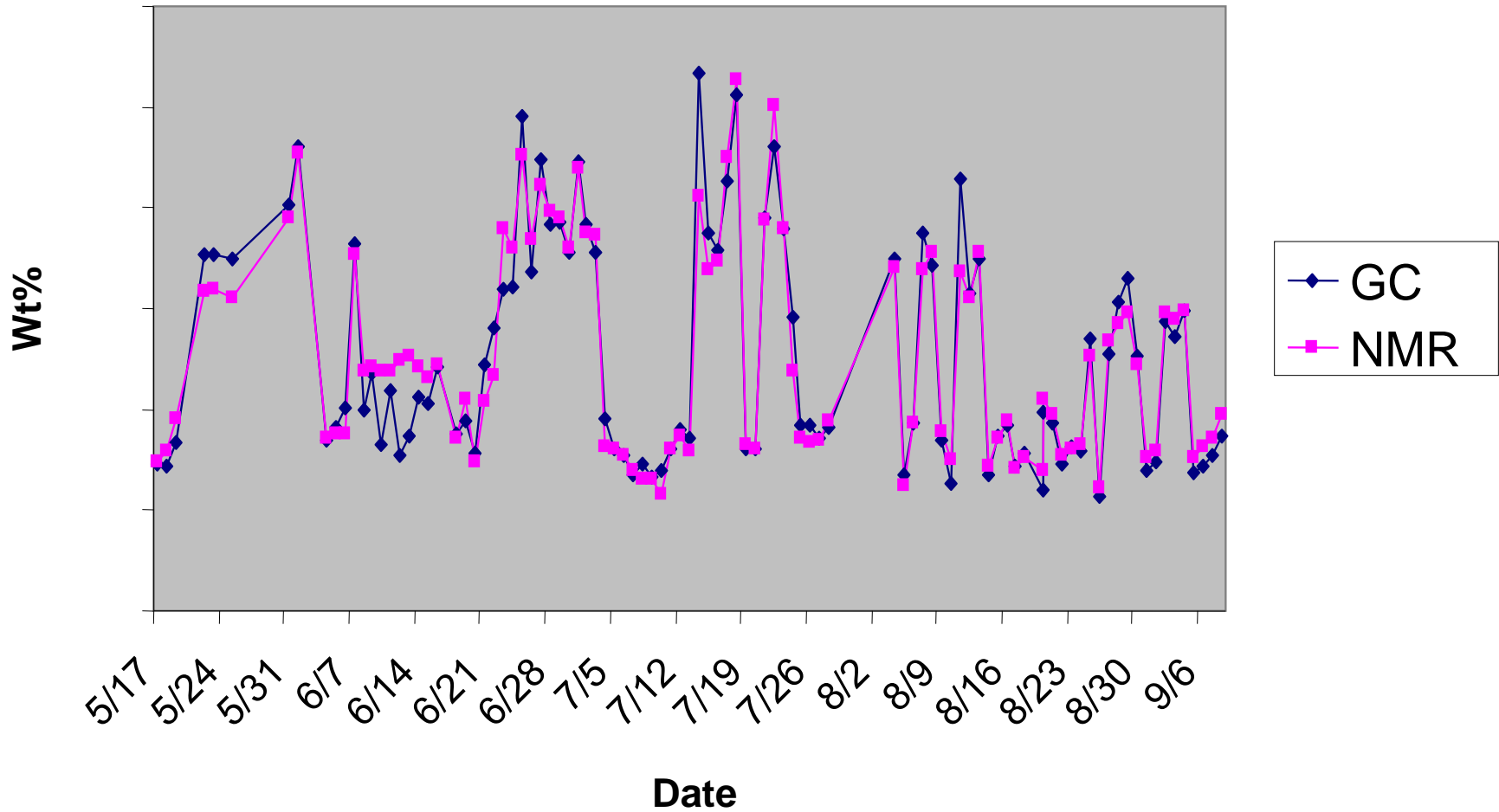


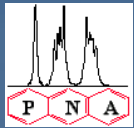
Iso-C5 Paraffin



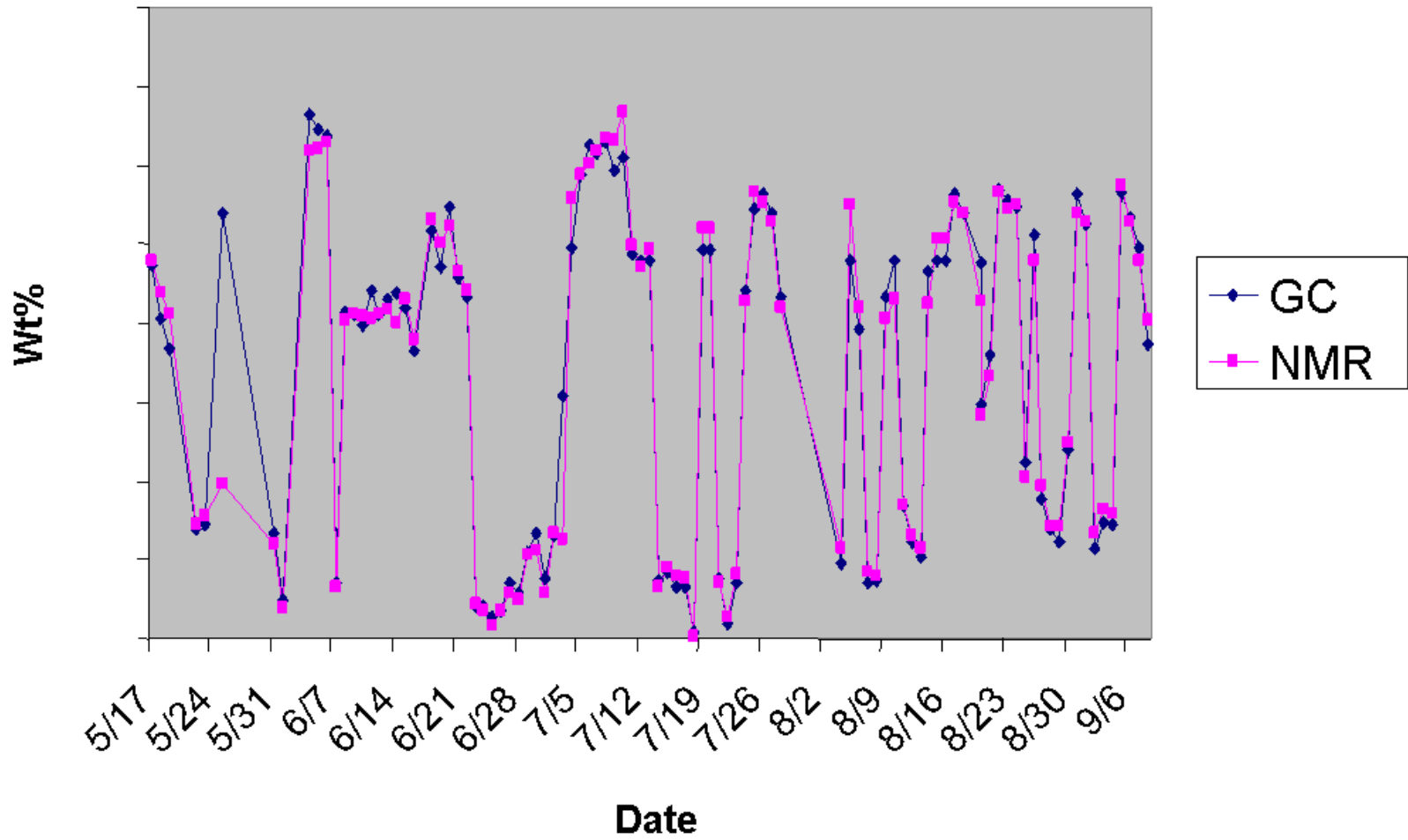


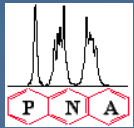
Cyclopentane



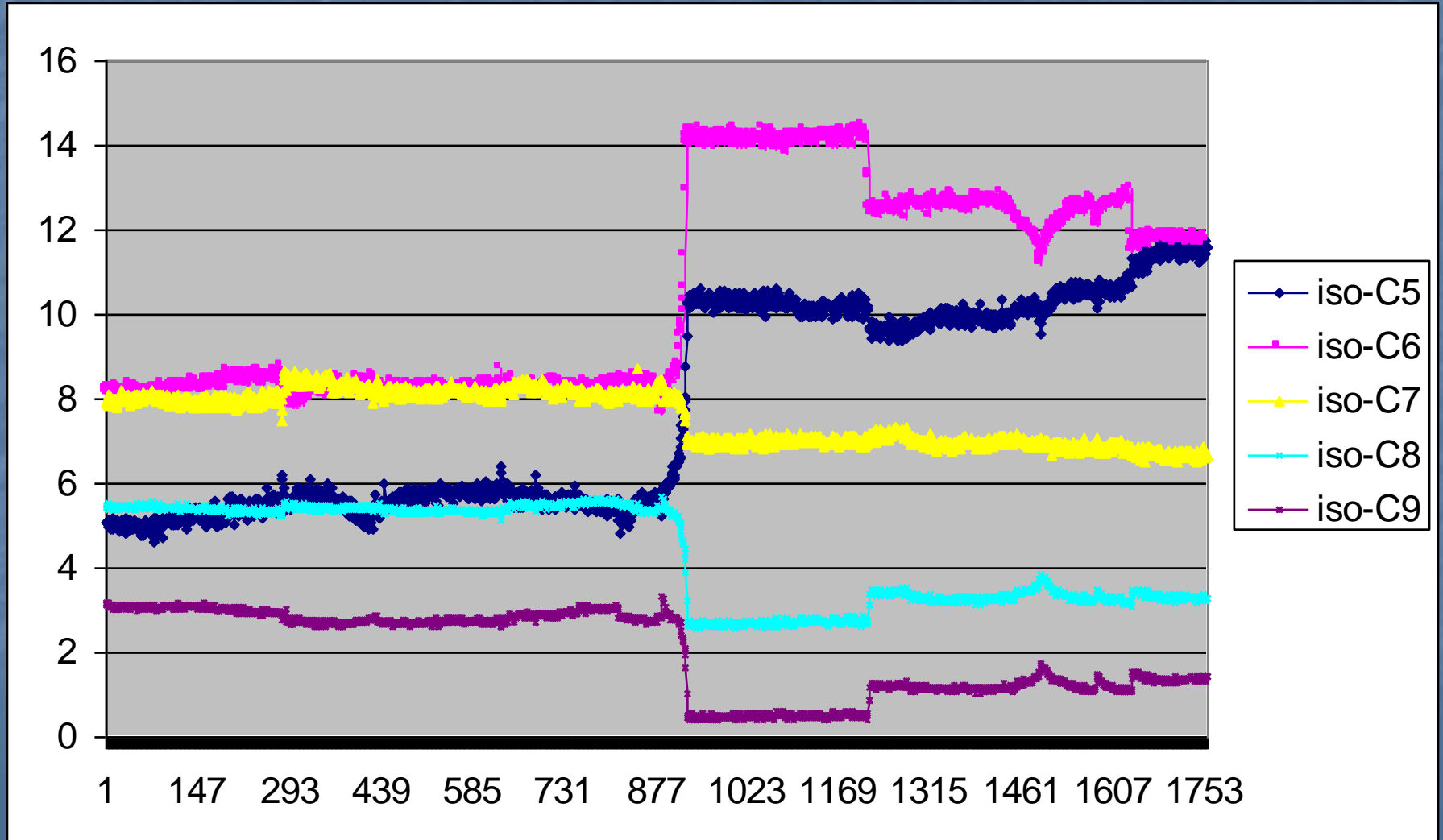


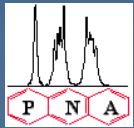
Xylenes



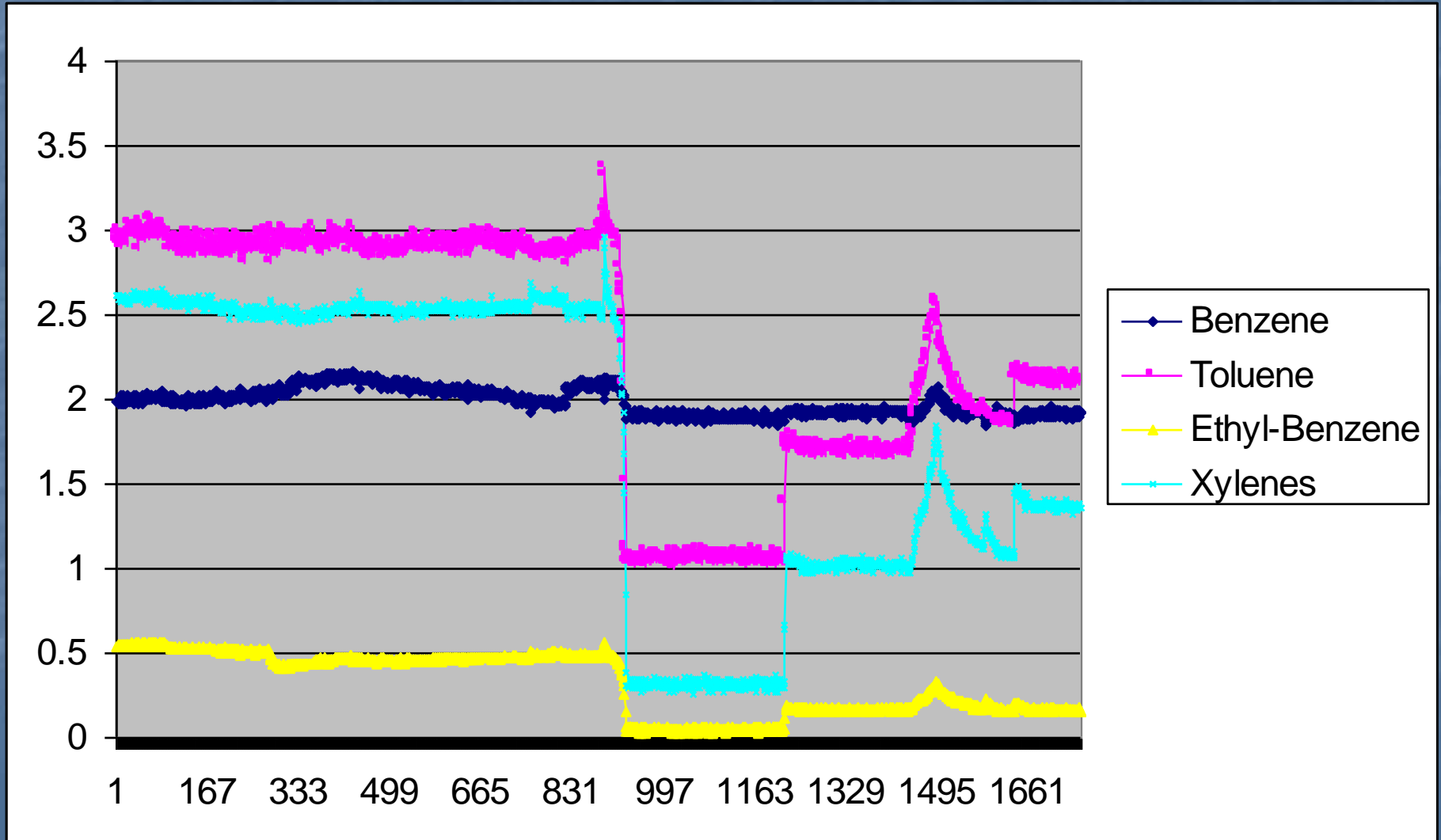


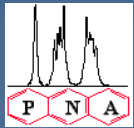
96 Hours of NMR Process Output – iso-Paraffin Components





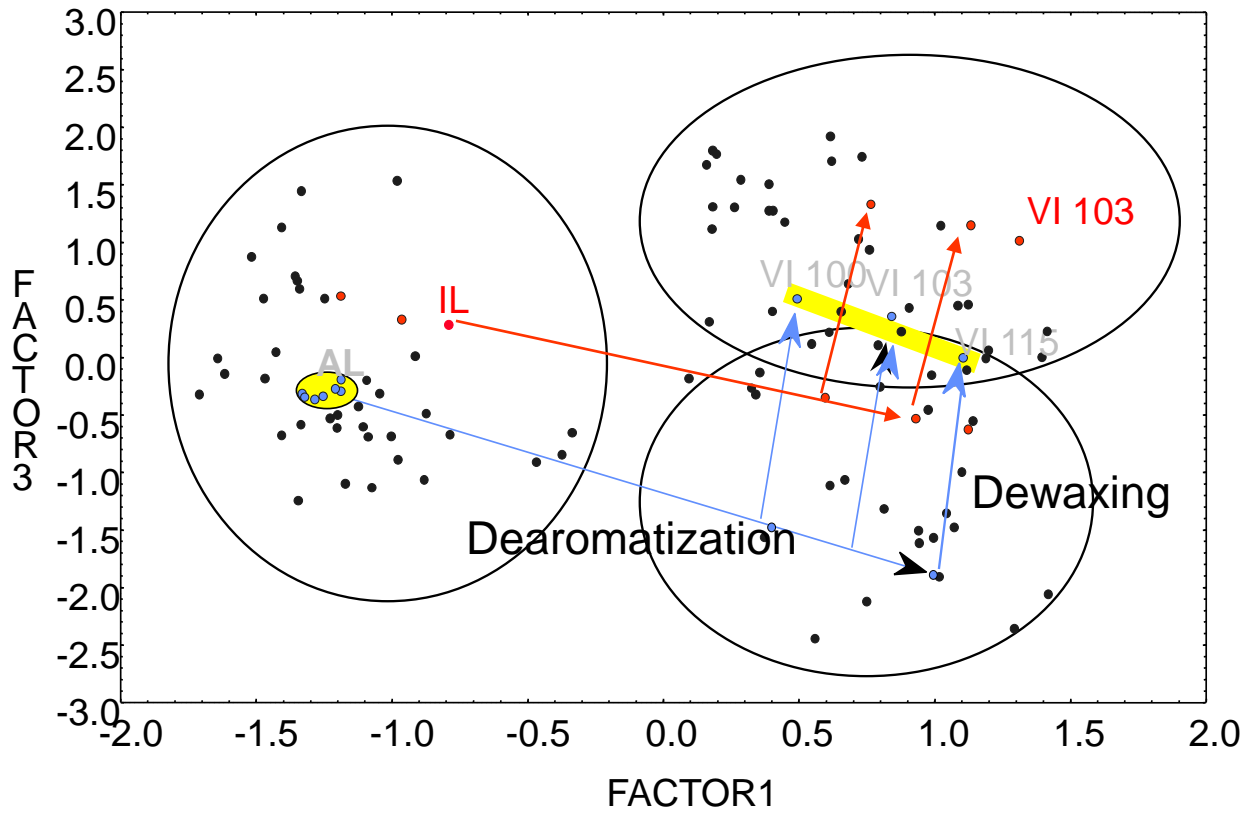
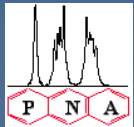
96 Hours of NMR Process Output – Aromatic Components



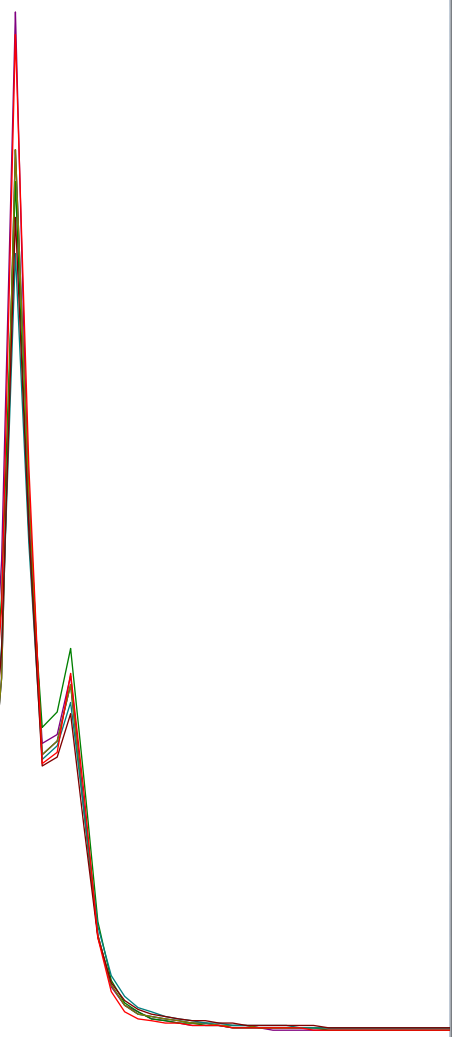


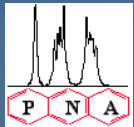
Online NMR Applications Timeline

- 1993 - Development of Laboratory Based process NMR Methodologies
- 1995 - BTU Analysis of Refinery Fuel Gas
- 1995 - Sulfuric Acid Strength in Emulsion Zone of Stratco Acid Alkylation Unit
- 1999 - Diesel Blending System
- 1999 - Reformer Control System
- 2000 - Naphtha Cracker Feed Analyzer – Full GC PIONA
- 2000 - Crude Unit Analyzer
- 2000 - Crude Blending System
- 2001 - Gasoline Blending System,
- 2001 - Base Oil Manufacturing Analyzer
- 2002 - FCC Unit Analyzer

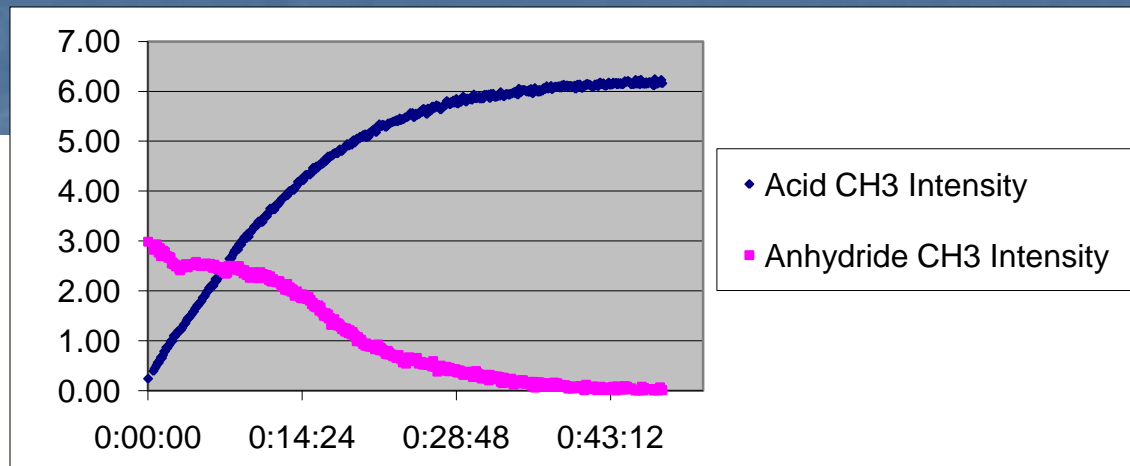


Base Oil Manufacturing – NMR Control



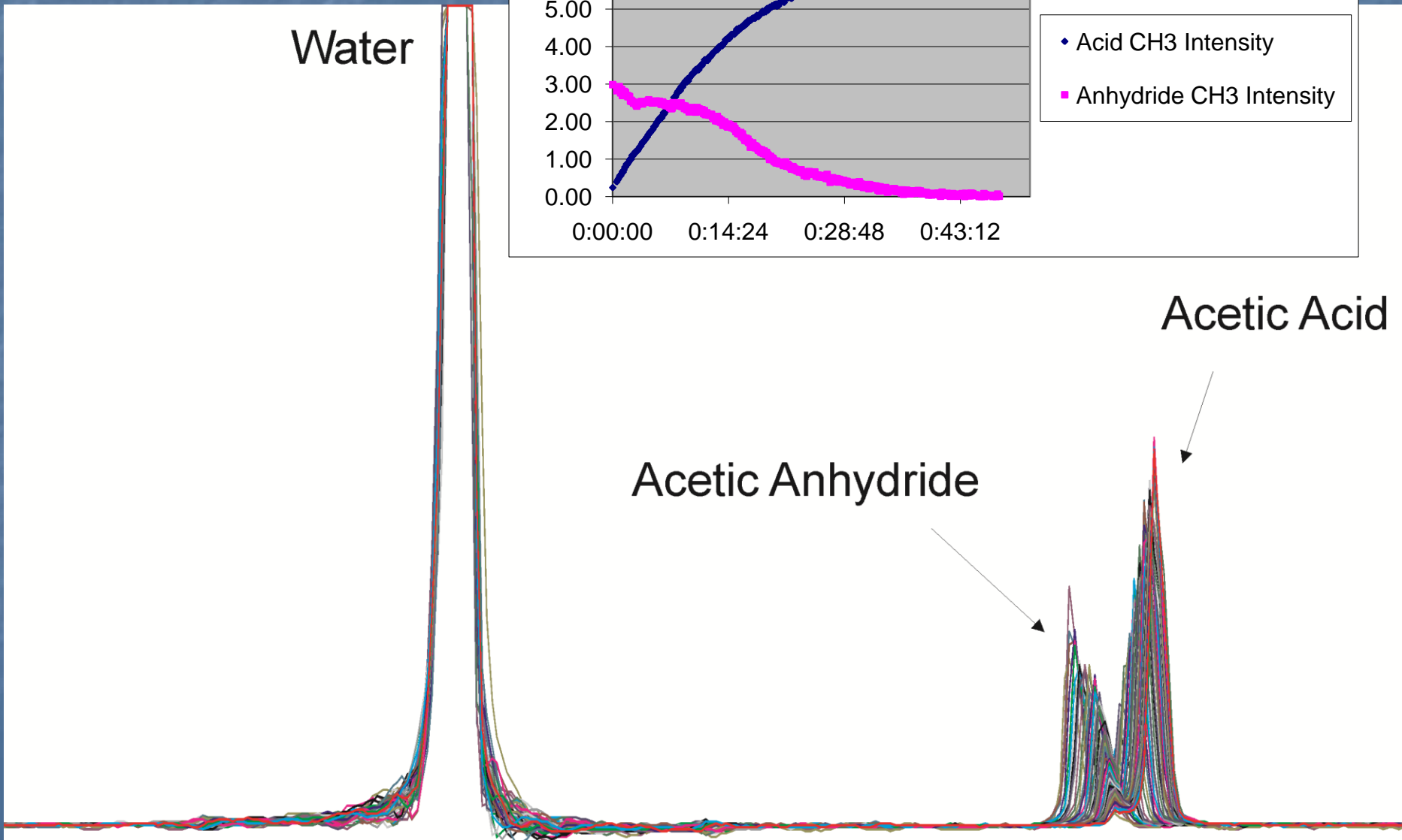


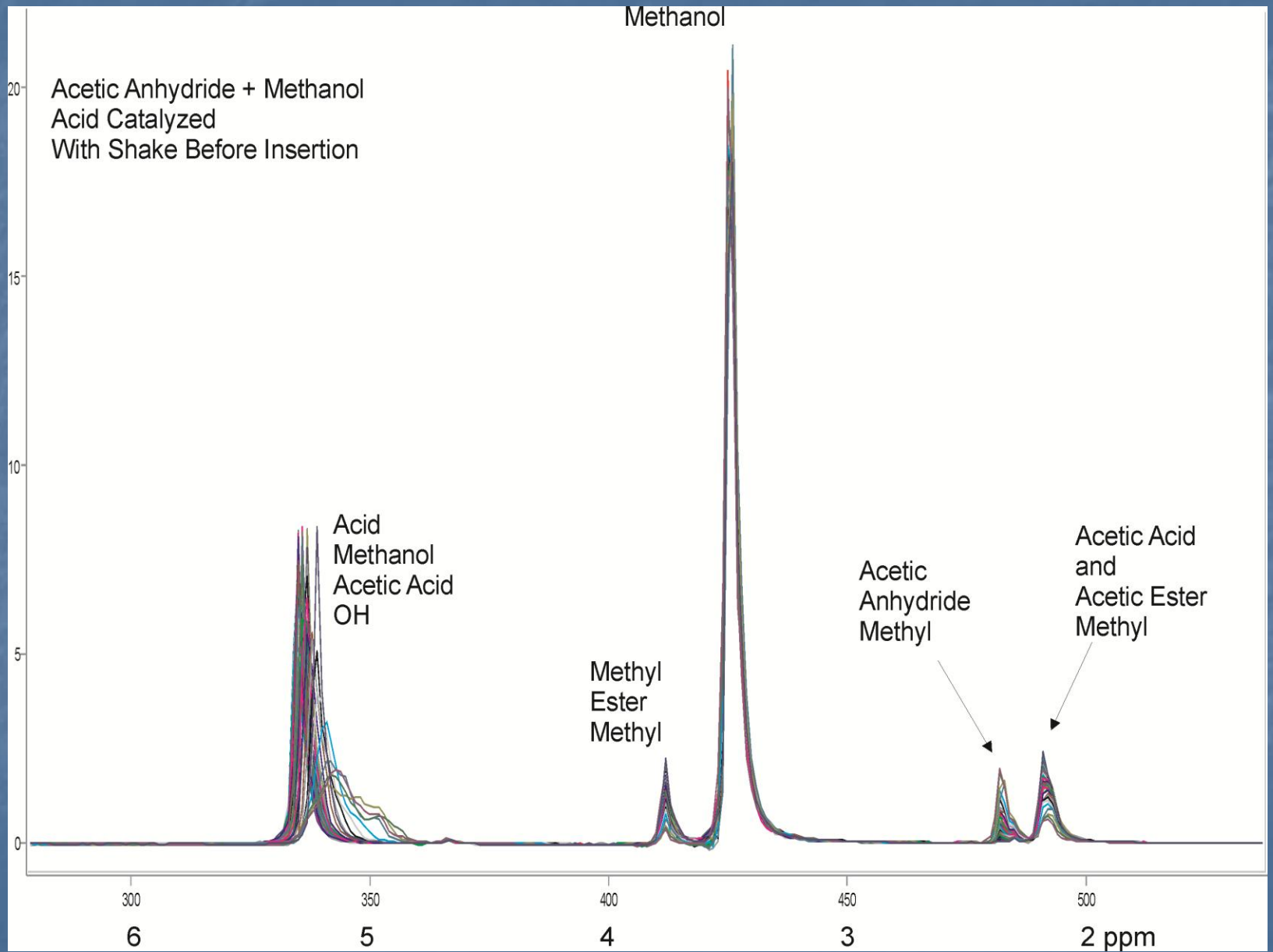
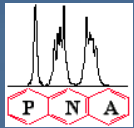
Water

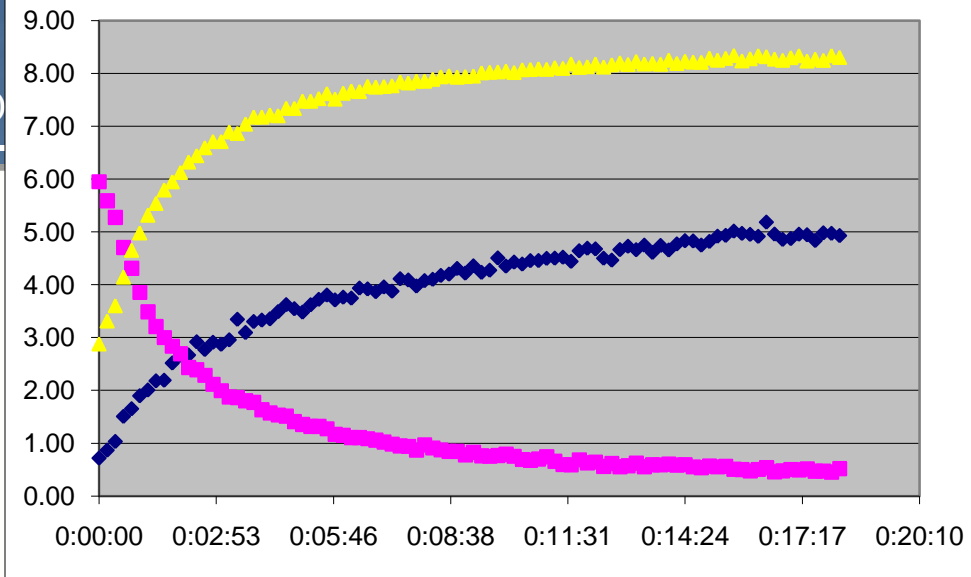
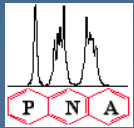


Acetic Acid

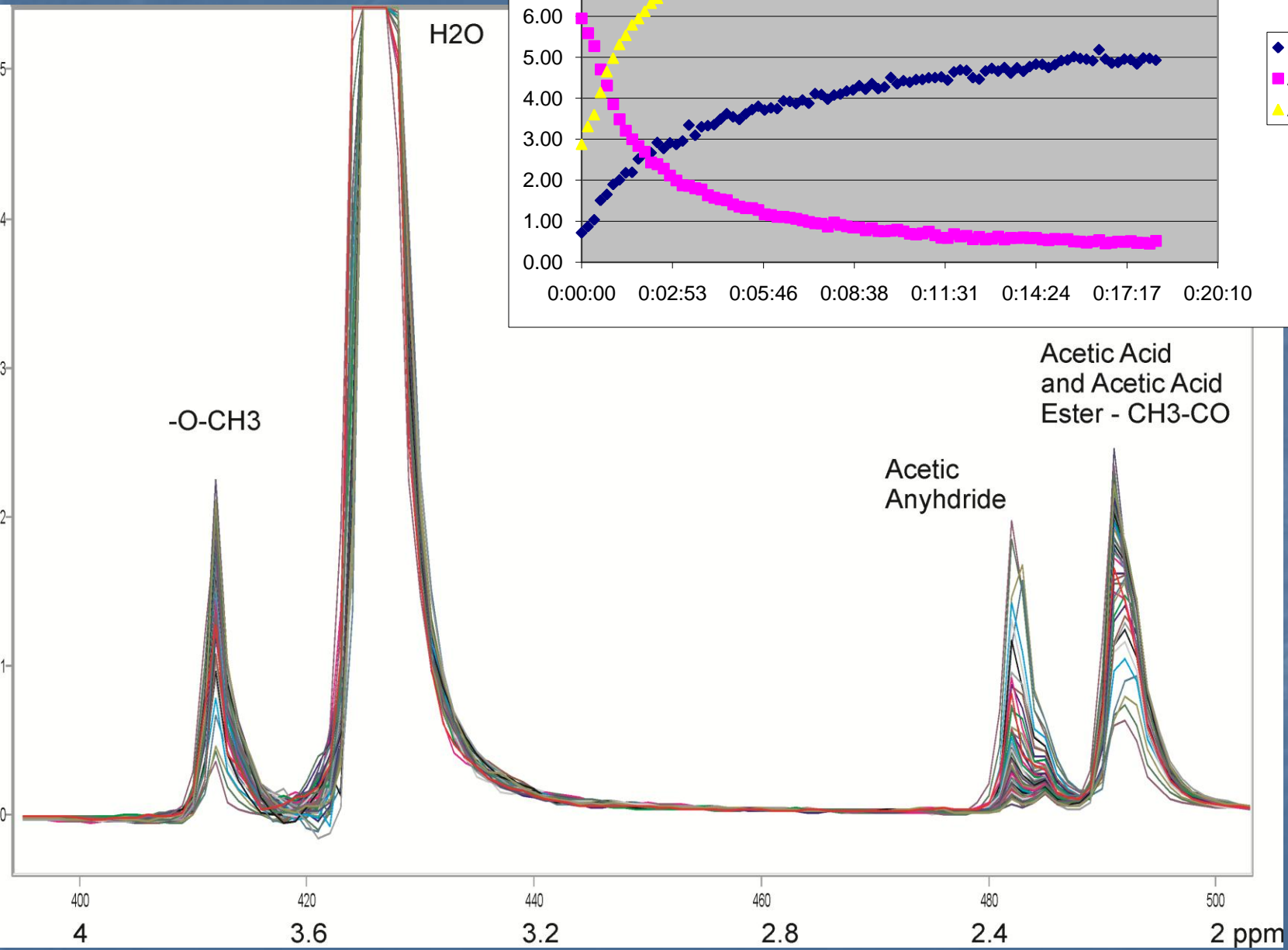
Acetic Anhydride

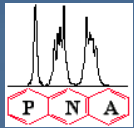






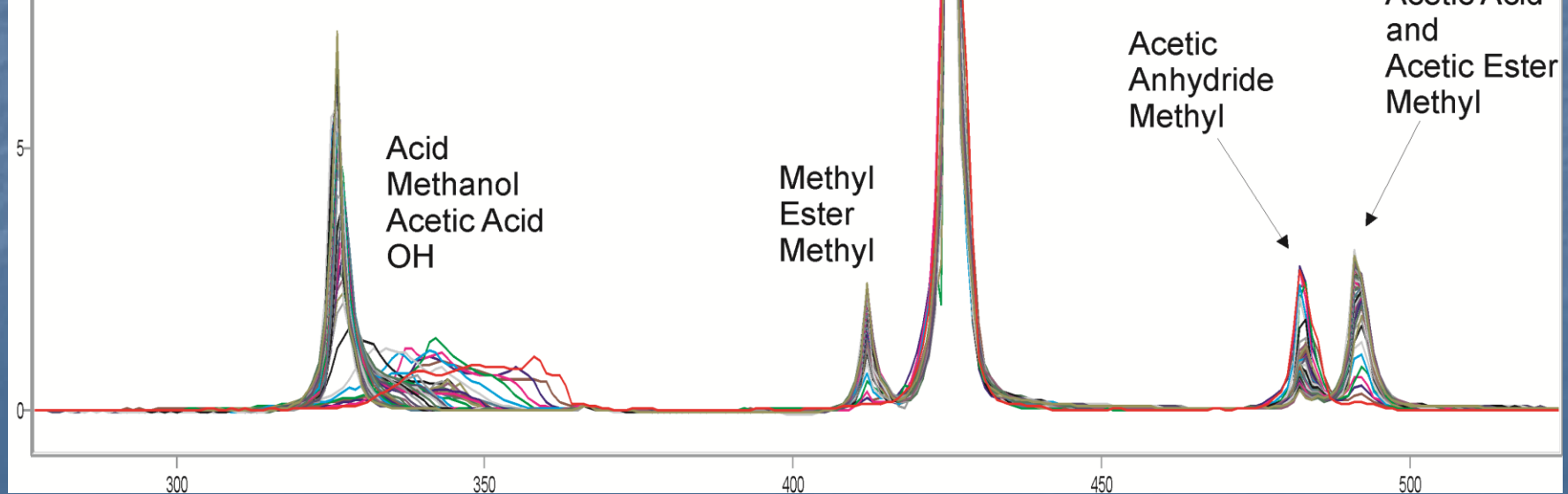
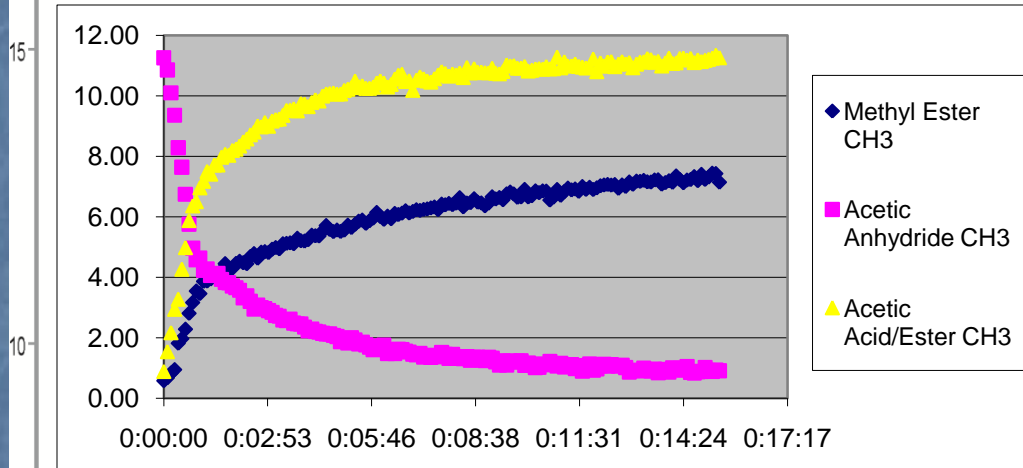
- ◆ Methyl Ester CH3
- Acetic Anhydride CH3
- ▲ Acetic Acid/Ester CH3

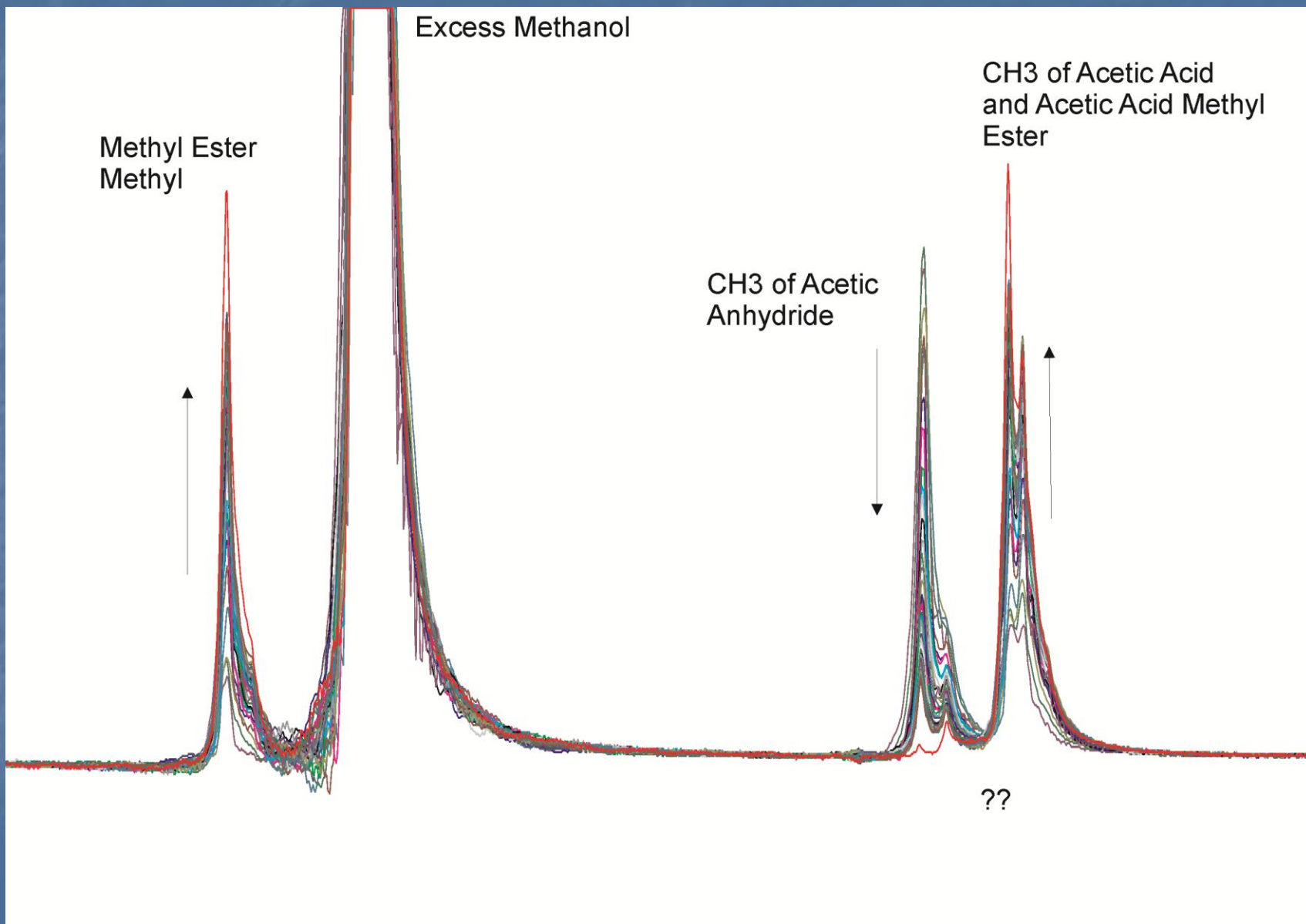
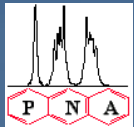


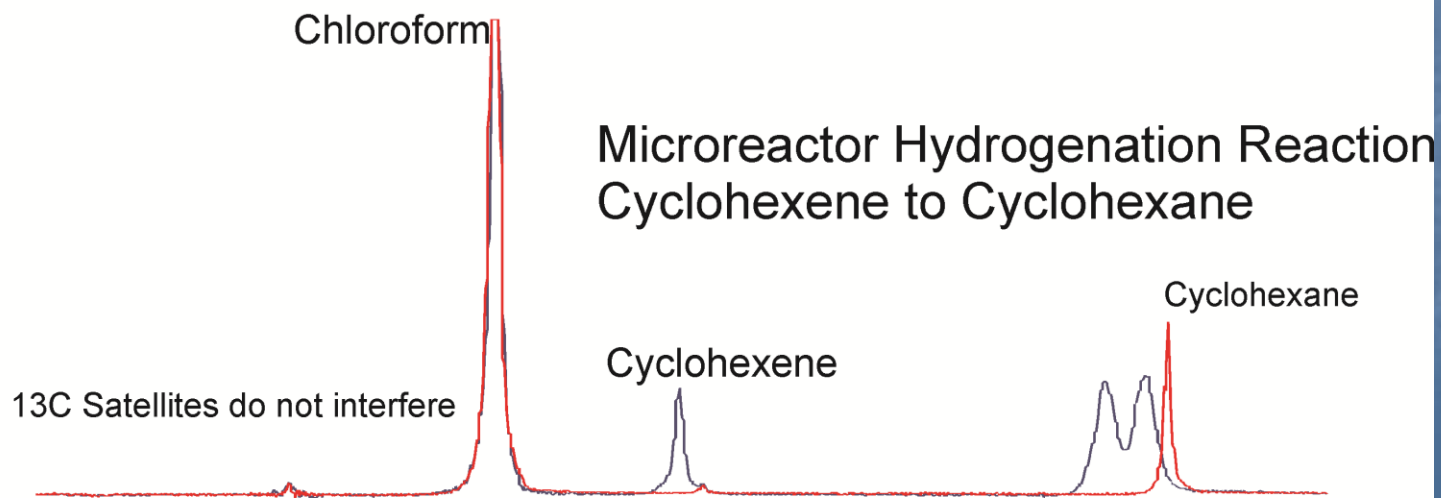
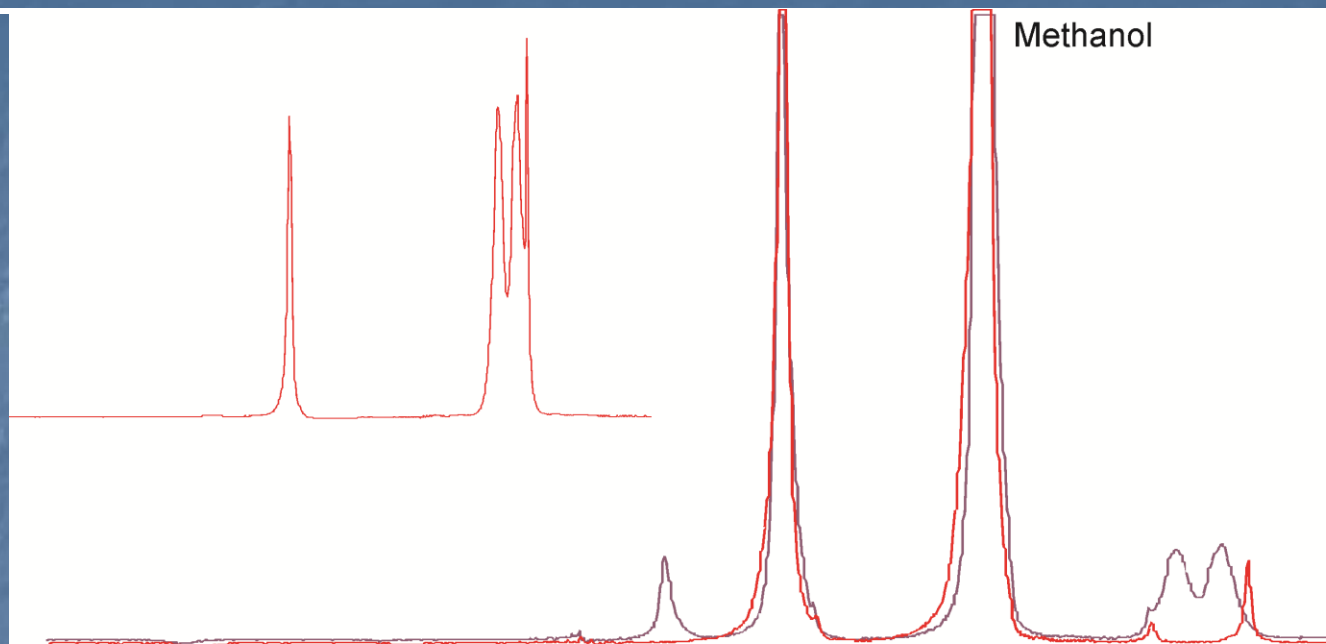
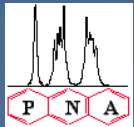


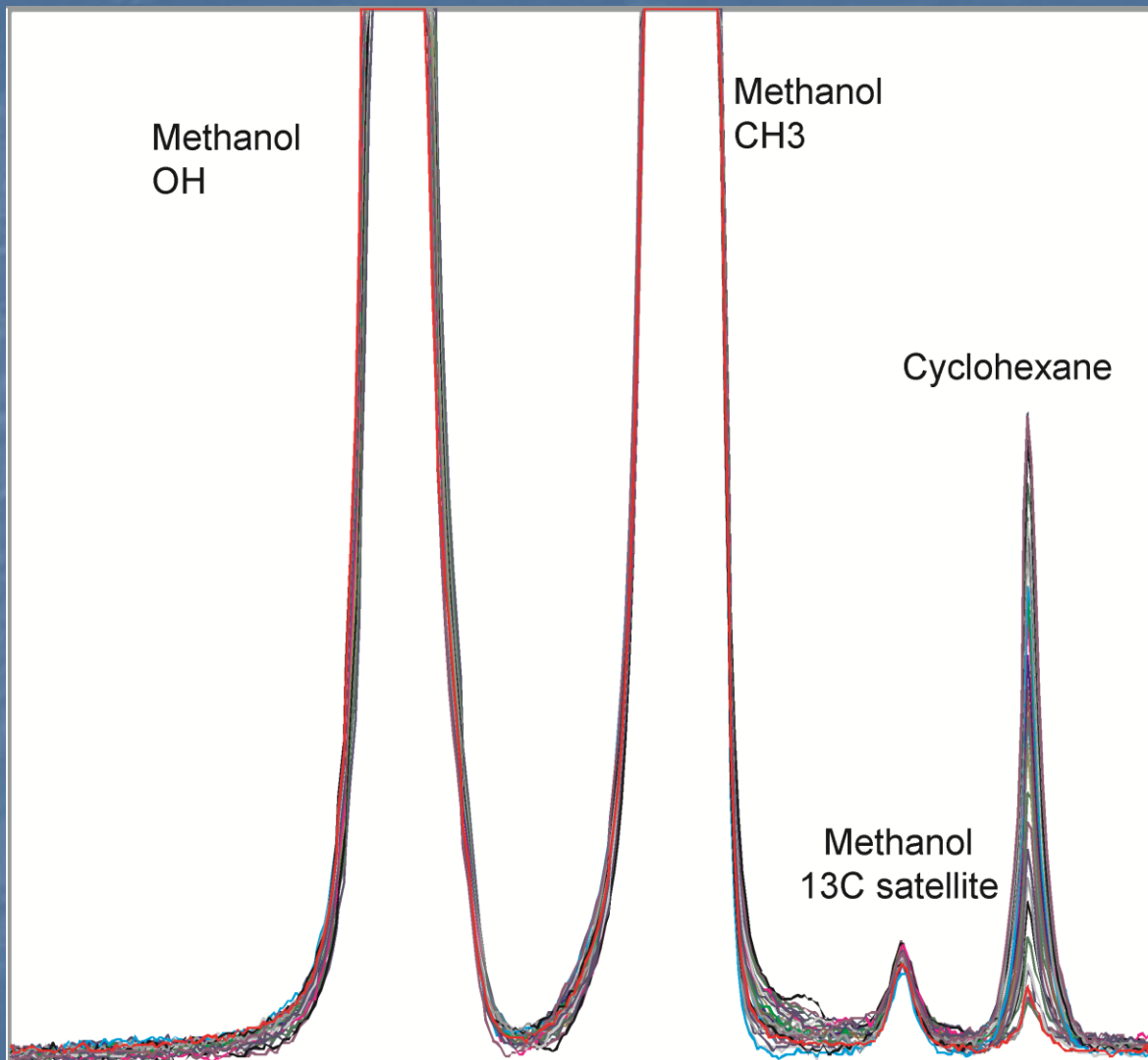
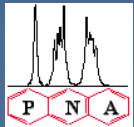
Acetic Anhydride + Methanol
Acid Catalyzed
No Shaking

Methanol









Continuous Flow (10 ml/min).
Starting Cyclohexane concentration 0.08 gm/18 ml MeOH.
Final Cyclohexane concentration 0.4 gm in 18 ml MeOH.
Cyclohexane was added in 0.01 gm increments every 12 seconds with no mixing.
Total run time: 9 minutes.



Acknowledgements

Paul Giammatteo
– PNA

Qualion NMR – Israel

Tal Cohen – ASPECT Italia