Process NMR Applications in the Refinery Utilization, Closed Loop Control, and Value Added Statements

Presented By
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Danbury, Connecticut

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Delaware ACS Process Analytical Topical Group/SAS

Company: Process NMR Associates, LLC

Founded : 1997

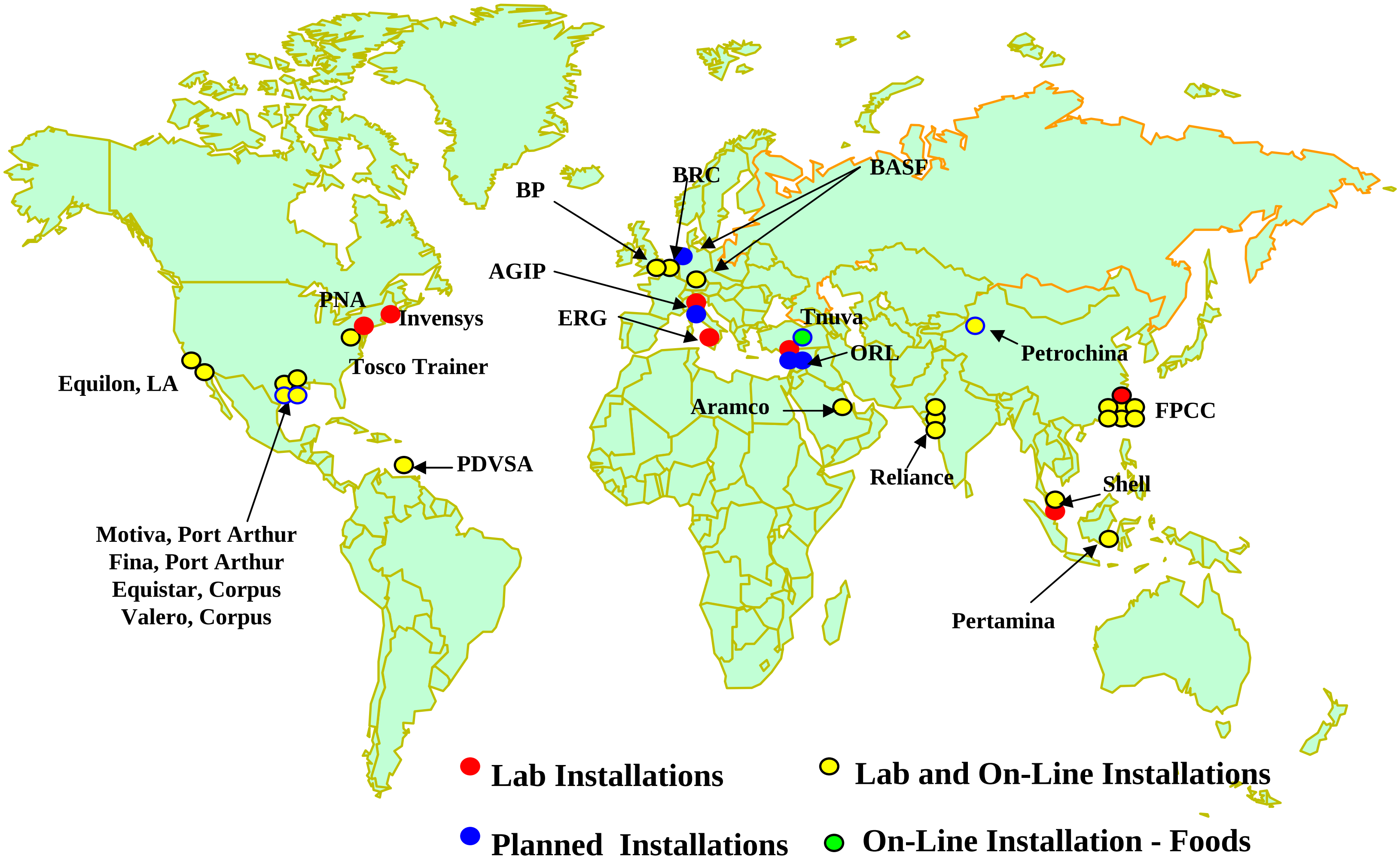
Personnel: 2 Ph.D. Chemists

Background: Analytical and Process Spectroscopy
in Petroleum and Petrochemical (Texaco Inc.)

Facilities: 2 Invensys 58 MHz Process MRA Units
300 MHz NMR (Liquids)
200 MHz NMR (Solids)

Business: Application Development for Invensys Process MRA
Analytical NMR Services for Commercial and Academic Customers

Invensys Process NMR Installations



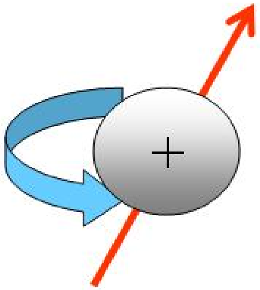
Presentation Overview

- NMR Basics – Briefly
- Advantages/Disadvantages as a Process Spectroscopy
- Applications
  1. Reformer Unit Control
  2. Crude Distillation Unit Control and Optimization
  3. Naphtha Steam Cracking Control and Optimization
- Application Snippets

  Aromaticity – FCC, Base Oil Manufacture
  Styrene-Butadiene Rubbers
  Aromatics
- Conclusion

Nuclear Magnetic Resonance Spectroscopy - The Basics

Involves Magnetic Energy of Nuclei

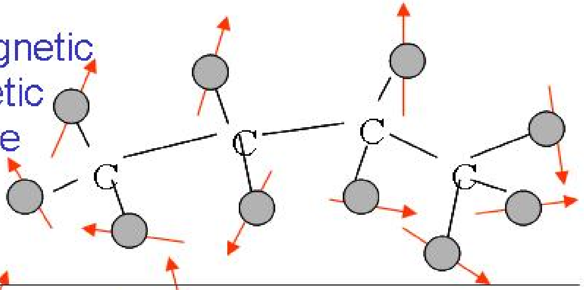


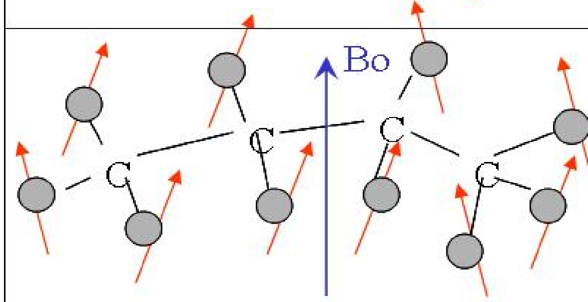
$\mathbf{m}$(Magnetic Moment)

Hydrogen Atom
(Proton)

Proton is spinning -
magnetic moment generated

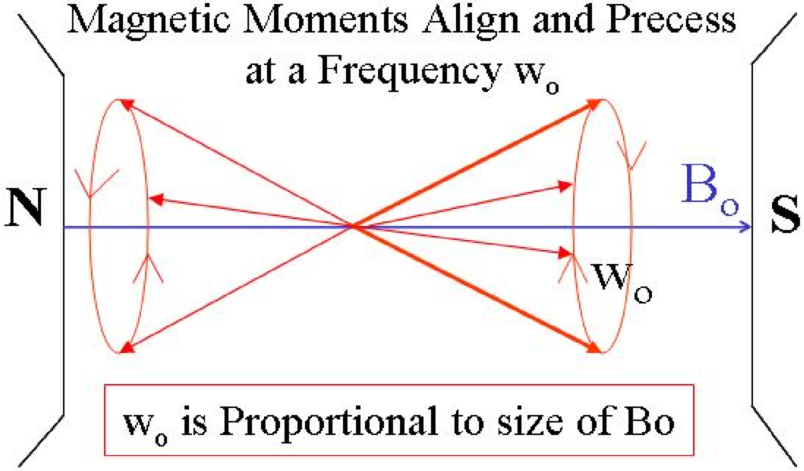
With no magnetic field, magnetic moments are random





In Strong Magnetic Field (Bo), magnetic moments align along Bo

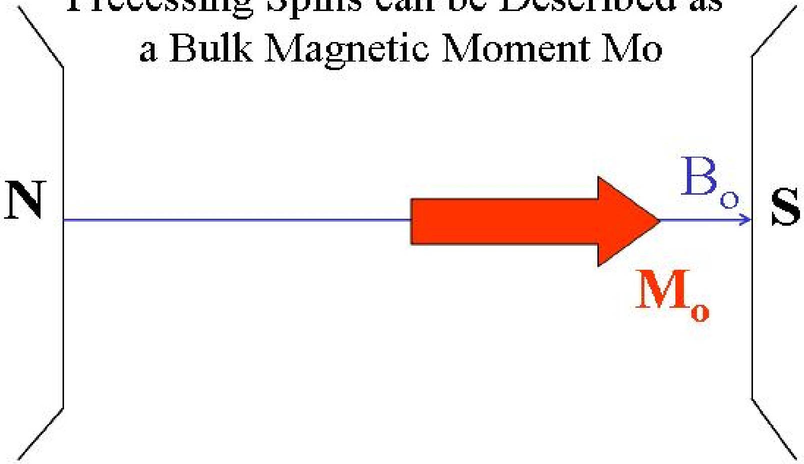
Magnetic Moments Align and Precess at a Frequency w_o



w_o is Proportional to size of Bo

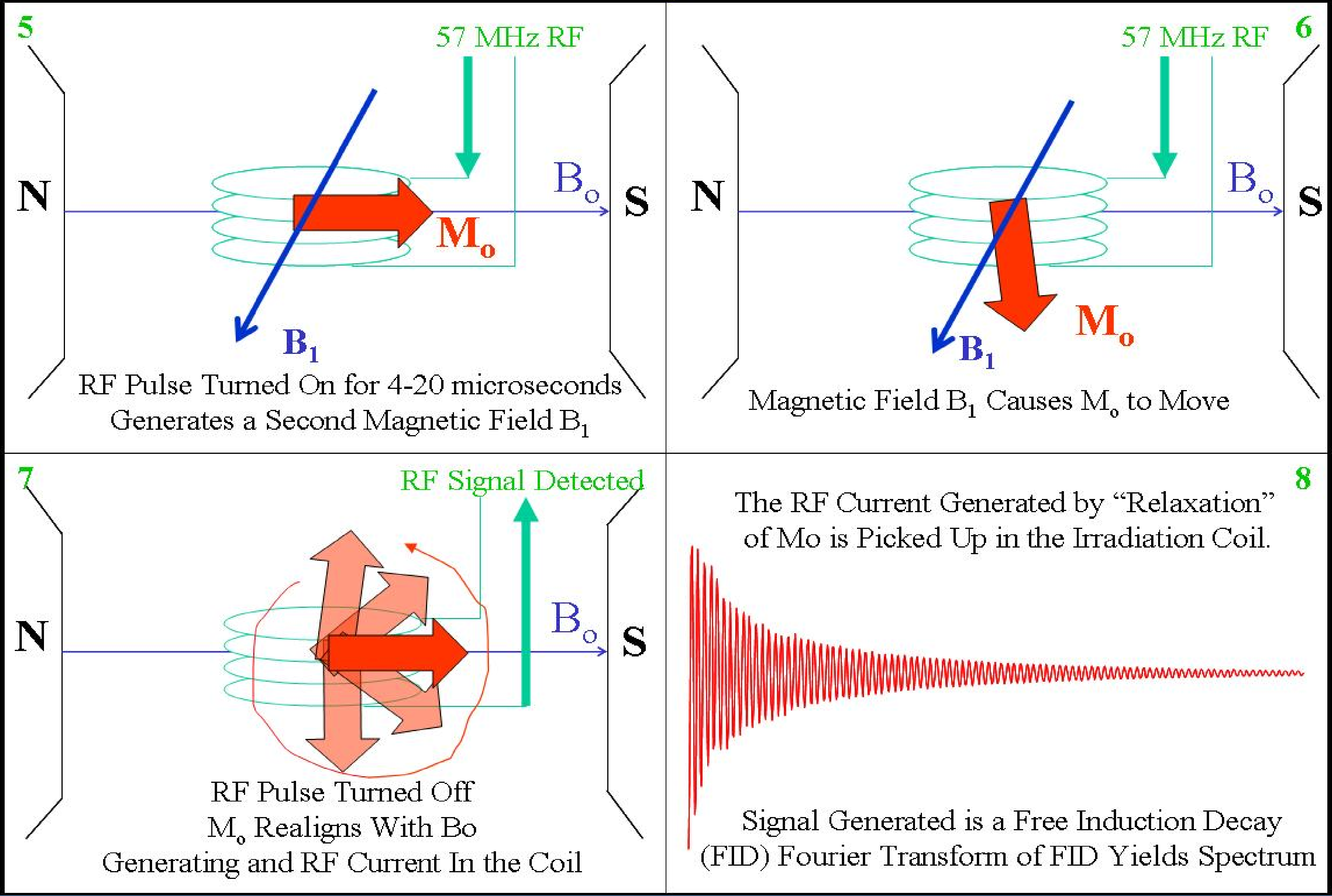
Bo = 1.35 Tesla w_o = 58 MHz

Precessing Spins can be Described as a Bulk Magnetic Moment Mo



Mo = Summation of Individual Magnetic Moments

NMR Experiment



RF Pulse Turned On for 4-20 microseconds
Generates a Second Magnetic Field B_1

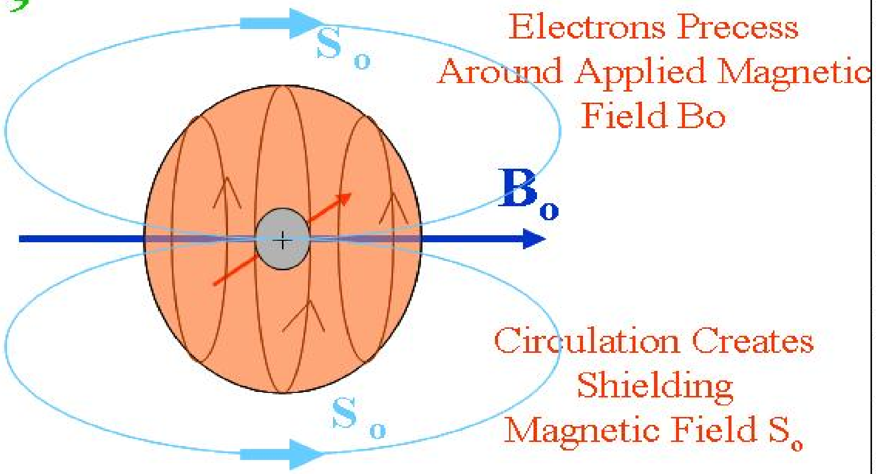
Magnetic Field B_1 Causes M_o to Move

RF Pulse Turned Off
M_o Realigns With Bo
Generating and RF Current In the Coil

The RF Current Generated by “Relaxation” of Mo is Picked Up in the Irradiation Coil.

Signal Generated is a Free Induction Decay (FID) Fourier Transform of FID Yields Spectrum

Chemical Information From NMR Spectroscopy



Electrons Precess Around Applied Magnetic Field Bo

Circulation Creates Shielding Magnetic Field S_o

NMR Chemical Shift

Differences in Electronic Environment Correspond Directly to Chemical Differences

The Shielding Effect of S_o Leads to Differences in the Nuclear Precession Frequency w_o

Hydrogens in Different Chemical Environments Yield Signals at $w_o \pm s$ (shielding effect)

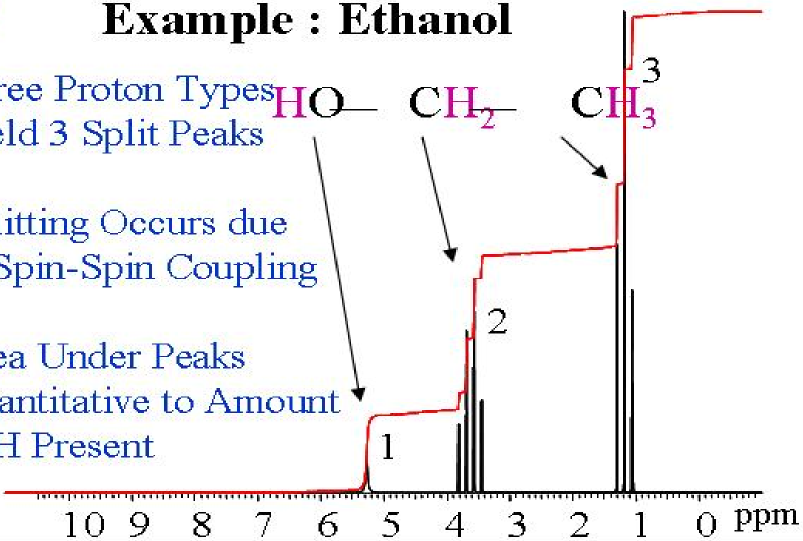
This “s” term is referred to as the chemical shift. At 57 MHz this shielding effect is maximally 600 Hz

Example : Ethanol

Three Proton Types Yield 3 Split Peaks

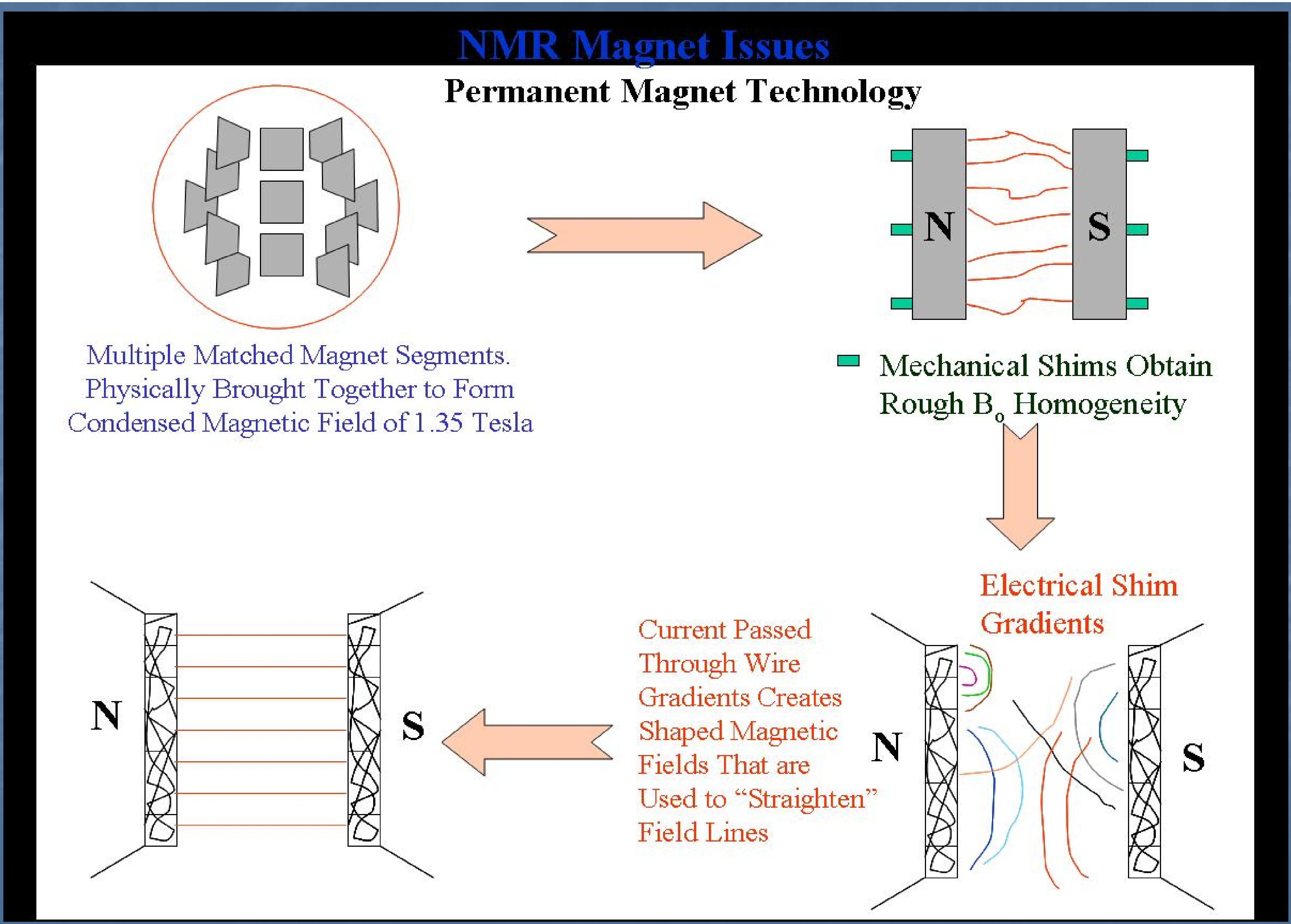
Splitting Occurs due to Spin-Spin Coupling

Area Under Peaks Quantitative to Amount of H Present



NMR Spectral Response

- Linear Response Across Entire Spectral Range
- Peak Position and Intensity Unaffected by Temperature
- Non-Optical Spectroscopy - No Cell Fouling
- Radiofrequency Irradiation of Entire Sample Volume - No Wall Contamination Issues
- Water - Readily Excluded From Modeling



NMR Magnet Issues

Permanent Magnet Technology

Multiple Matched Magnet Segments.
Physically Brought Together to Form
Condensed Magnetic Field of 1.35 Tesla

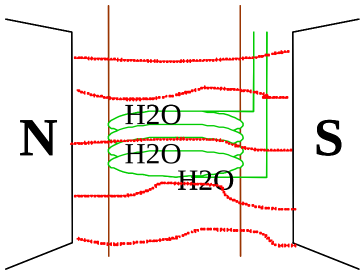
🟩 Mechanical Shims Obtain Rough B_o Homogeneity

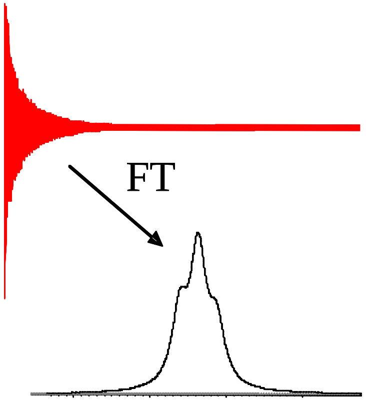
Electrical Shim Gradients

Current Passed Through Wire Gradients Creates Shaped Magnetic Fields That are Used to “Straighten” Field Lines

NMR Spectroscopy Why Shim? NMR Imaging (MRI)

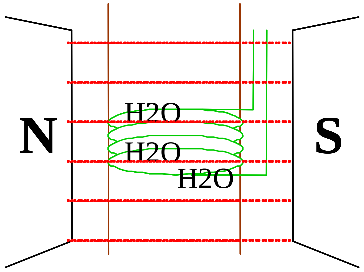
Example : H_2O in Line

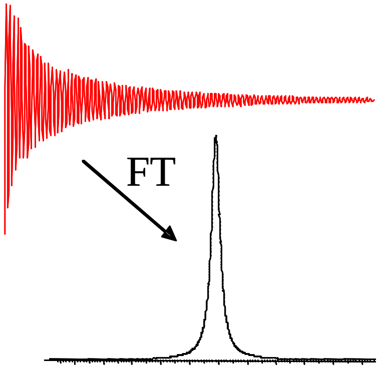




Bad Shim
Inhomogeneous Field

Bad Shim or 3 Different H-Types?

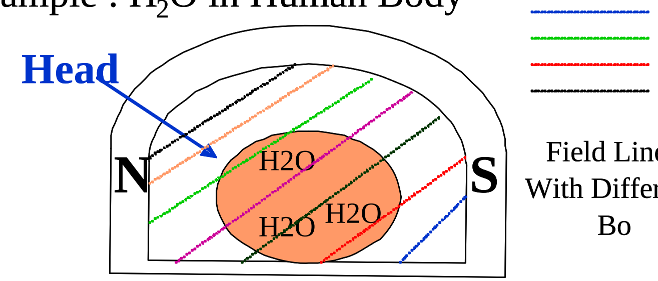




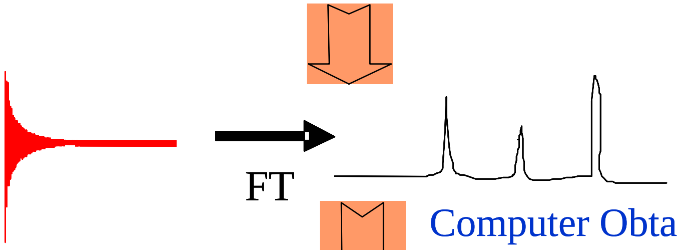
Good Shim
Homogeneous Field

H_2O Should Give One Resonance if Shim is Good

Example : H_2O in Human Body

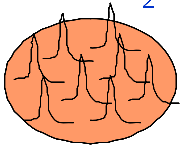


Field Lines
With Different
Bo

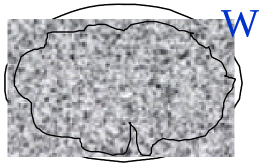


Computer Obtains Spatial Location of H_2O in Head

In MRI Large Shims are Utilized to Distort the Magnetic Field in a Known Manner in Order to Make the H_2O Peak Position Spatially Dependent



Computer Generates Image Based on Water Location



NMR Innovations Developed to Bring NMR On-Line

- Permanent Magnet Stability and Design
- Shimming Protocols
- Flow-Through Probe Technology
- Post Processing Developments
  - Robust auto-phasing routines
  - Frequency Domain Averaging
  - Post-processing monitoring of each constituent spectrum for heavy stream analyses where sediment/rust may be present.

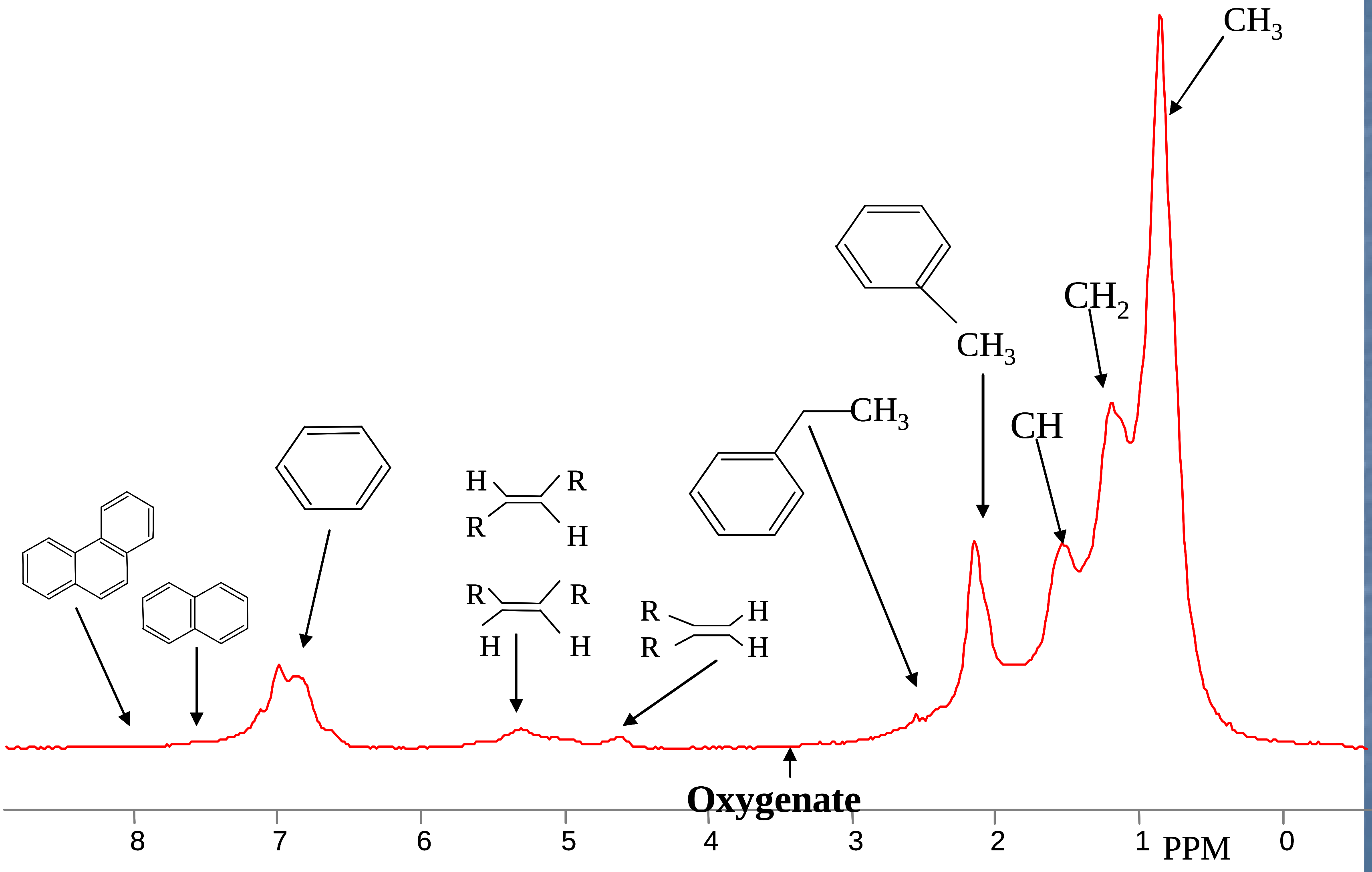
Advantages and Disadvantages of NMR Applied to Process

Advantages:

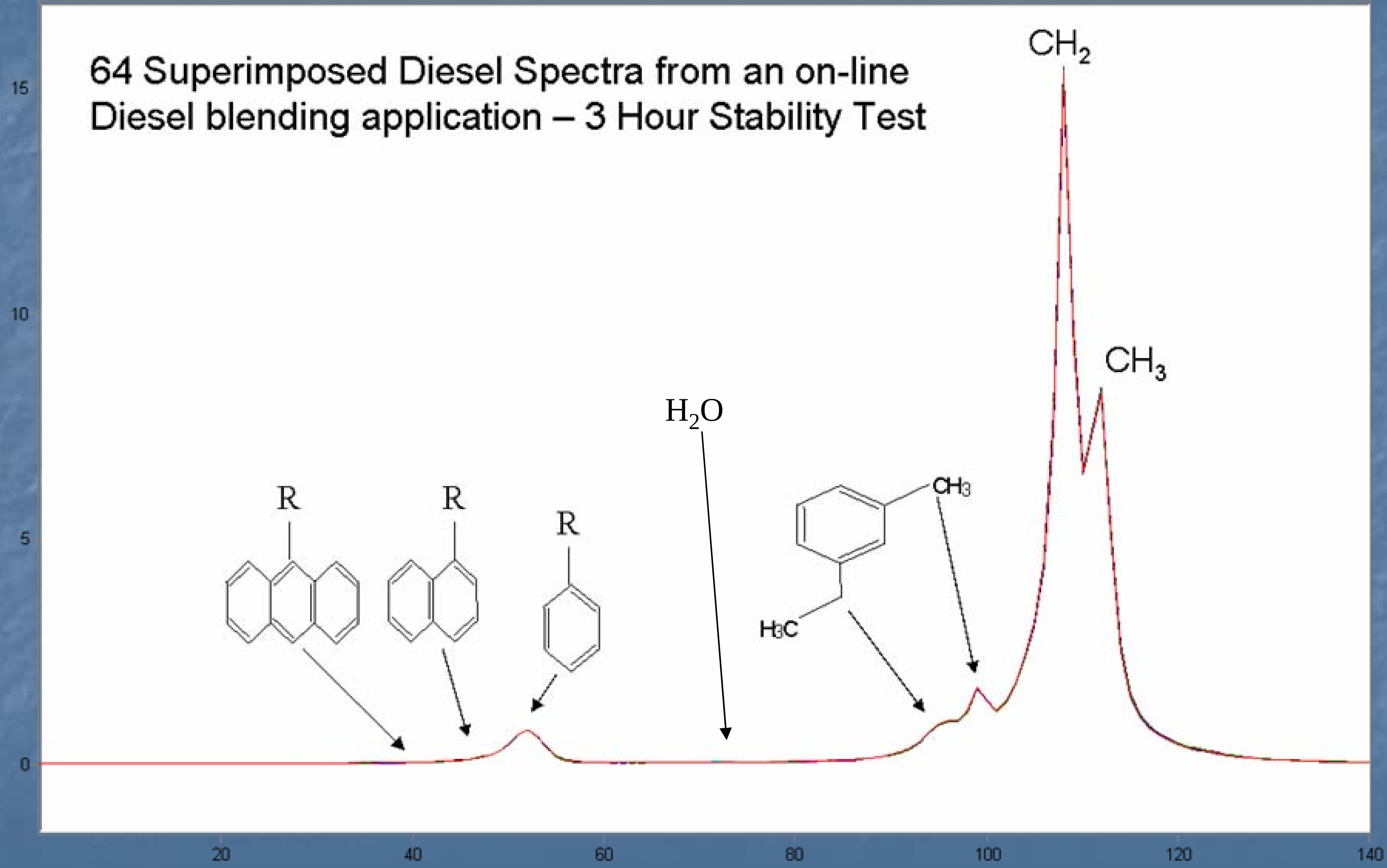
Non-Optical Spectroscopy
No Spectral Temperature Dependence
Minimal Sampling Requirements
Spectral Response to Sample Chemistry is Linear
Chemical Regions of NMR Spectra are Orthogonal
Entire Volume is Sampled by the RF Experiment
Water is in Distinct Region and can be digitally removed
Detailed Hydrocarbon information is readily observed.
Fundamental Chemical Information Can be Derived Directly from Spectrum.
Colored/Black Samples Readily Observed

Disadvantages:

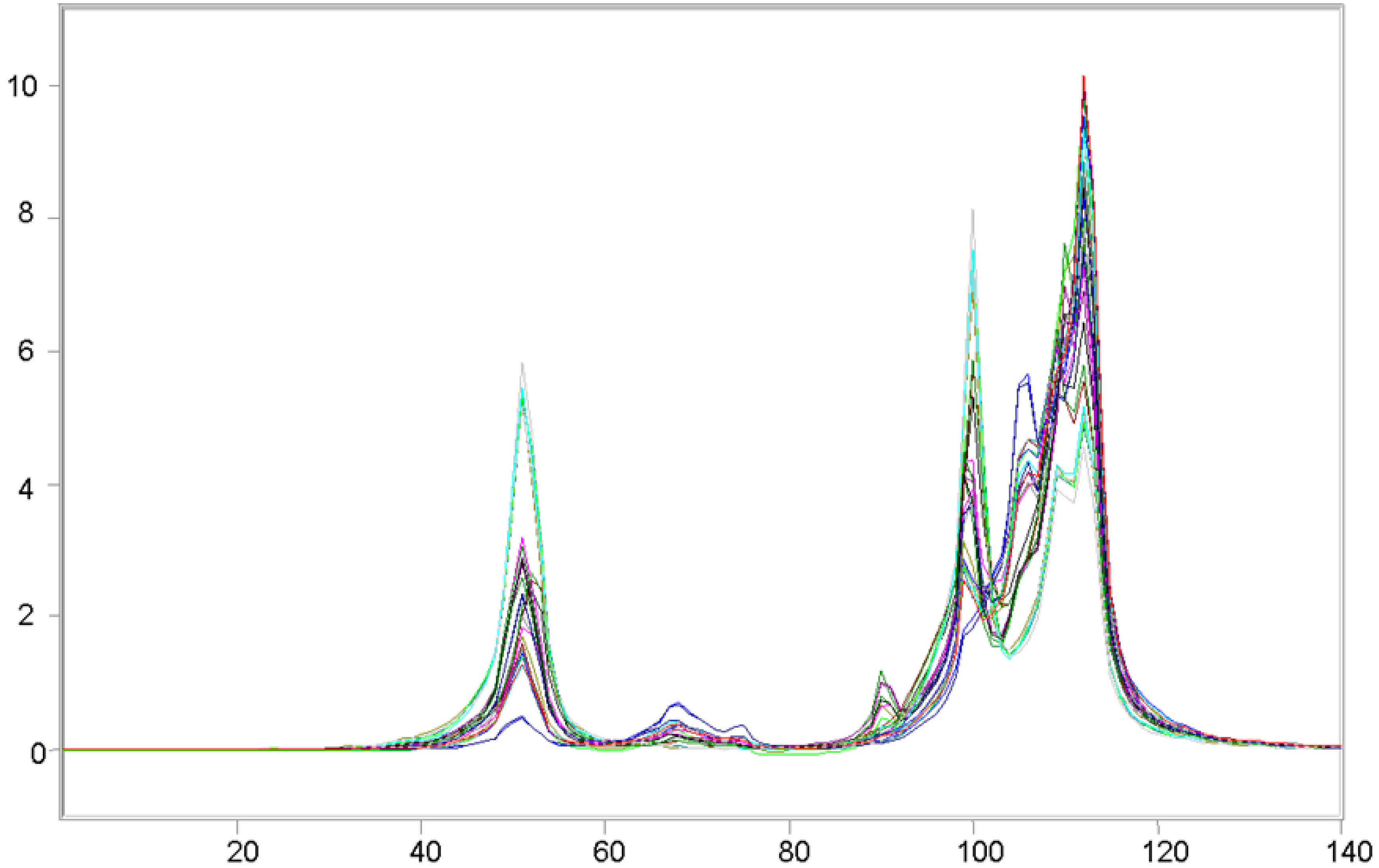
Solids Cannot be Observed
Individual Molecular Component Sensitivity Not Observed Directly in the Spectrum.
Low Sensitivity to Impurities – Quantitative > 1000 ppm.
Sensitive to Ferro-magnetics.
Sample Viscosity Causes Resolution Changes
Non-Hydrogen Containing Species are Not Observed



H-Types Observed in a Gasoline ^{1}H NMR Spectrum


64 Superimposed Diesel Spectra from an on-line
Diesel blending application – 3 Hour Stability Test
CH2
CH3
H2O
R
R
R
CH3
H3C
15
10
5
0
20
40
60
80
100
120
140

Typical Variability Observed in Gasoline Blending



Application: Closed Loop Reformer Control

Reformer Capacity: 34,000 Barrels per Day

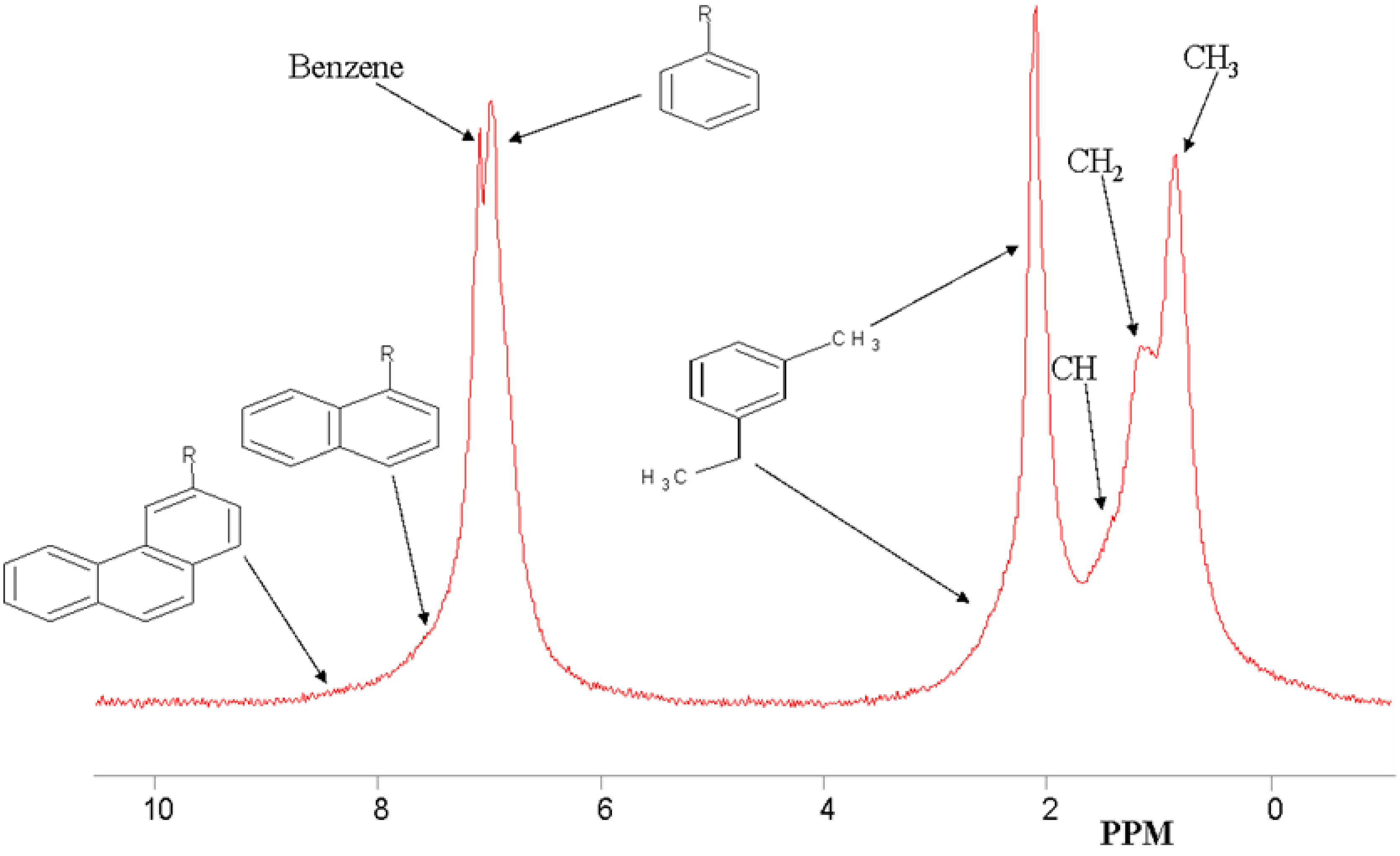
Control Strategy: Control on MON and Benzene Content

NMR Analysis: 2 Minute Analysis

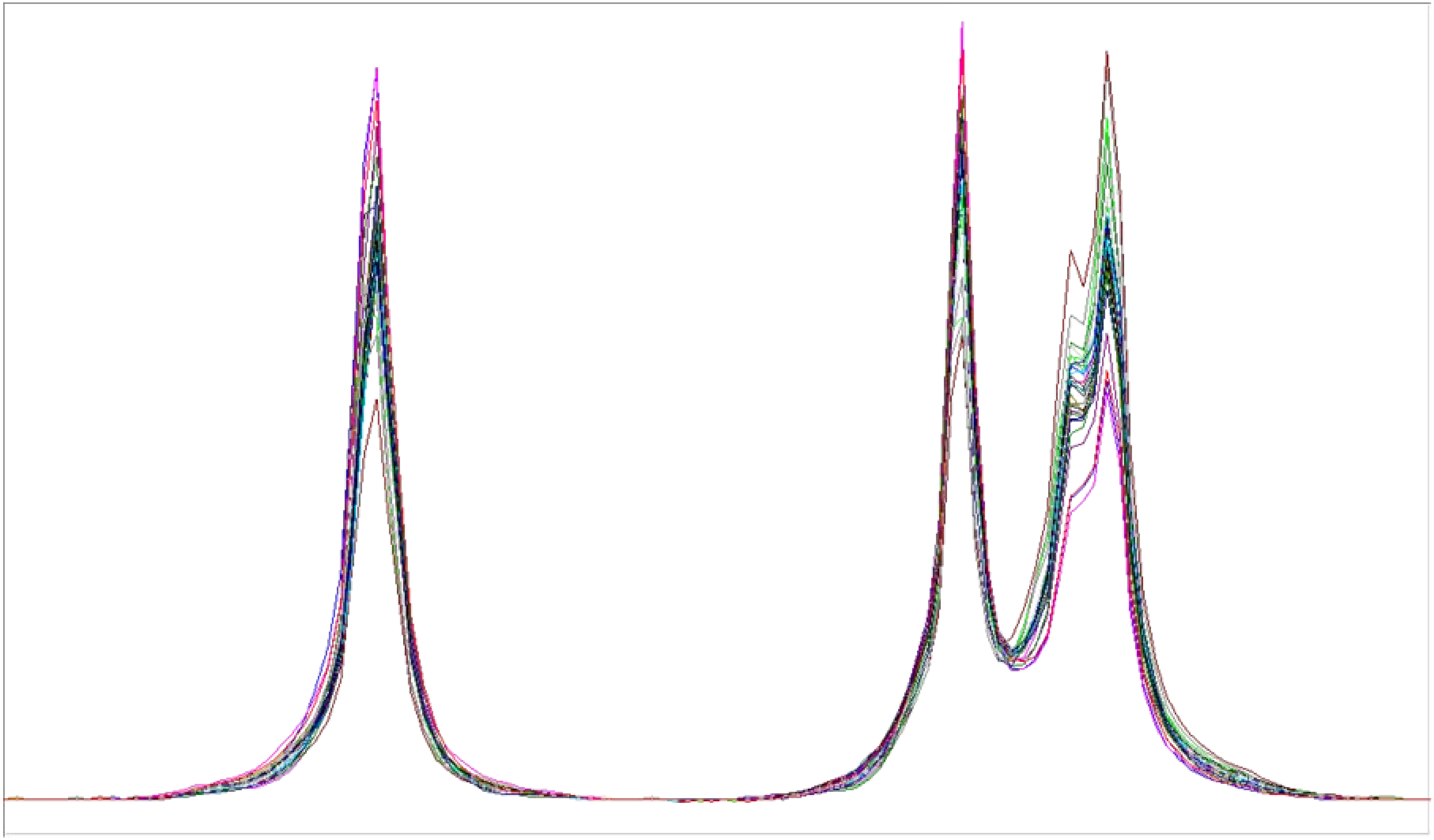
NMR PLS Outputs: RON
MON
Benzene
Total Aromatics

Value Added: Maximize Benzene Content of Reformate at 1 Wt%
Conservatively 4 cents per Barrel (Can Be Much More)

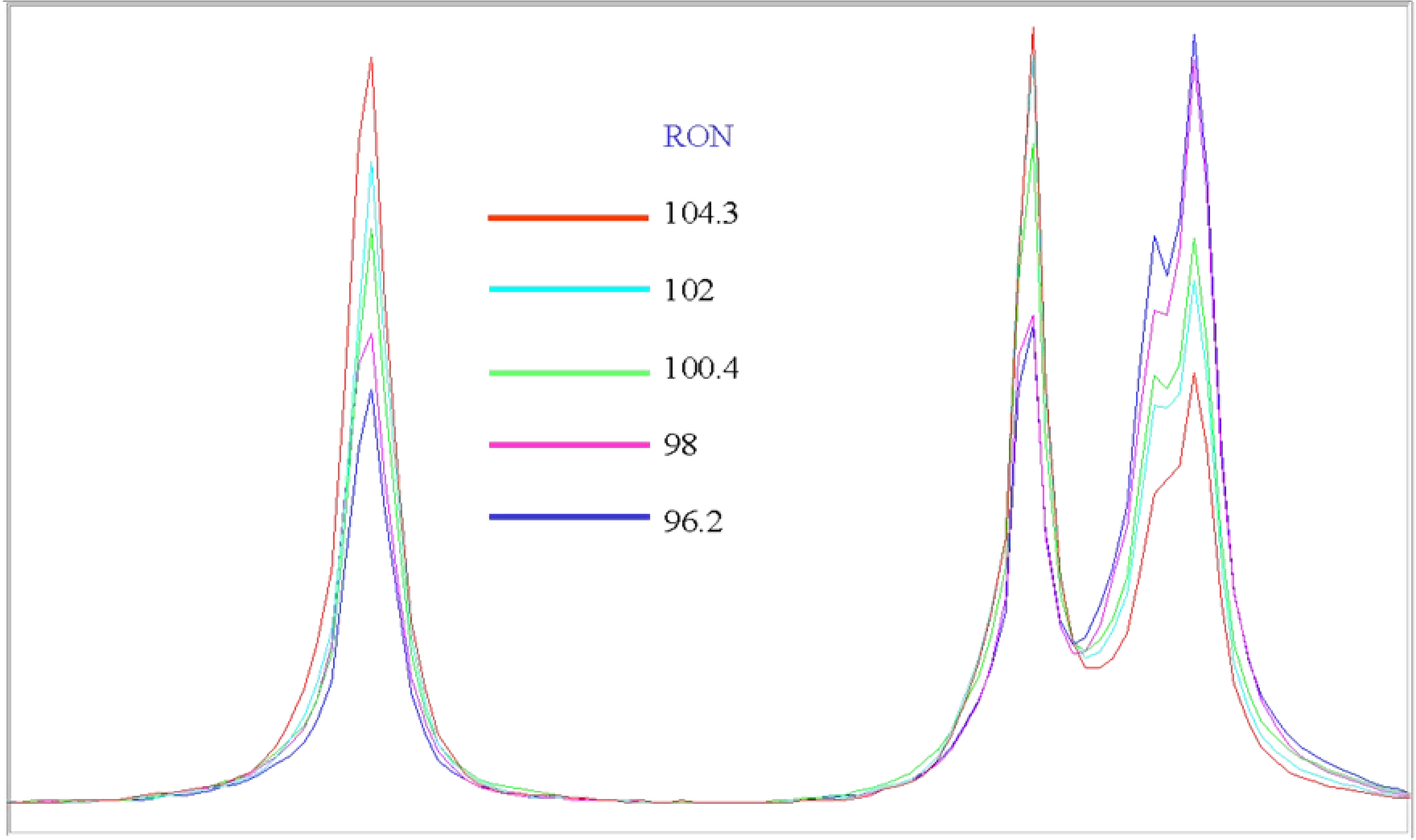
Performance : NMR Available 98%+ For Past Year
Models Unchanged for 2 Years
Value Gained From Control $10,000 - $35,000 / Week



Chemical Breakdown of ^{1}H NMR Spectrum of Reformate

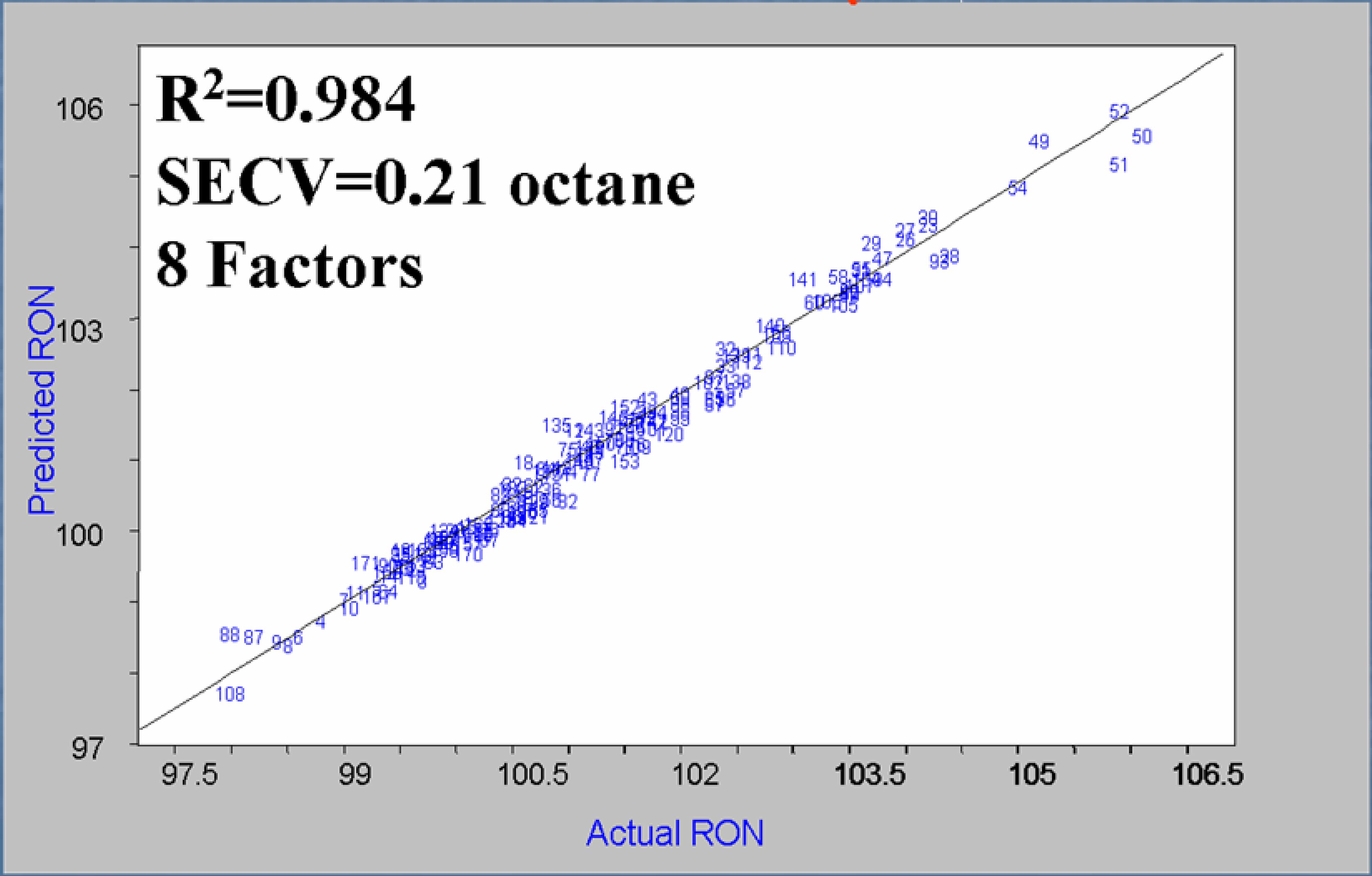


Typical Variation of Processed NMR Data Observed in Reformate Data Set



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

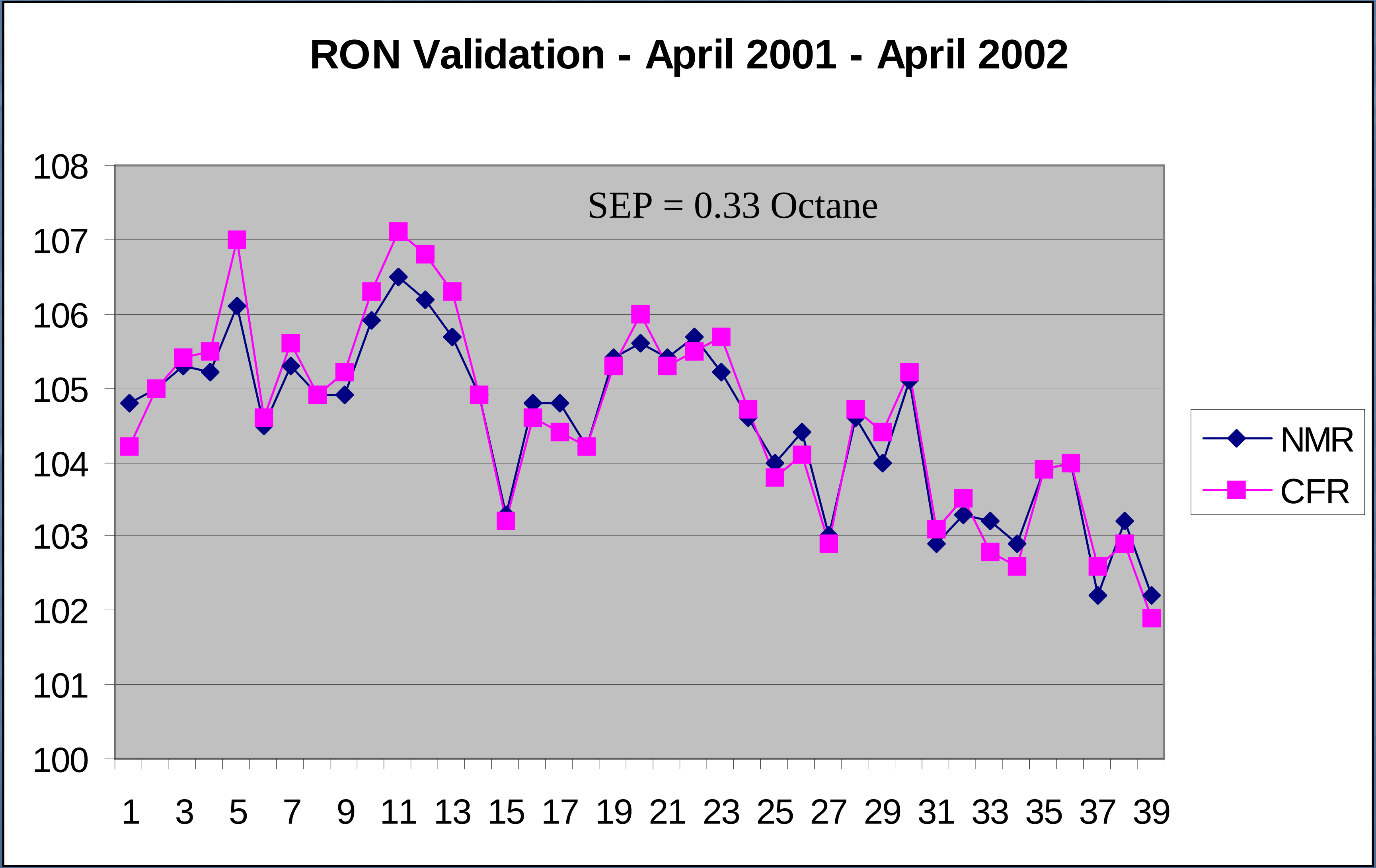
Current Model on System



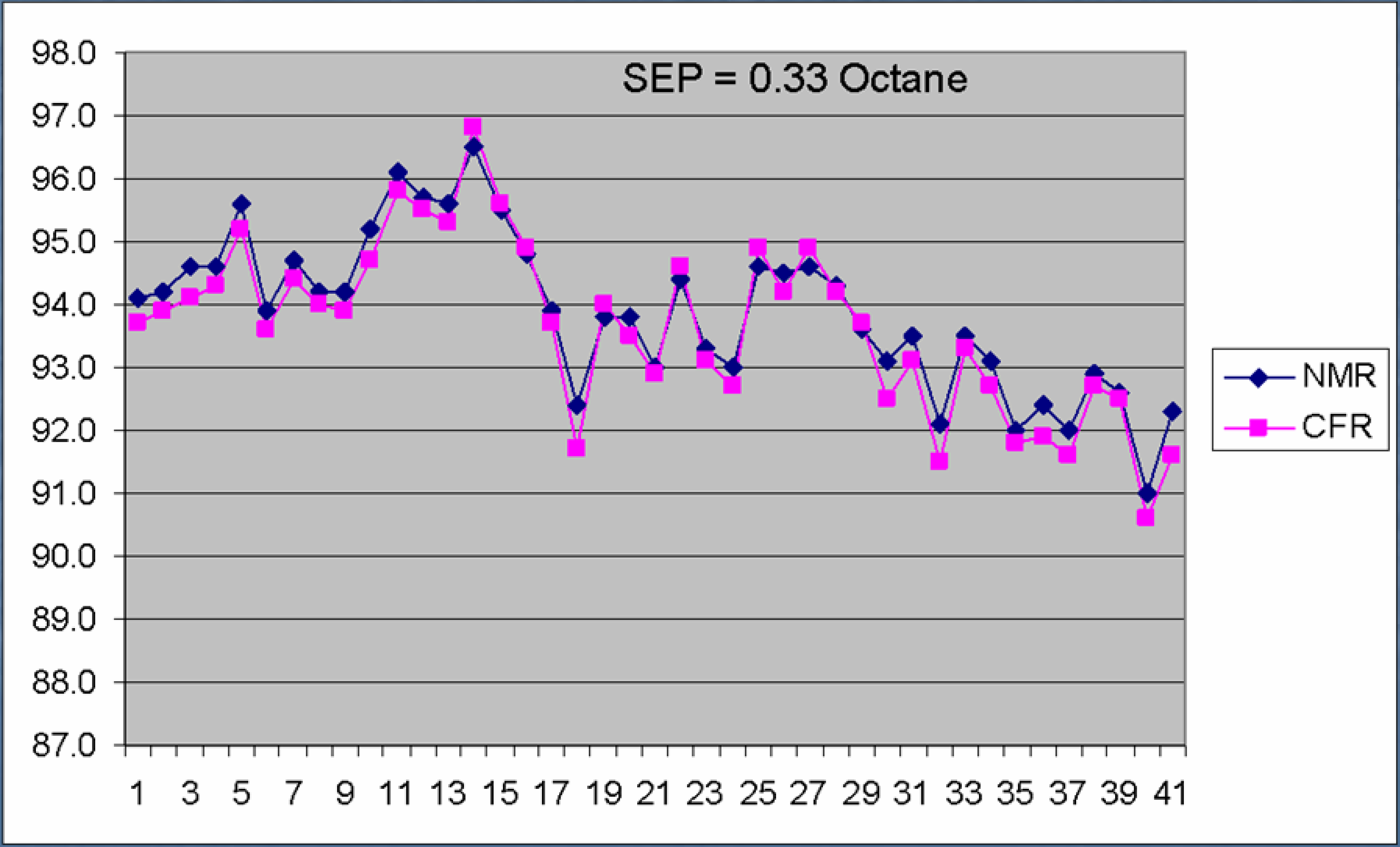
R^2=0.984

SECV=0.21 octane

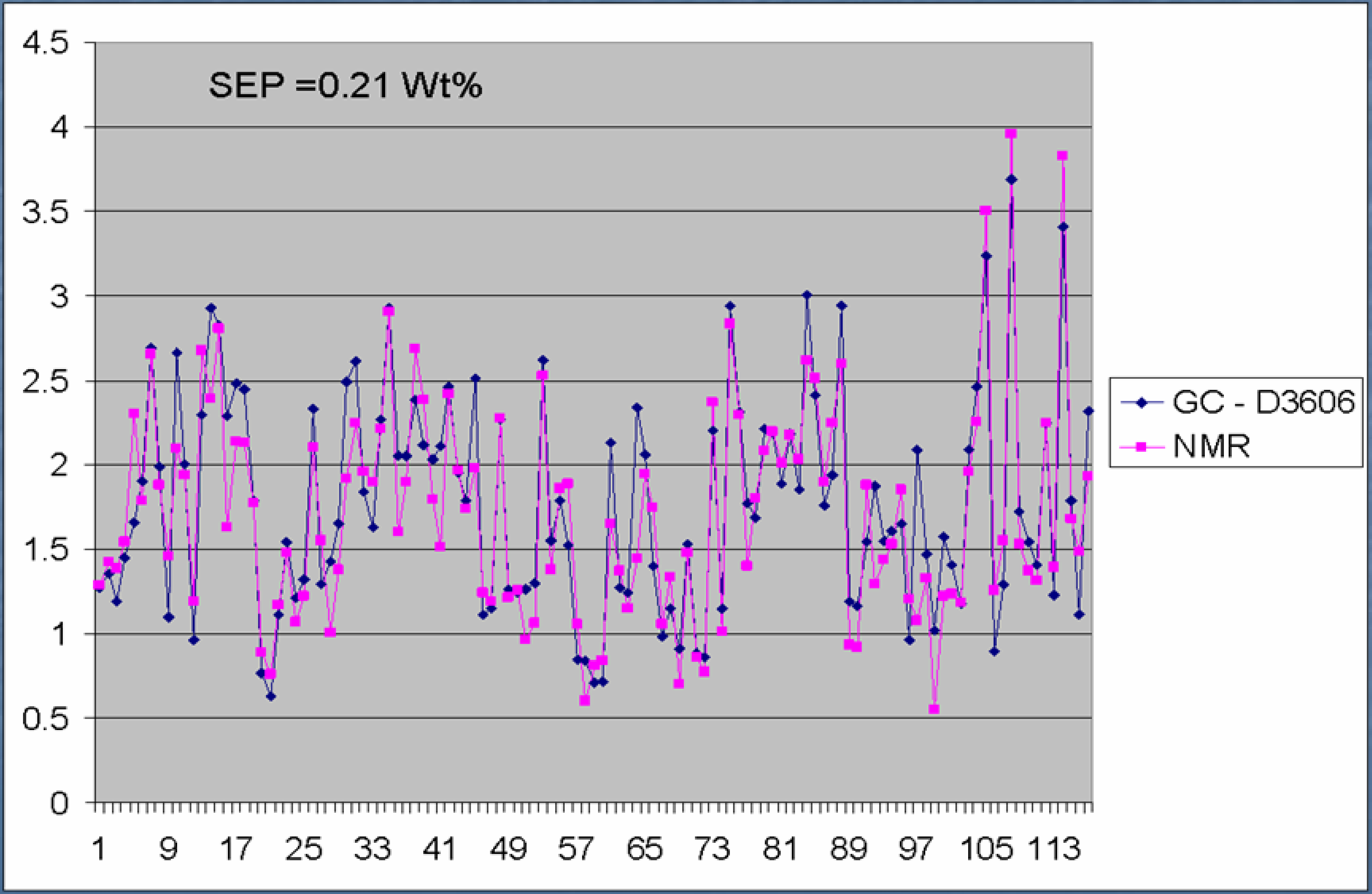
8 Factors


RON Validation - April 2001 - April 2002
SEP = 0.33 Octane
108
107
106
105
104
103
102
101
100
1
3
5
7
9
11
13
15
17
19
21
23
25
27
29
31
33
35
37
39
NMR
CFR

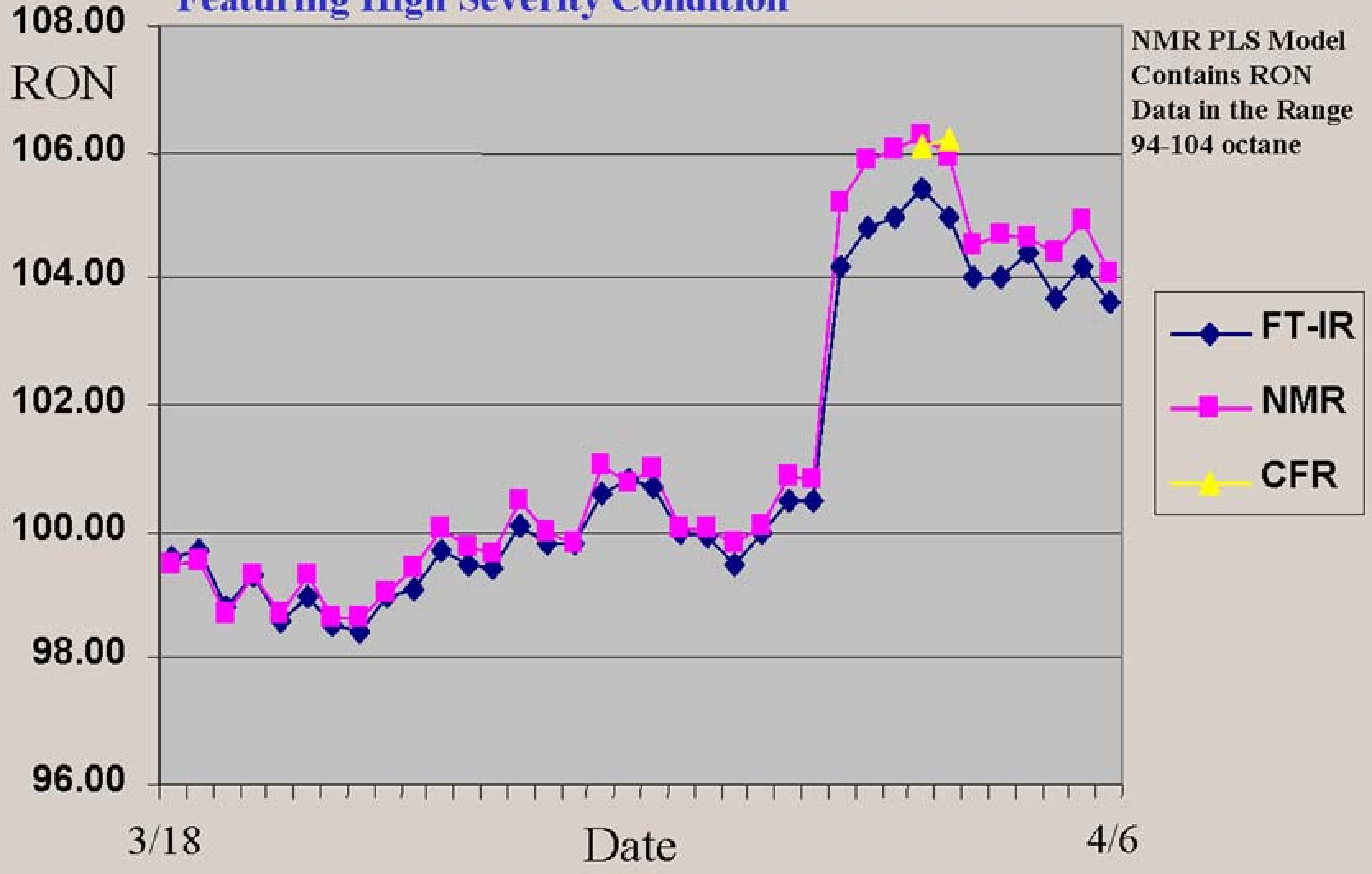
NMR Weekly Validation Performance April 2001 – April 2002



Benzene Validation October 1, 2001 – April 30, 2002



Comparison of Lab, Online-NMR and CFR for Period March 18-April 6 Featuring High Severity Condition



NMR PLS Model
Contains RON
Data in the Range
94-104 octane

Application: Crude Distillation Unit Optimization and Control

Crude Unit Capacity: 180,000 Barrels per Day

Control Strategy: Control on Kero Freeze Point
Crude Tower Optimization

NMR Analysis: 15 Minute Cycle
NMR Results into ROMEO CDU Optimization Package

NMR PLS Outputs: Naphtha – T10, T50, T90, EP
Kero – Freeze, Flash
Crude – API, Sulfur, TBP (38, 105, 165, 365, 565C)

Value Added: Kero - Approach Freeze Point Limit – Worth $600K/Year
CDU Optimization- Conservatively 4 cents per Barrel

Performance : NMR Available 98% Except for February

SSC

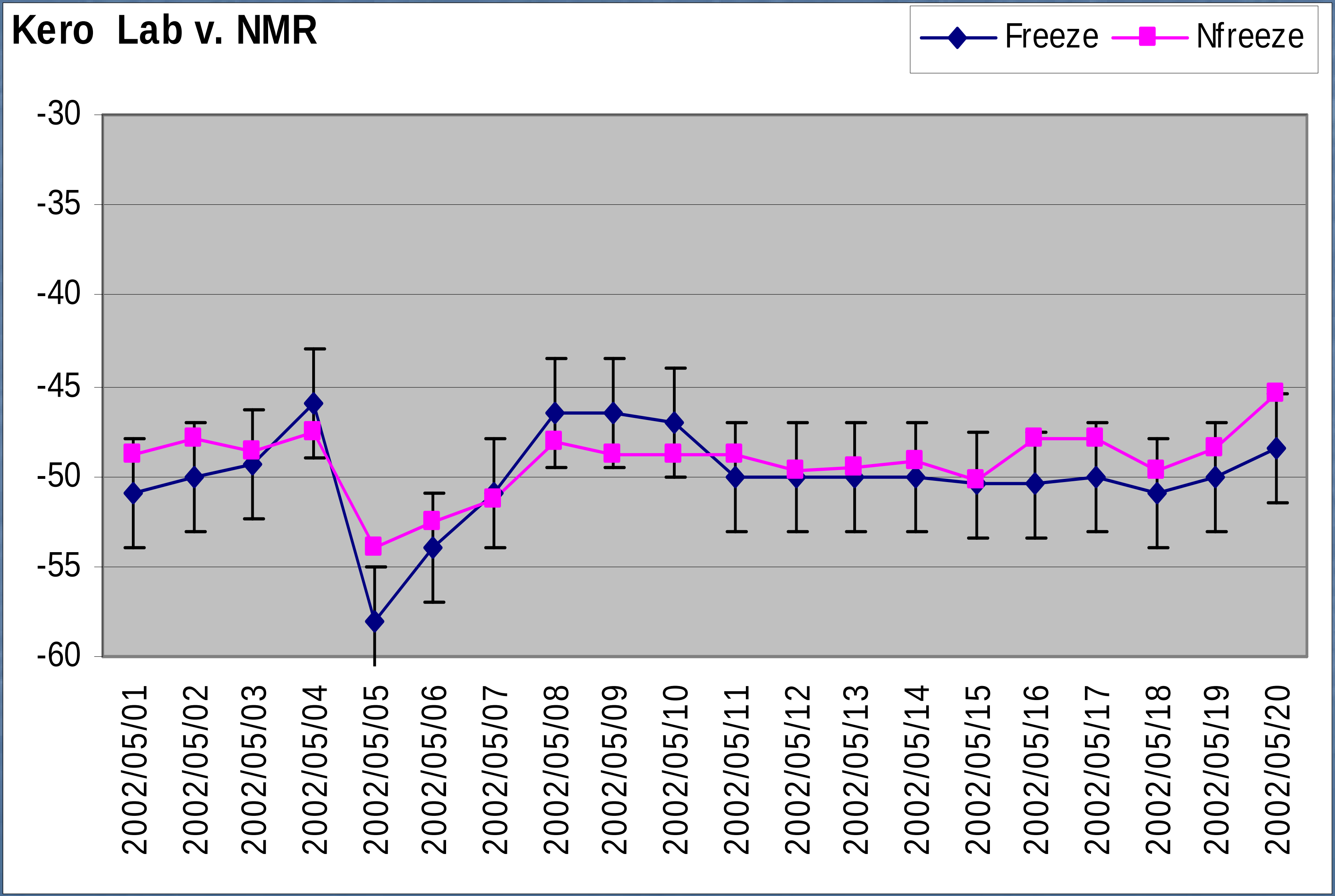
&

MRA

Crude Fast Loop Heater

MRA Sample System

- **Crude Brought into NMR at 70C (Crude Fast Loop Heater)**
- **Kerosene and Naphtha Also Brought to NMR at 70C (Sample Heater With PID Control at NMR SSC**
- **All Samples are routed to crude sample return and Pass Through CDU Again**
- **Double Block-and-Bleed and Flushing Protocol to Prevent Cross Contamination of Light Ends With Crude.**


Kero Lab v. NMR
Freeze
Nfreeze
-30
-35
-40
-45
-50
-55
-60
2002/05/01
2002/05/02
2002/05/03
2002/05/04
2002/05/05
2002/05/06
2002/05/07
2002/05/08
2002/05/09
2002/05/10
2002/05/11
2002/05/12
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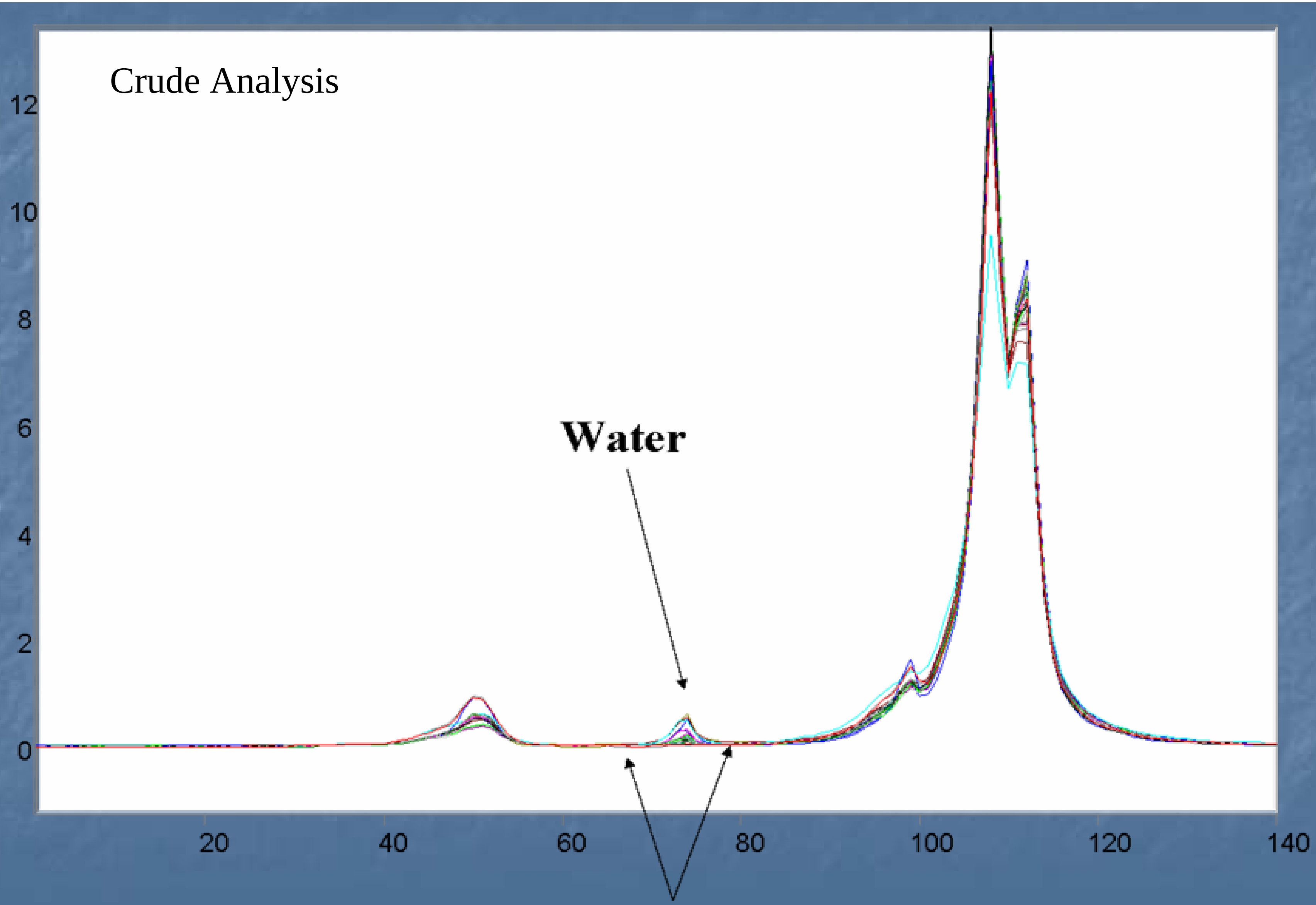
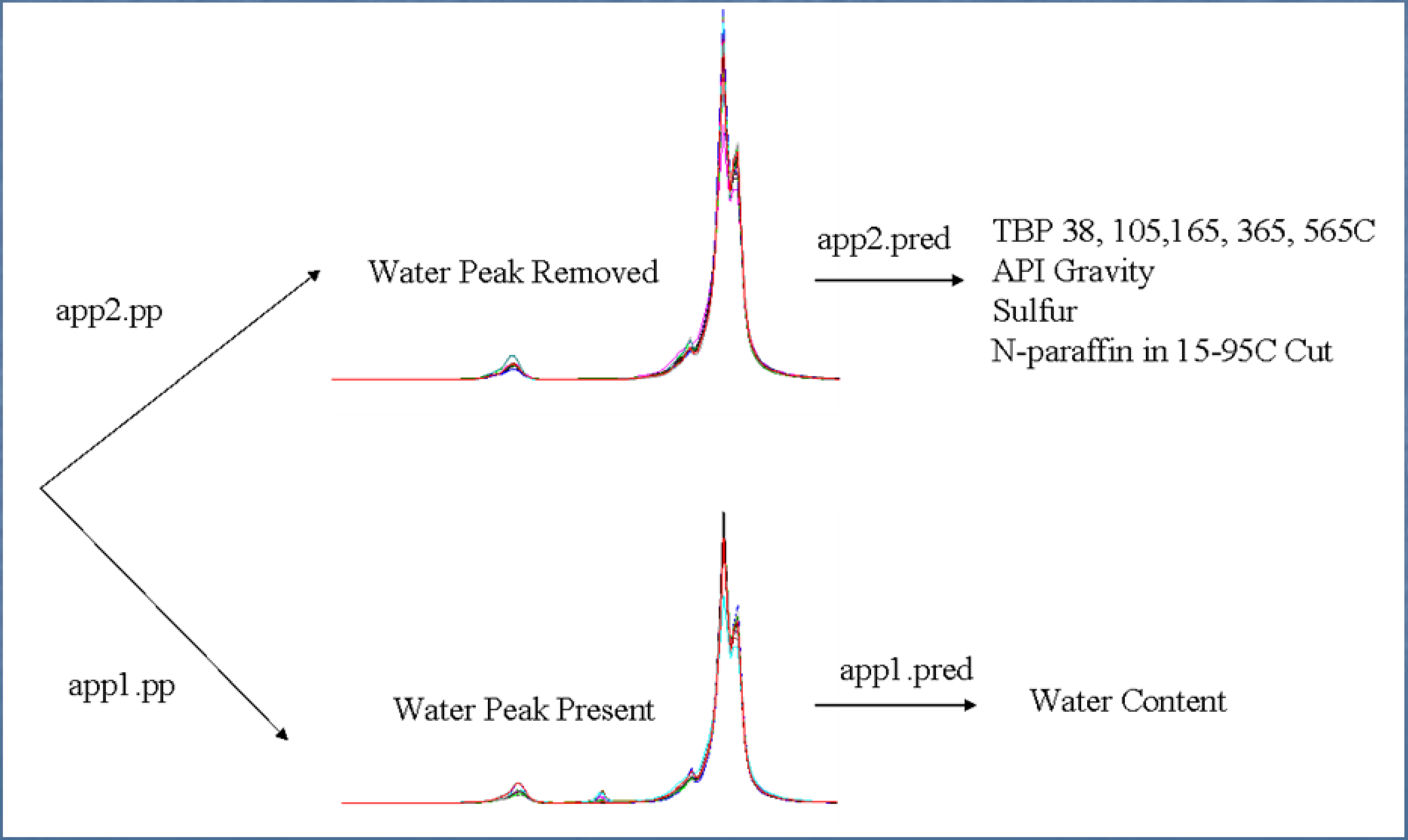
2002/05/16
2002/05/17
2002/05/18
2002/05/19
2002/05/20



Points 67 and 79 are linearly connected to remove water peak and the data is re-normalized

Experimental Design For Implementation on Each Crude NMR



app2.pp

Water Peak Removed

app2.pred

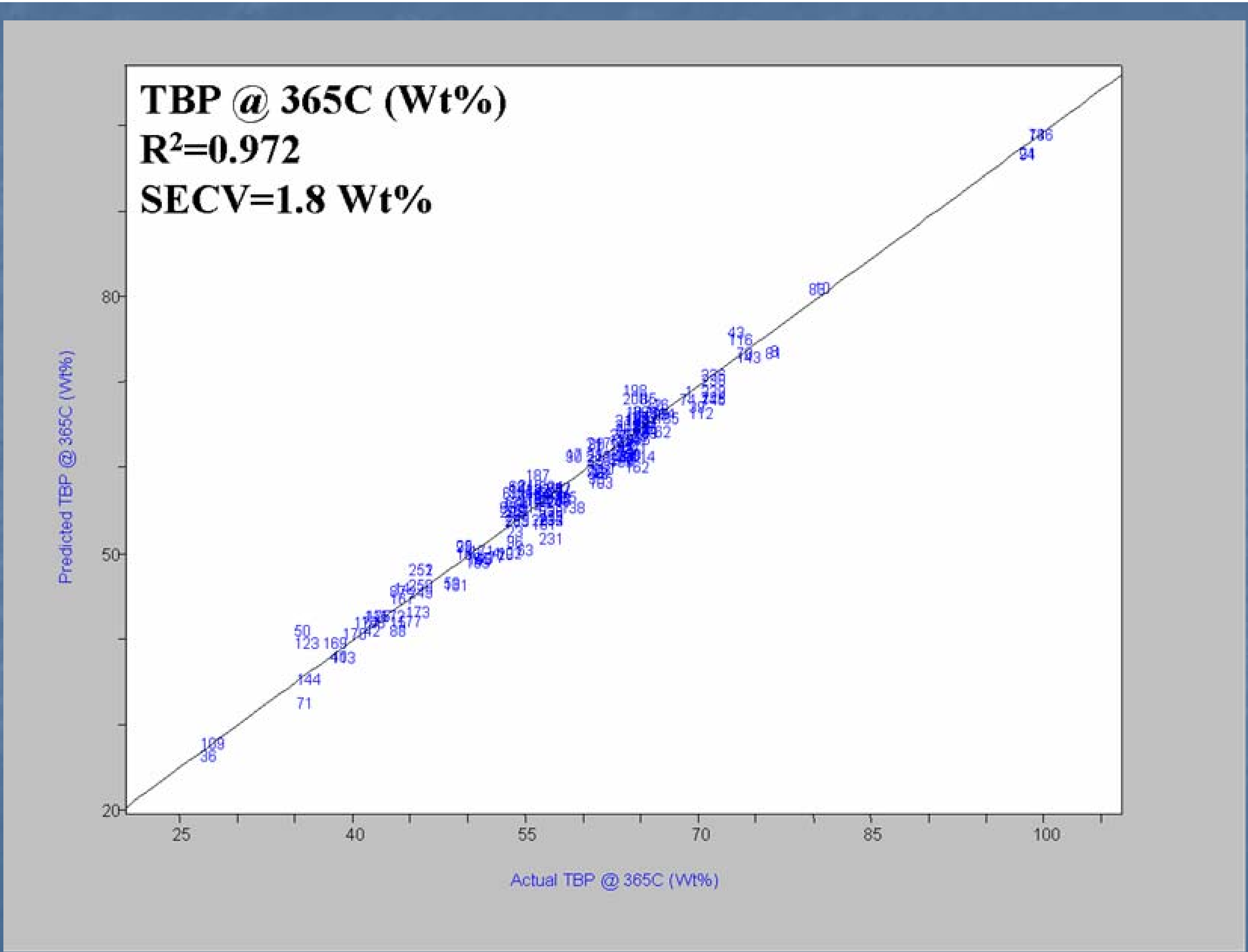
TBP 38, 105,165, 365, 565C
API Gravity
Sulfur
N-paraffin in 15-95C Cut

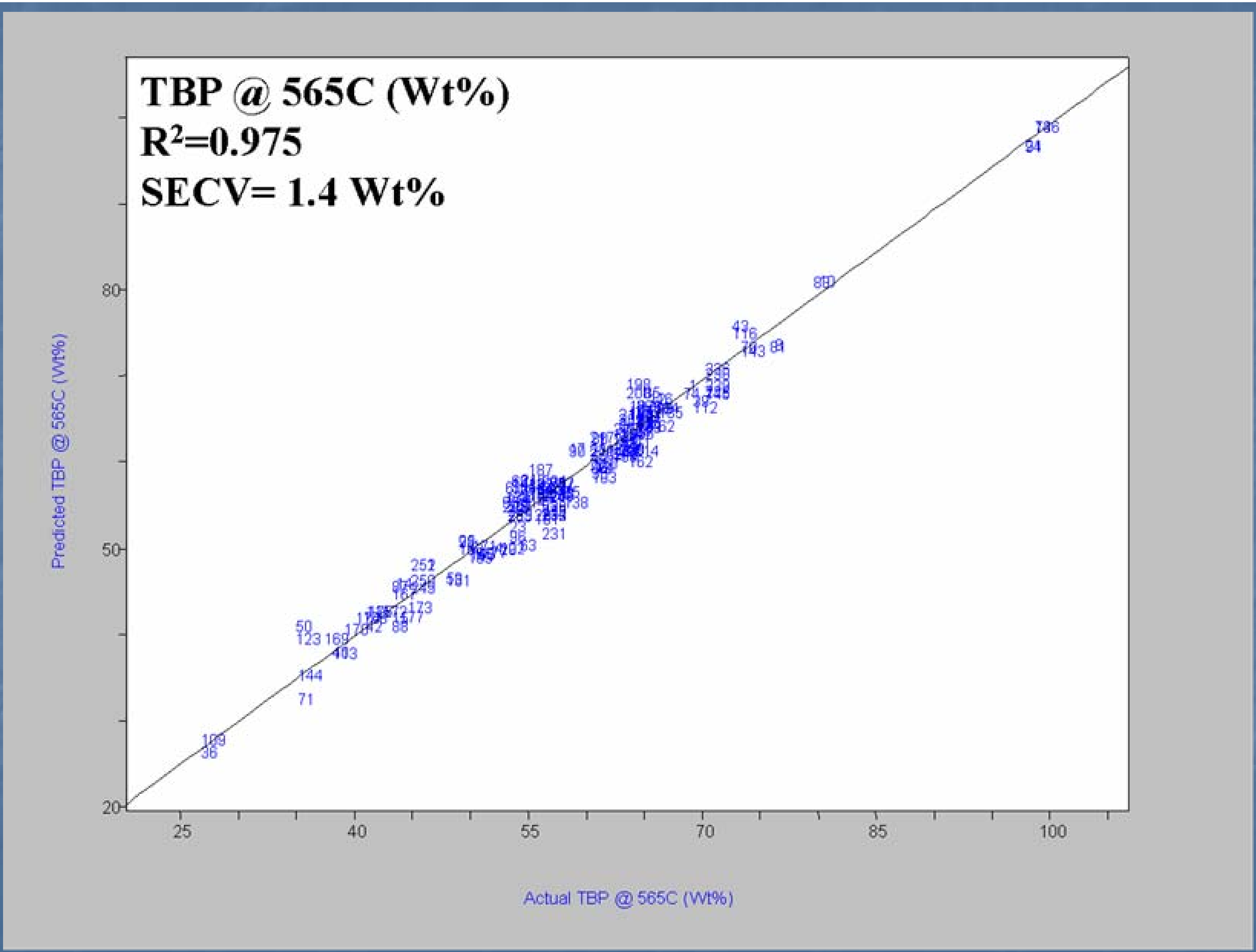
app1.pp

Water Peak Present

app1.pred

Water Content

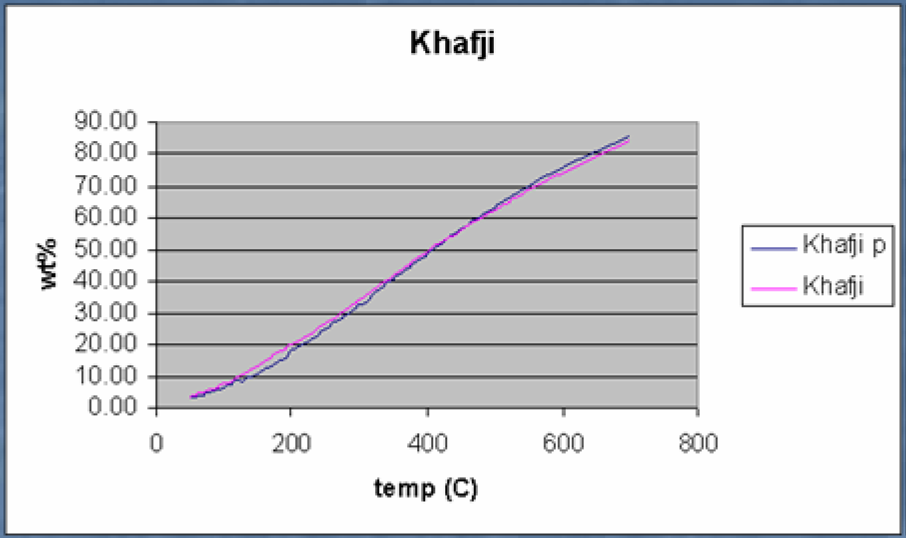

TBP @ 365C (Wt%)
R²=0.972
SECV=1.8 Wt%
Predicted TBP @ 365C (Wt%)
80
50
20
25
40
55
70
85
100
Actual TBP @ 365C (Wt%)

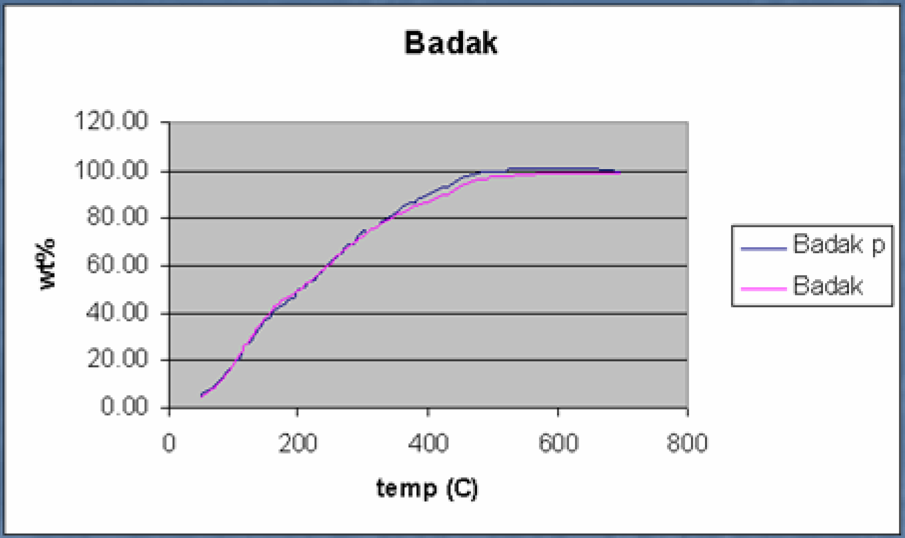


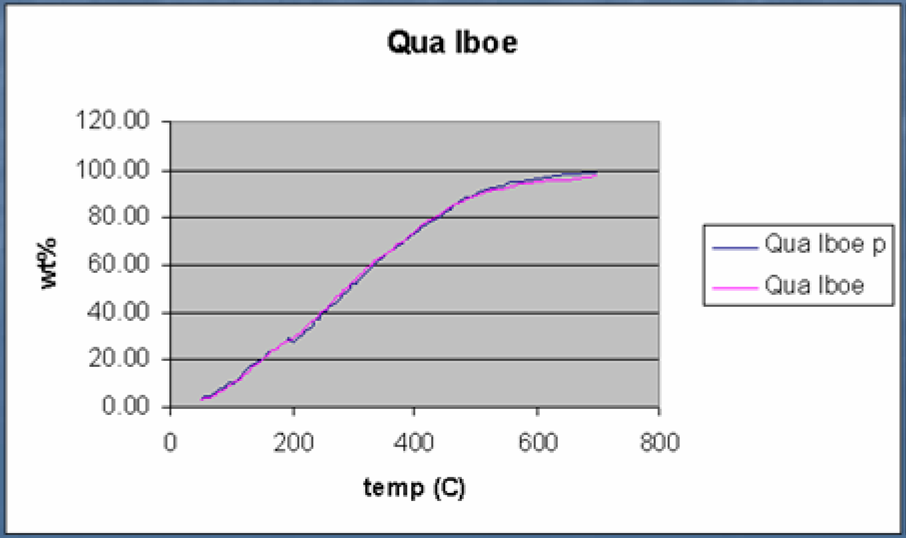
TBP @ 565C (Wt%)

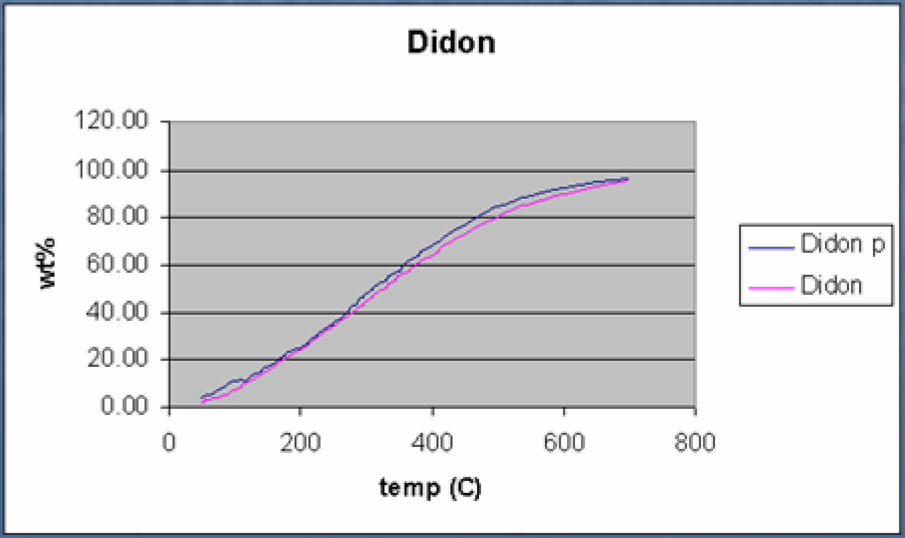
R^2=0.975

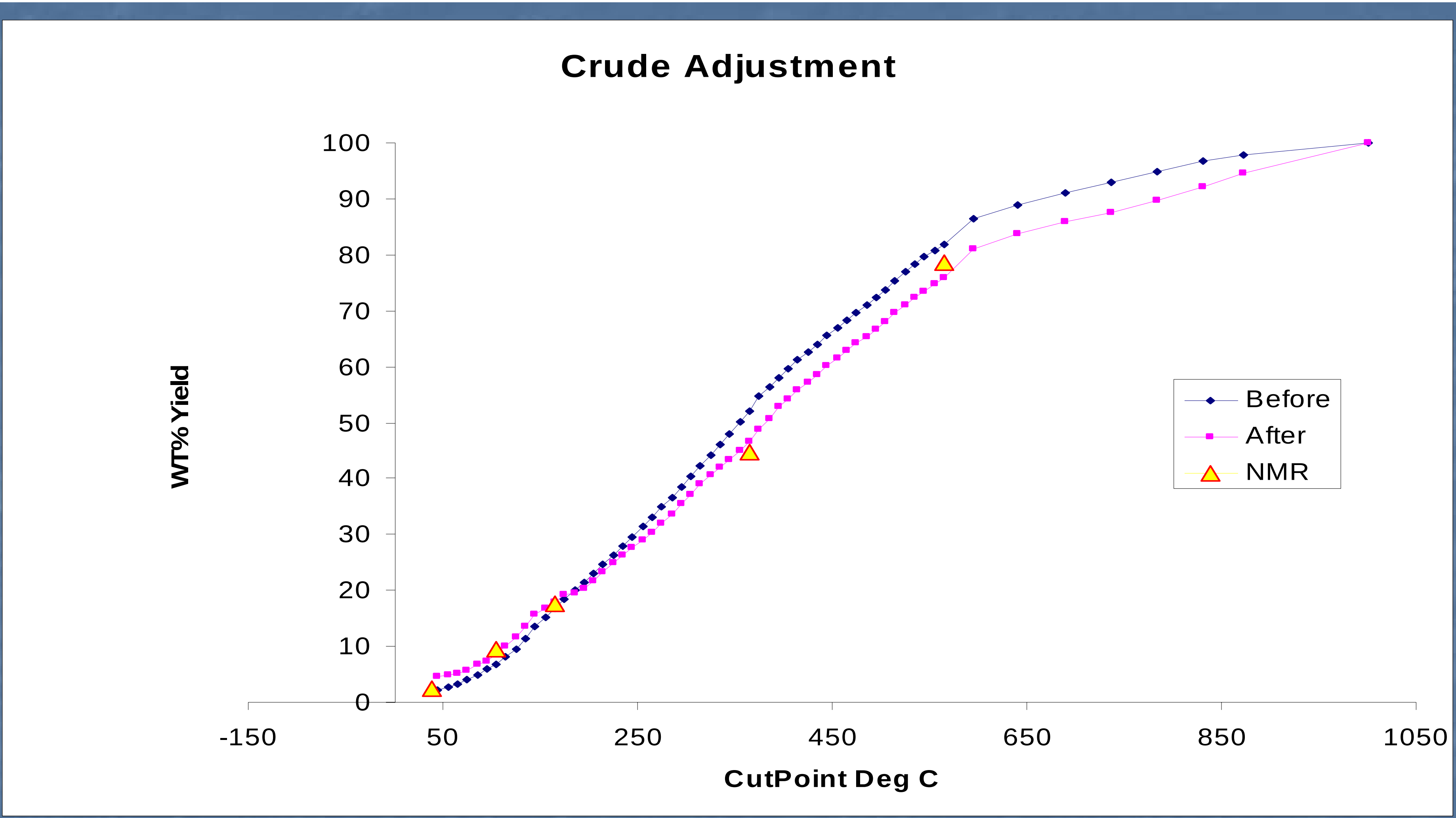
SECV= 1.4 Wt%


Khafji
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
wt%
0
200
400
600
800
temp (C)
Khafji p
Khafji


Badak
120.00
100.00
80.00
60.00
40.00
20.00
0.00
wt%
0
200
400
600
800
temp (C)
Badak p
Badak


Qua Iboe
120.00
100.00
80.00
60.00
40.00
20.00
0.00
wt%
0
200
400
600
800
temp (C)
Qua Iboe p
Qua Iboe


Didon
120.00
100.00
80.00
60.00
40.00
20.00
0.00
wt%
0
200
400
600
800
temp (C)
Didon p
Didon



Crude Reconciliation

Application: Steam Cracking Optimization

Cracker Facility Capacity: 600,000 Tonnes per Year

Control Strategy: Feed Forward Detailed Hydrocarbon Analysis to SPYRO
Optimization Package

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

NMR PLS Outputs: Naphtha – Detailed PIONA
c4-c10 n-paraffin, i-paraffin, aromatics, naphthenes

Value Added: Unit Optimization - $150K /year
4 Units Now Being Optimized ($600K/year)

Performance : NMR Available 98%+ Since August 2000
Models Updated in a Limited Manner

Steam Cracker Optimization - Project Timeline

Feasibility Performed (30 Samples) – December 1999

Further Model Expansion (90 Samples) – December 1999-March 2000

Online System Installed – April 2000

On-Line Localization and Further Model Expansion (65 Sampes)– May to July 2000

Validation Period – 1 Month 100% Availability Within Specified Accuracy Limit - Aug 2000

System Validated and Accepted – September 2000

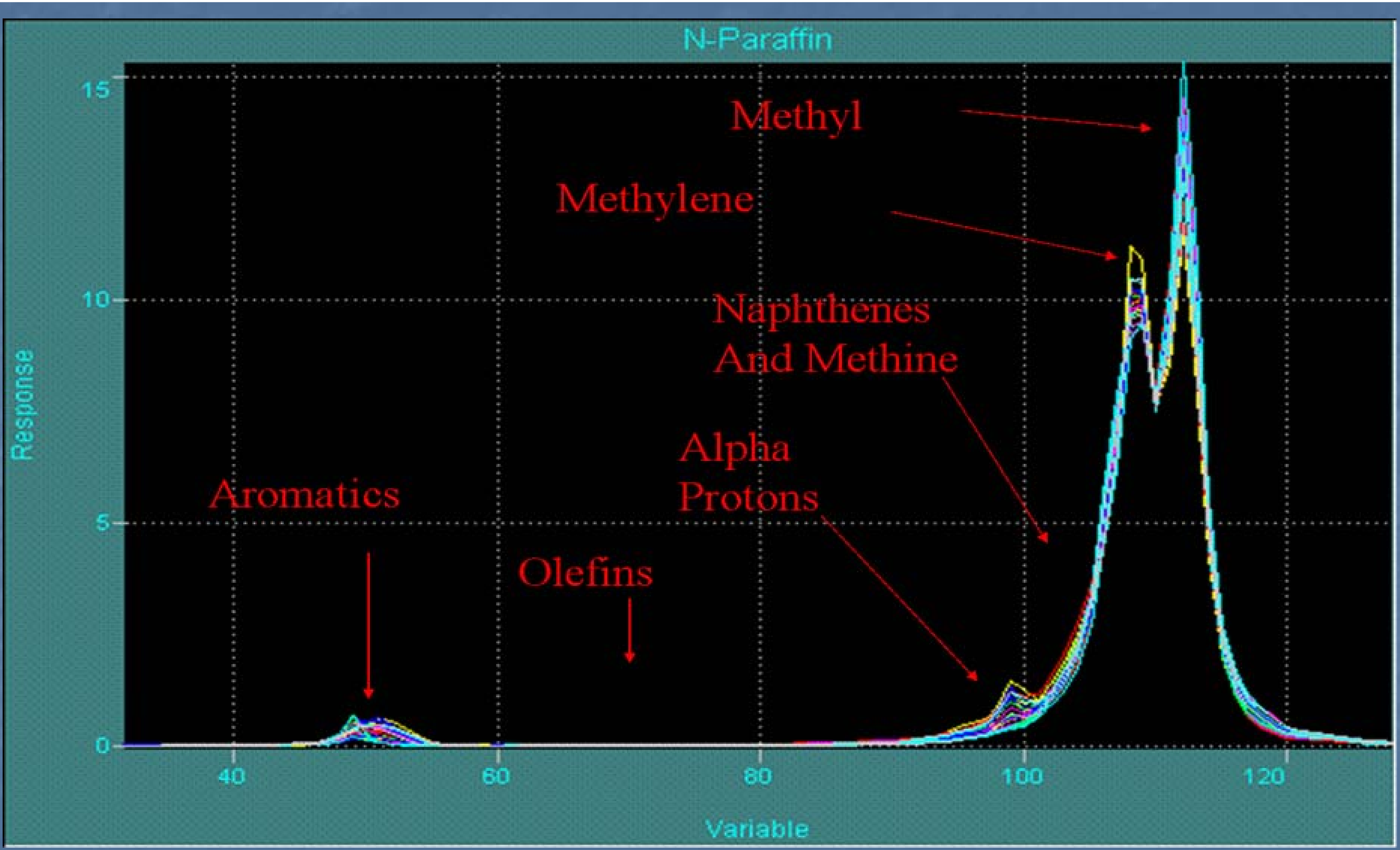
Add Validation Period Samples to Models – (Models now contain 215 Samples)

NMR Put on Control (Detailed PIONA into SPYRO Model for Unit Optimization) Oct 2000

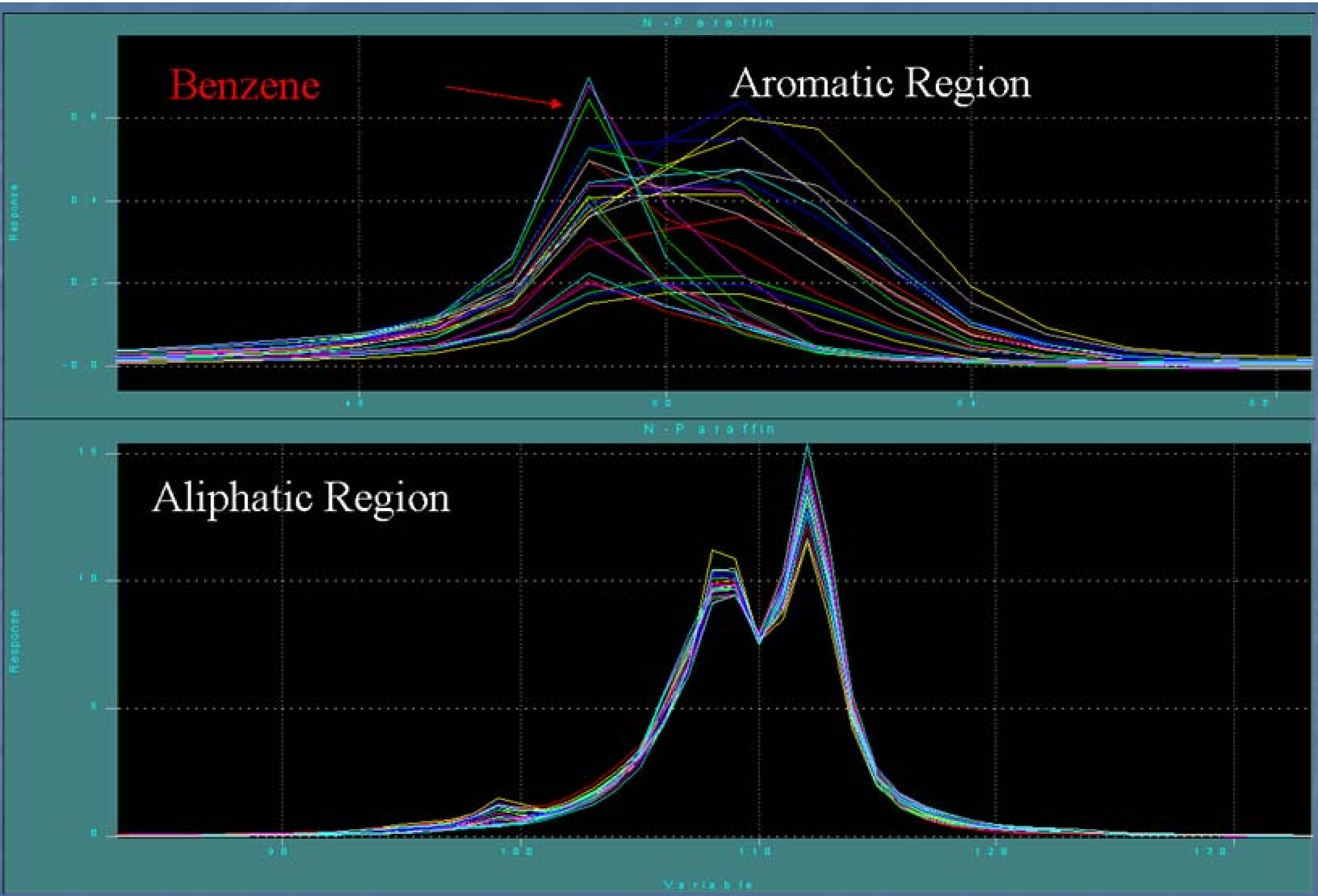
Models have been performing relatively untouched (6 parameters updated on 4 occasions) since end of validation period.

98+% Availability September 2000 – May 2002

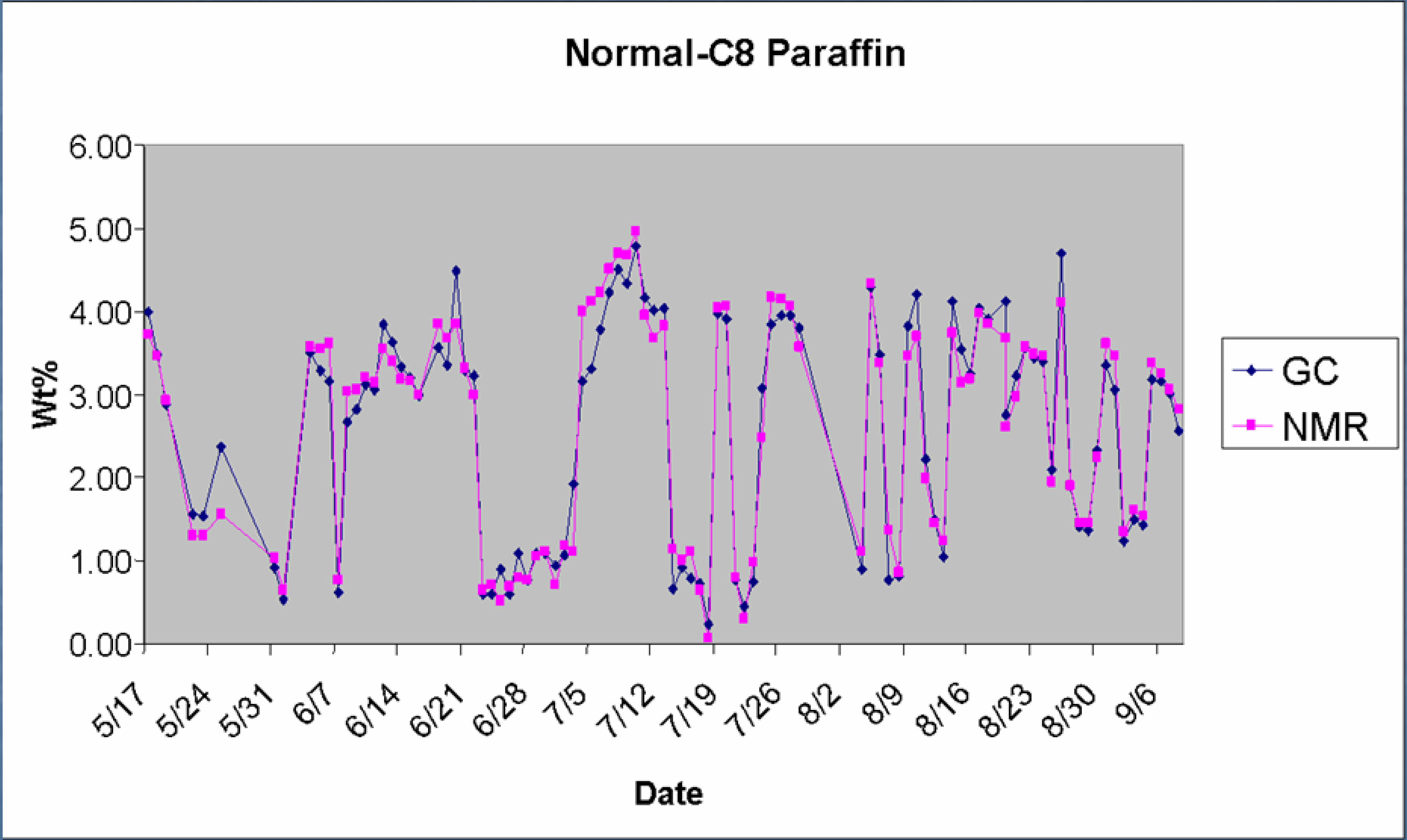
March 2002 – Three Further Feed-Streams Added to NMR

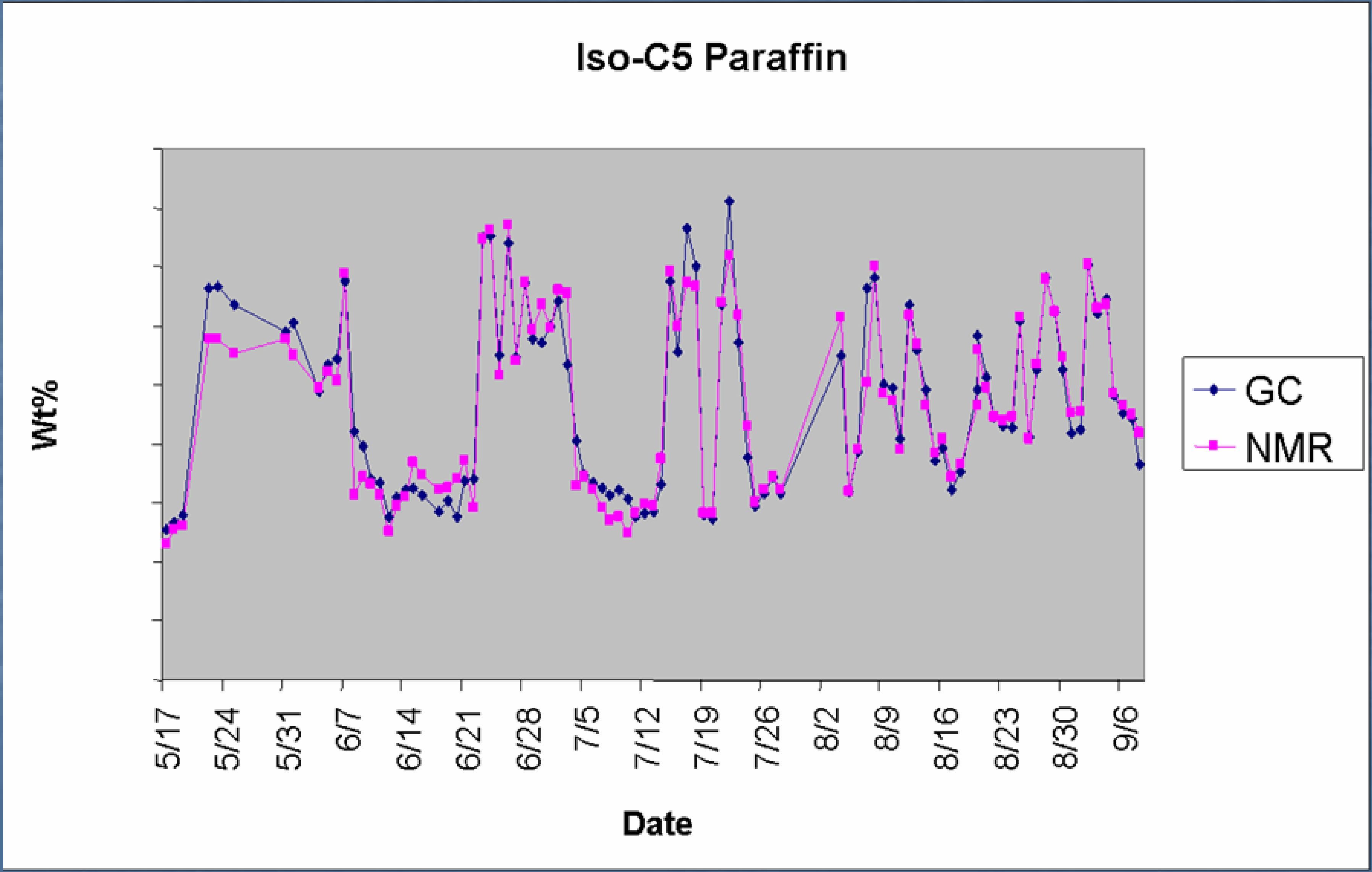


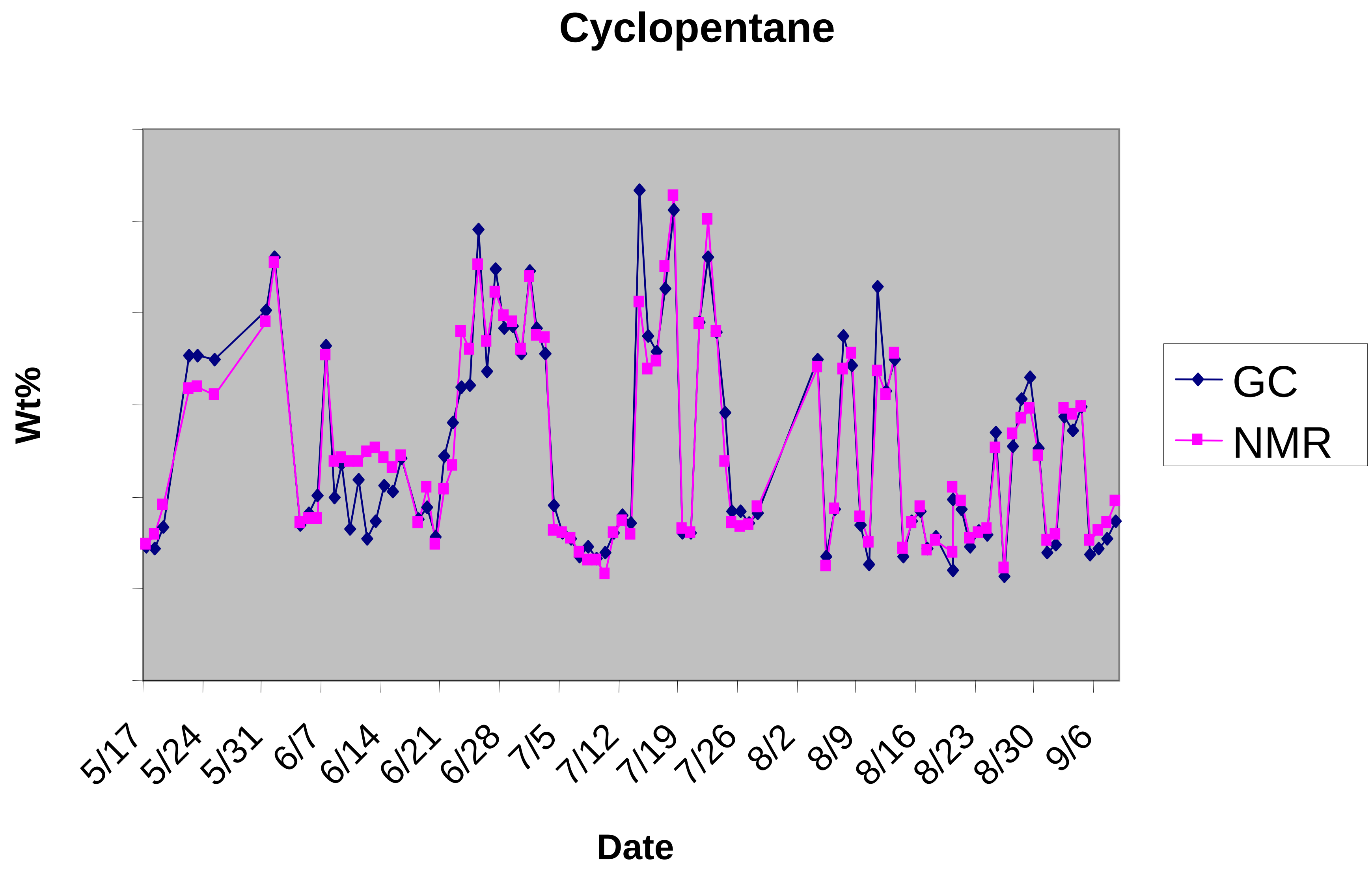
Spectral Variability Observed in Naphtha Samples

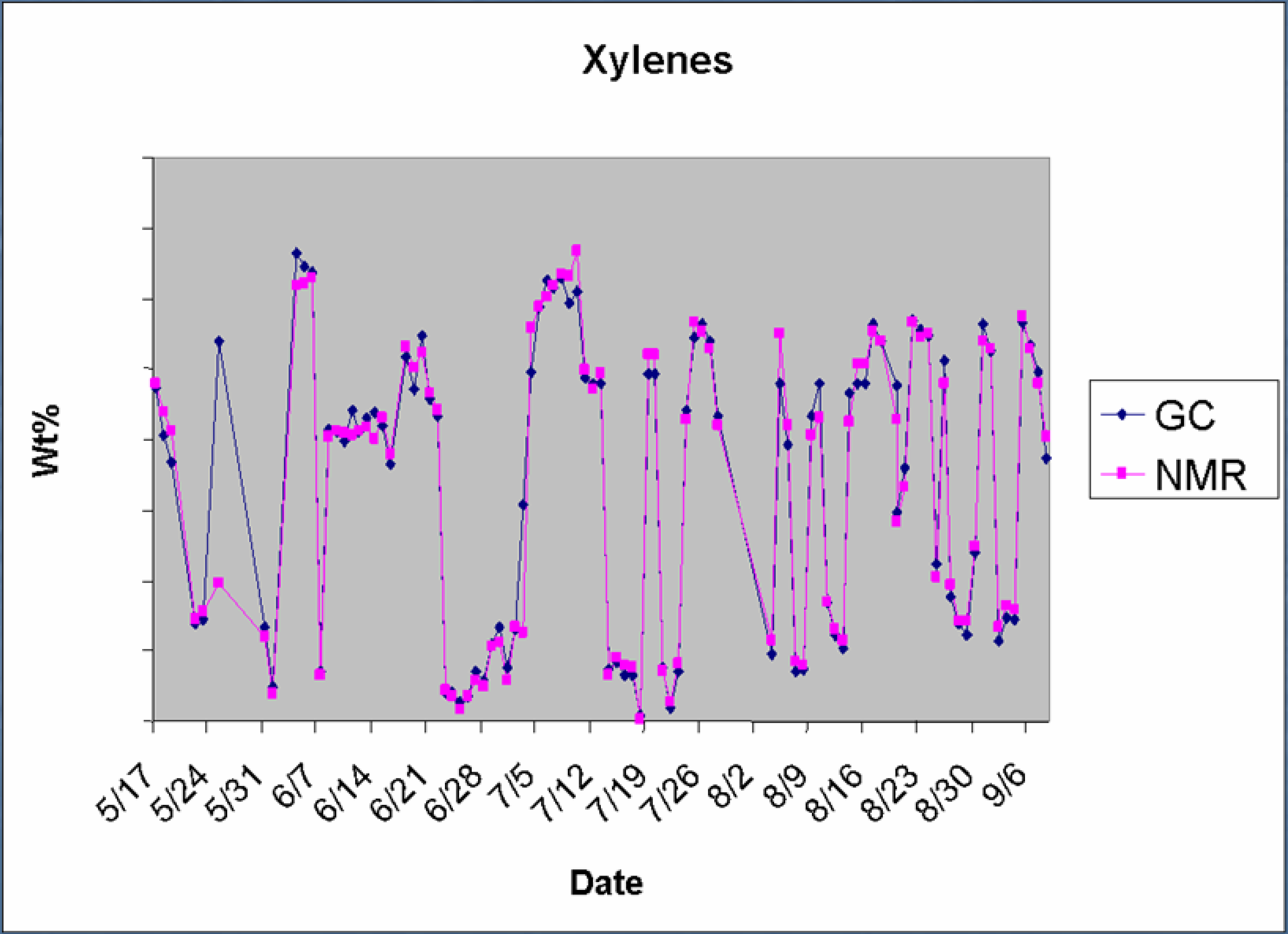


Spectral Variability in Aromatic and Aliphatic Regions


Normal-C8 Paraffin
6.00
5.00
4.00
3.00
2.00
1.00
0.00
Wt%
5/17
5/24
5/31
6/7
6/14
6/21
6/28
7/5
7/12
7/19
7/26
8/2
8/9
8/16
8/23
8/30
9/6
Date
GC
NMR


Iso-C5 Paraffin
Wt%
Date
5/17
5/24
5/31
6/7
6/14
6/21
6/28
7/5
7/12
7/19
7/26
8/2
8/9
8/16
8/23
8/30
9/6
GC
NMR


Cyclopentane
Wt%
5/17
5/24
5/31
6/7
6/14
6/21
6/28
7/5
7/12
7/19
7/26
8/2
8/9
8/16
8/23
8/30
9/6
Date
GC
NMR


Xylenes
Wt%
5/17
5/24
5/31
6/7
6/14
6/21
6/28
7/5
7/12
7/19
7/26
8/2
8/9
8/16
8/23
8/30
9/6
Date
GC
NMR

Single PLS Model for Each GC Component

Low Model Maintenance

SPYRO Optimization and APC Utilize Real Time Analysis

4 Crackers Now Covered by 1 NMR

Multiple GC Analyzers Replaced
Reduced Maintenance

Reduced Laboratory Participation

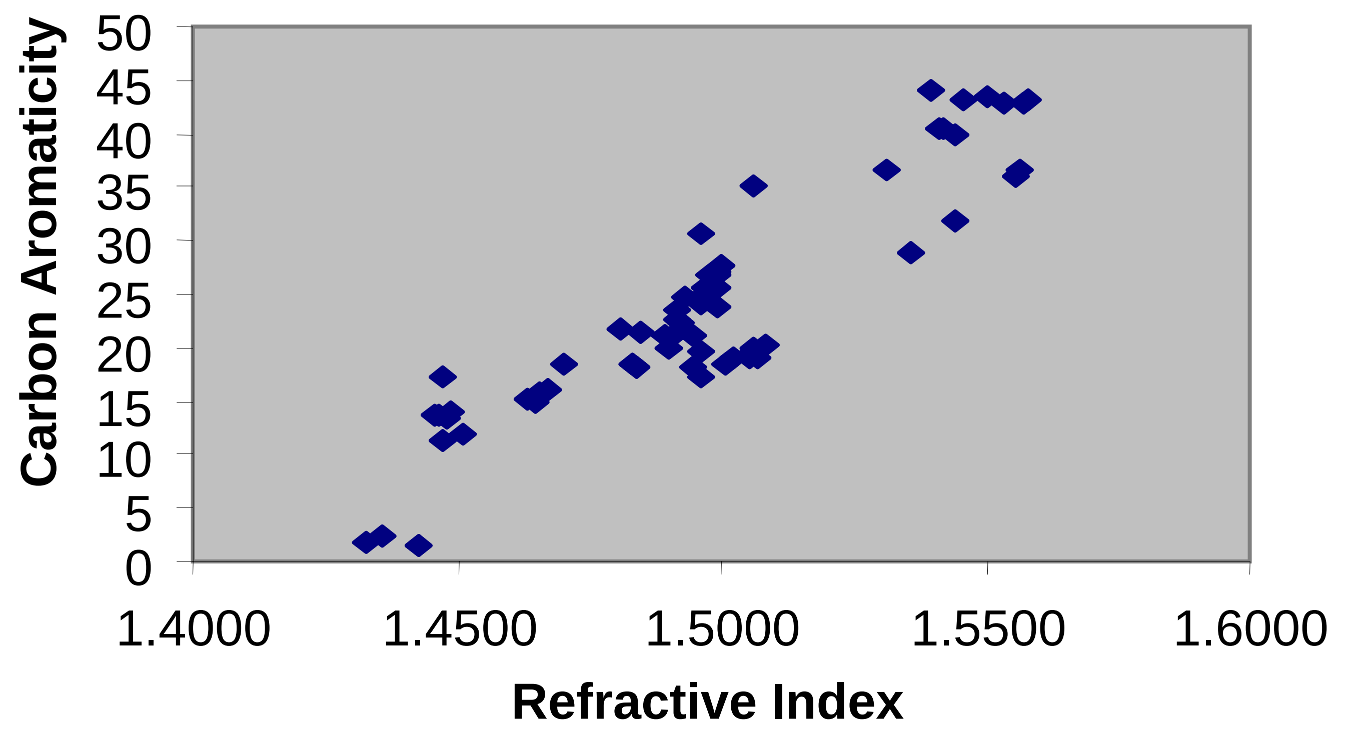
Other Installations:
Expanding Model Base to Cover Gas Oils and Mixed Naphtha/Gas Oil Blend Operation

Parameter	**R**	**Std Dev**	**Mean Dev**
n-c4	0.9340	0.52	0.067
n-c5	0.9761	0.73	-0.004
n-c6	0.9616	0.73	-0.093
n-c7	0.9840	0.33	-0.032
n-c8	0.9882	0.29	-0.008
n-c9	0.9918	0.18	-0.003
n-c10	0.9716	0.13	0.022
Total n-paraffin	0.9840	0.81	0.013
I-c4	0.8765	0.07	0.001
I-c5	0.9834	0.76	0.043
i-C6	0.9865	0.59	-0.050
i-C7	0.9119	0.46	-0.015
i-C8	0.9800	0.42	-0.035
i-C9	0.9905	0.26	0.010
i-C10	0.9866	0.24	0.013
i-C11	0.9613	0.08	-0.007
Total I-paraffin	0.9617	0.81	-0.011
cyclopentane	0.9821	0.14	-0.004
me-cyclopentane	0.9937	0.23	-0.018
Cyclohexane	0.9940	0.26	0.034
Methylcyclohexane	0.9872	0.29	0.001
Other C7-Nap	0.9025	0.32	-0.052
c8-Nap	0.9713	0.36	0.002
c9-Nap	0.9892	0.28	0.026
c10-Nap	0.8950	0.06	-0.001
Total Naphthenes	0.9794	0.83	0.019
Benzene	0.9950	0.10	0.006
Toluene	0.9920	0.17	0.007
Ethylbenzene	0.9902	0.04	0.002
Xylenes	0.9951	0.14	0.003
C9 - Arom	0.9875	0.16	0.006
C10-arom	0.9586	0.07	0.001
Total Aromatics	0.9967	0.31	0.022

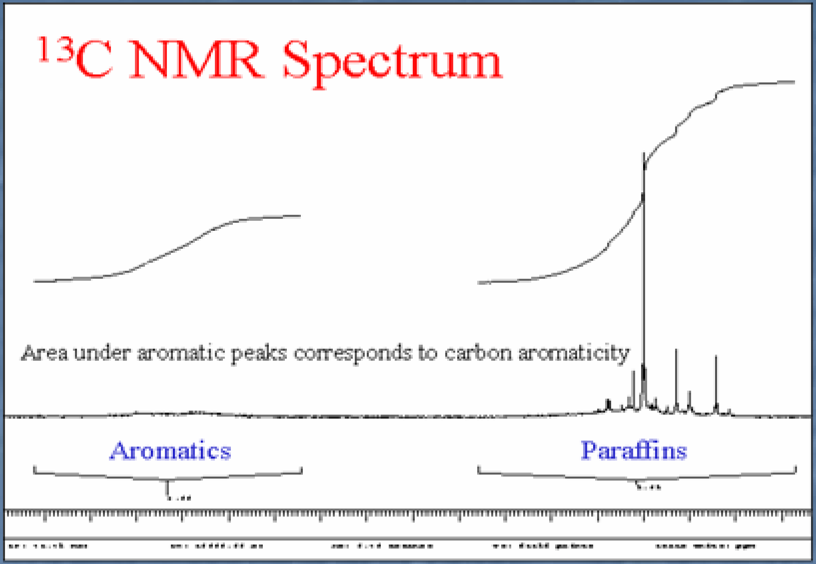
Application Snippets

FCC, RCC, Hydrotreating, Base Oil Manufacture

Correlation Between Carbon Aromaticity and Refractive Index



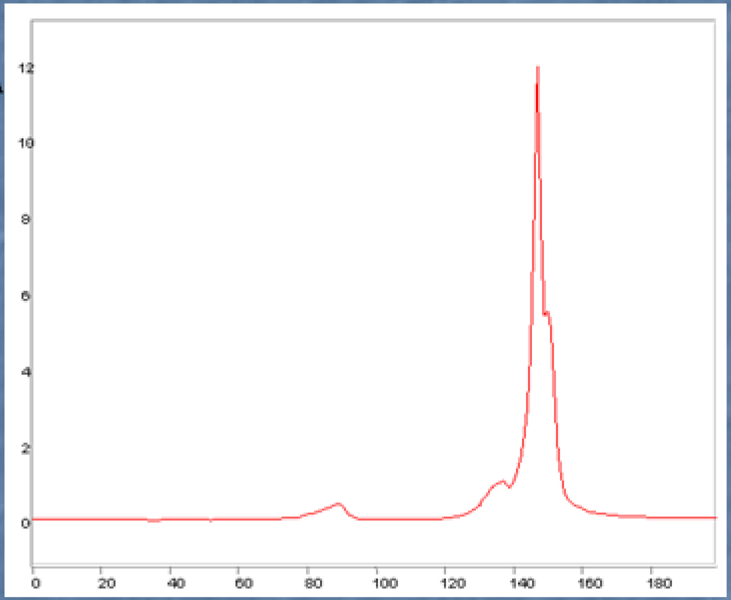
Why Measure Refractive Index When NMR Allows the Carbon Aromaticity to be Obtained Directly?

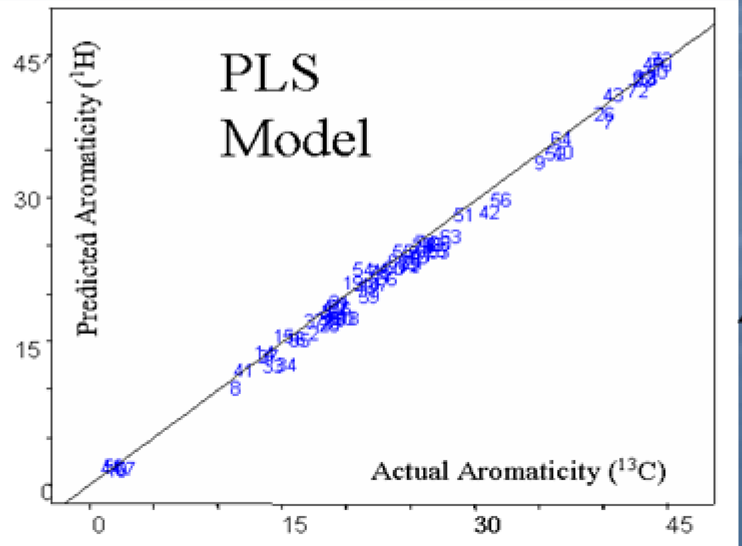


^{13}C NMR Spectrum

Area under aromatic peaks corresponds to carbon aromaticity

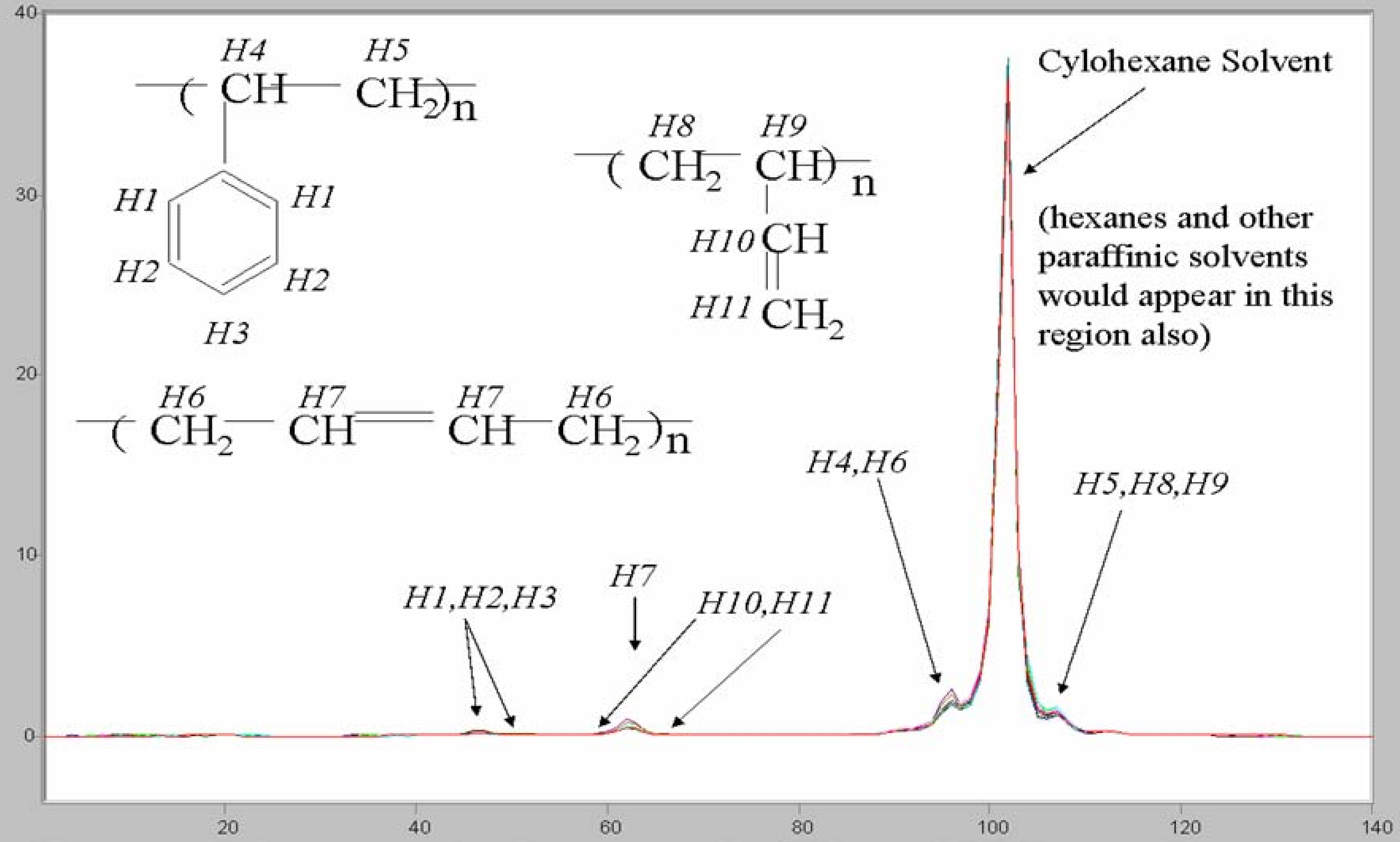
Correlate to 60 MHz
Foxboro ^1H NMR Using PLS Regression





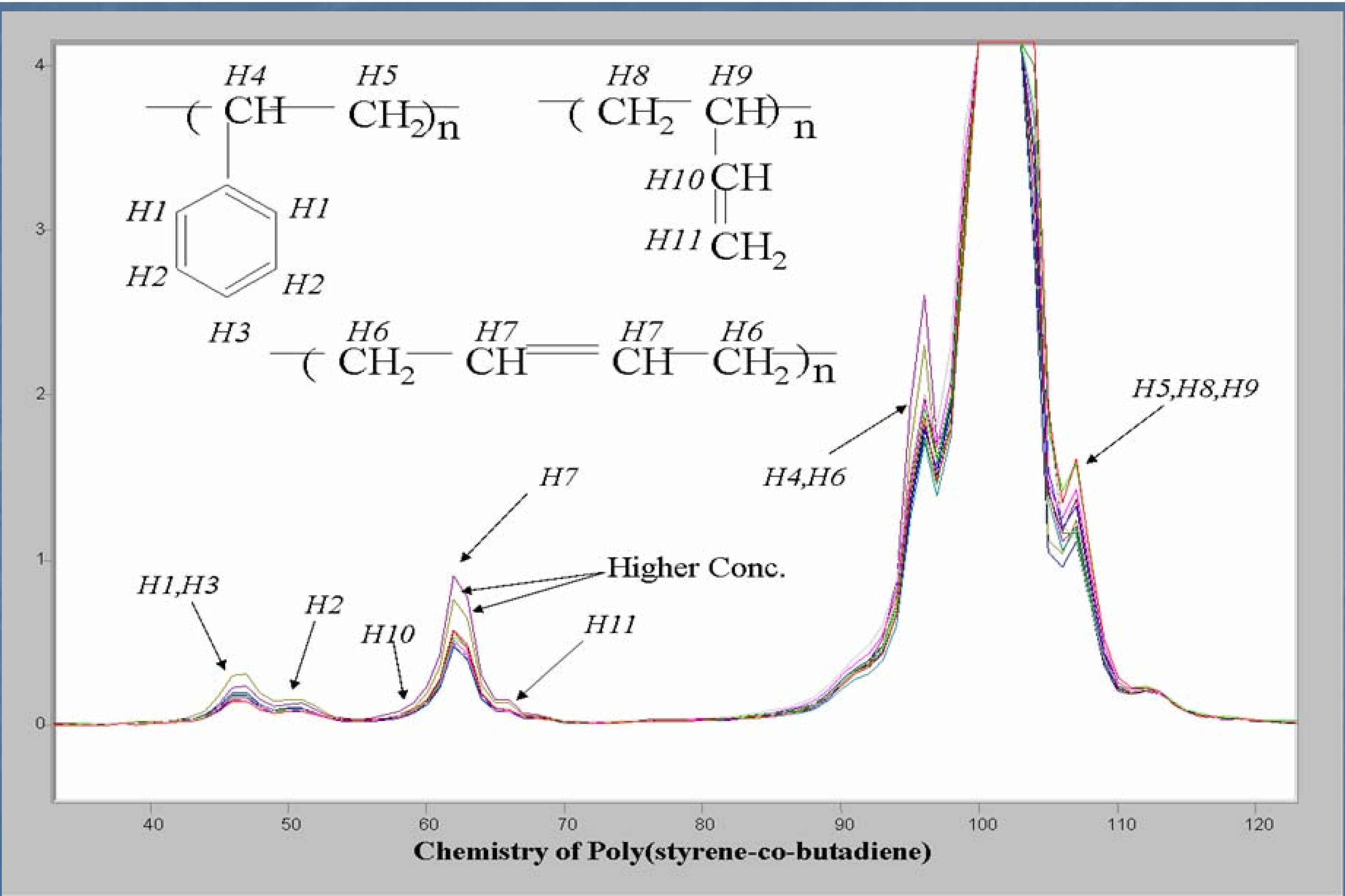
PLS Model

Process Samples



Chemistry of Poly(styrene-co-butadiene) observed by ^{1}H Process NMR (Processed Data)

Monomer Ratios



Selective Vinylidene Synthesis

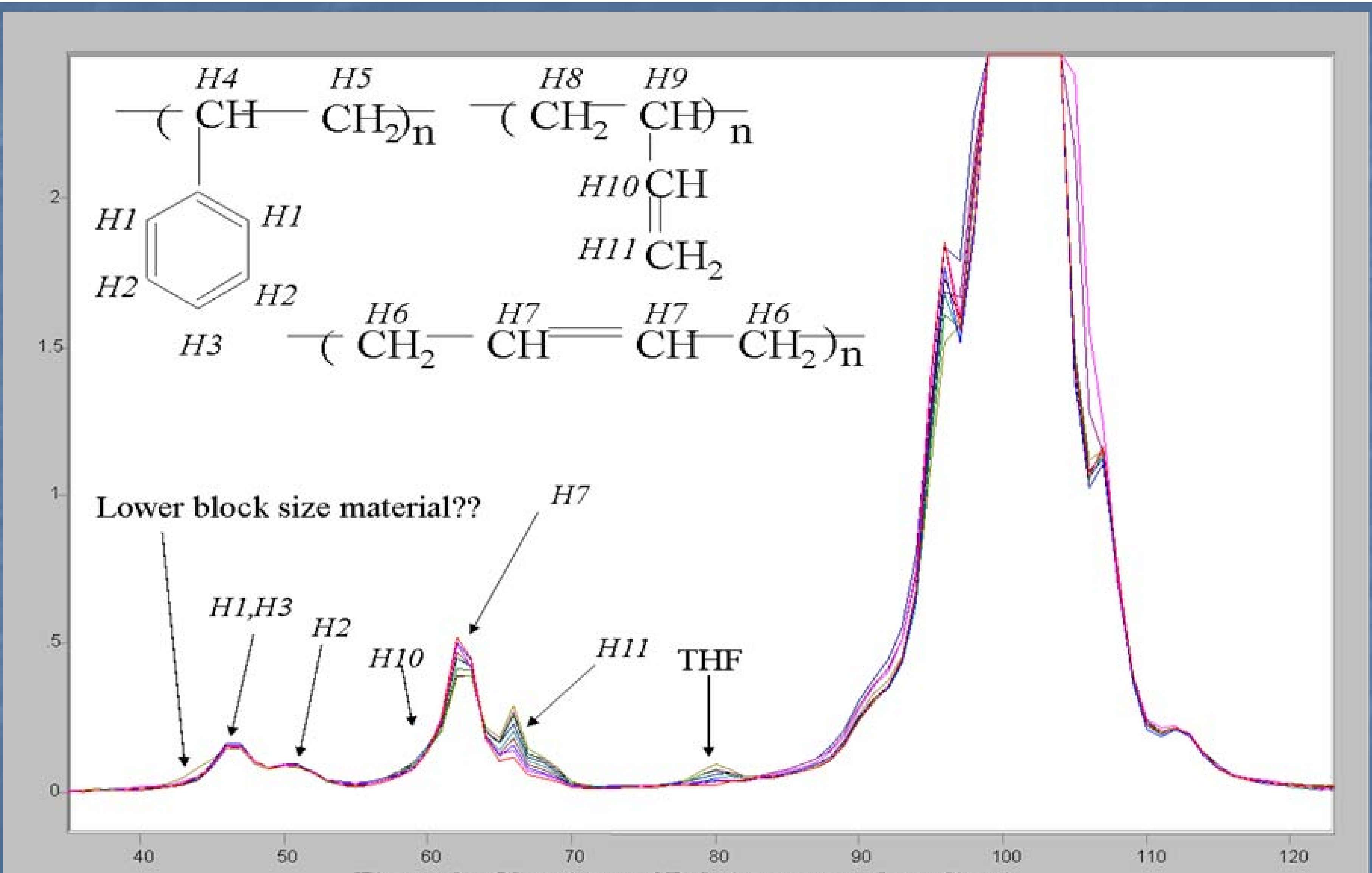
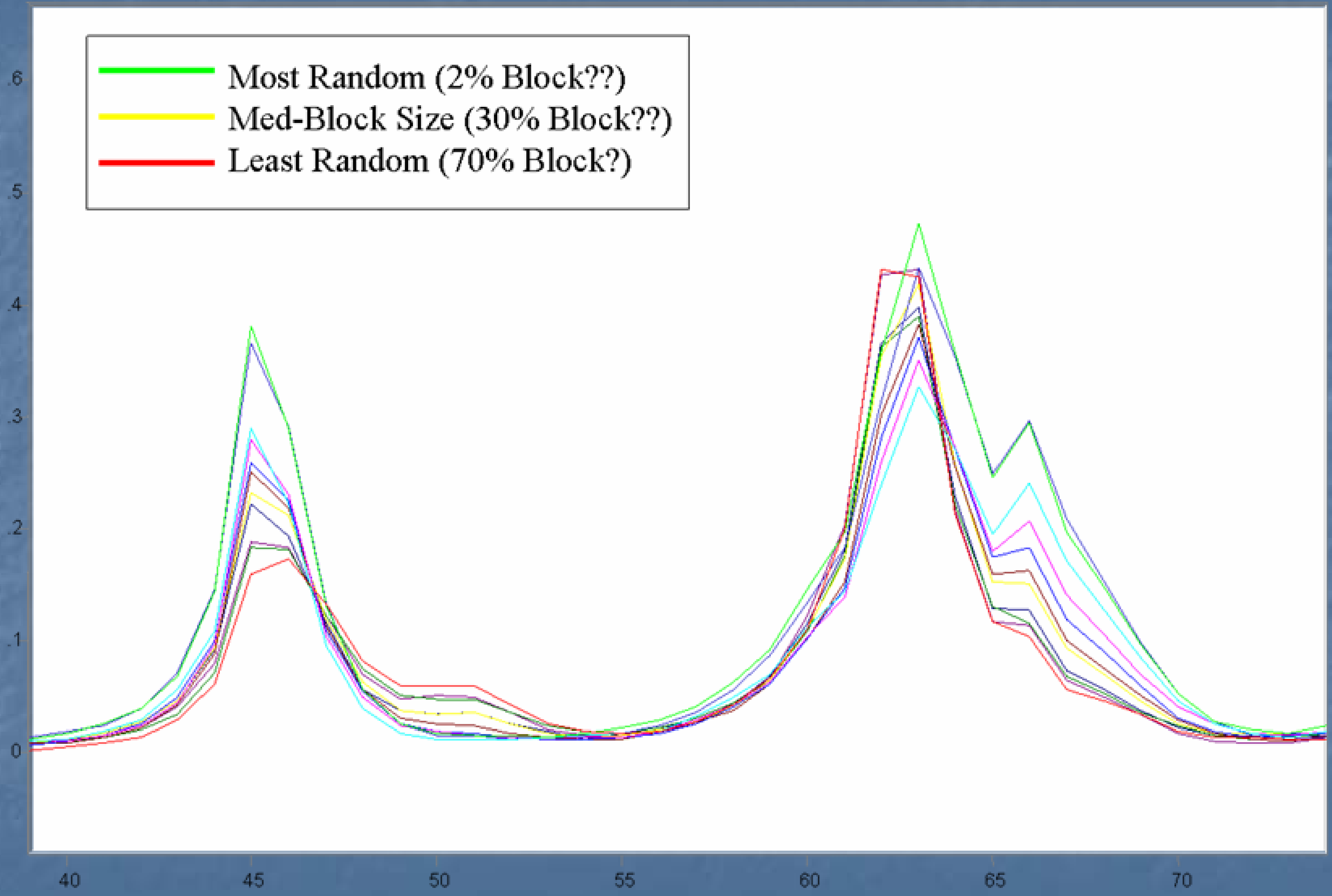
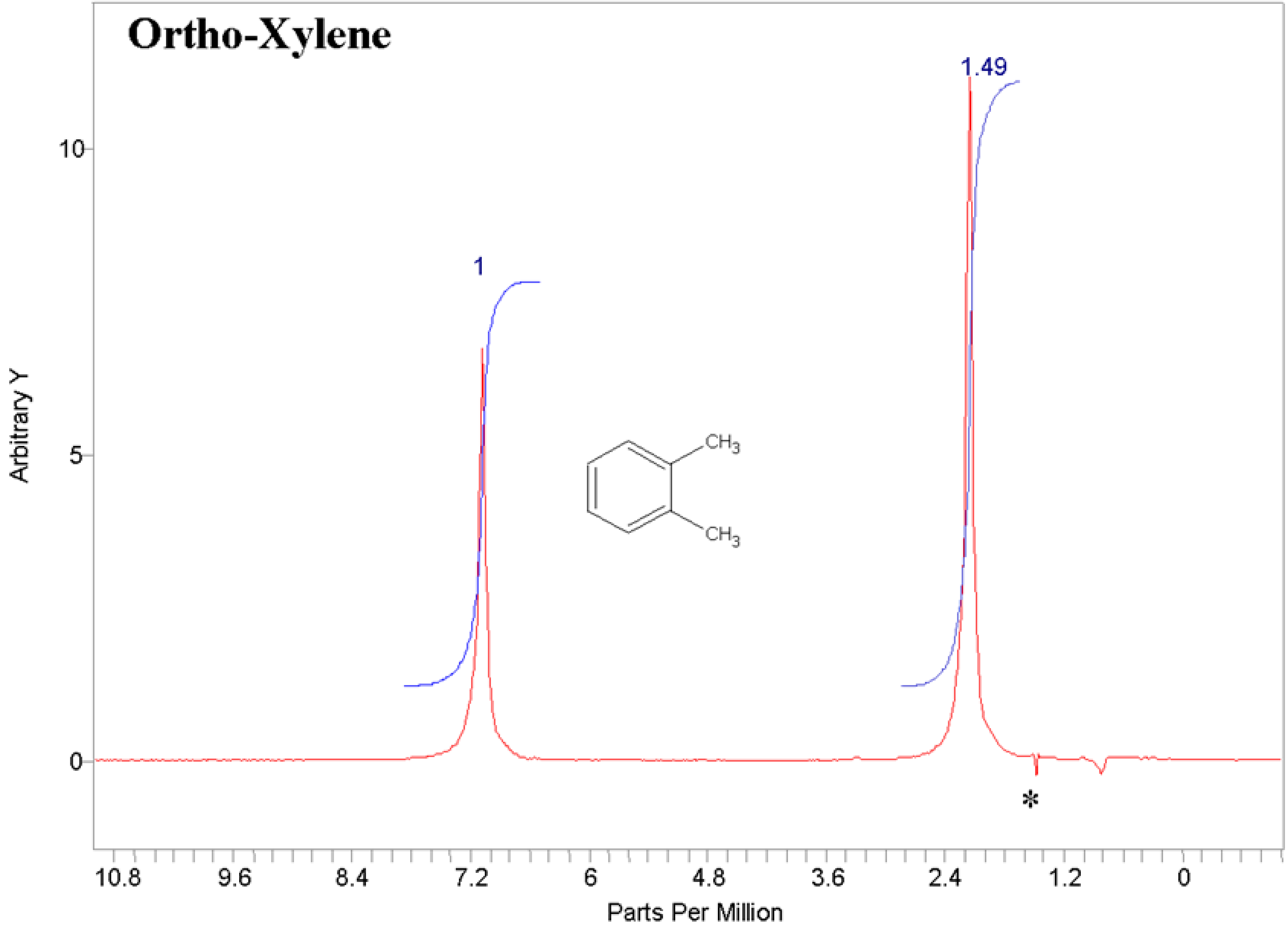


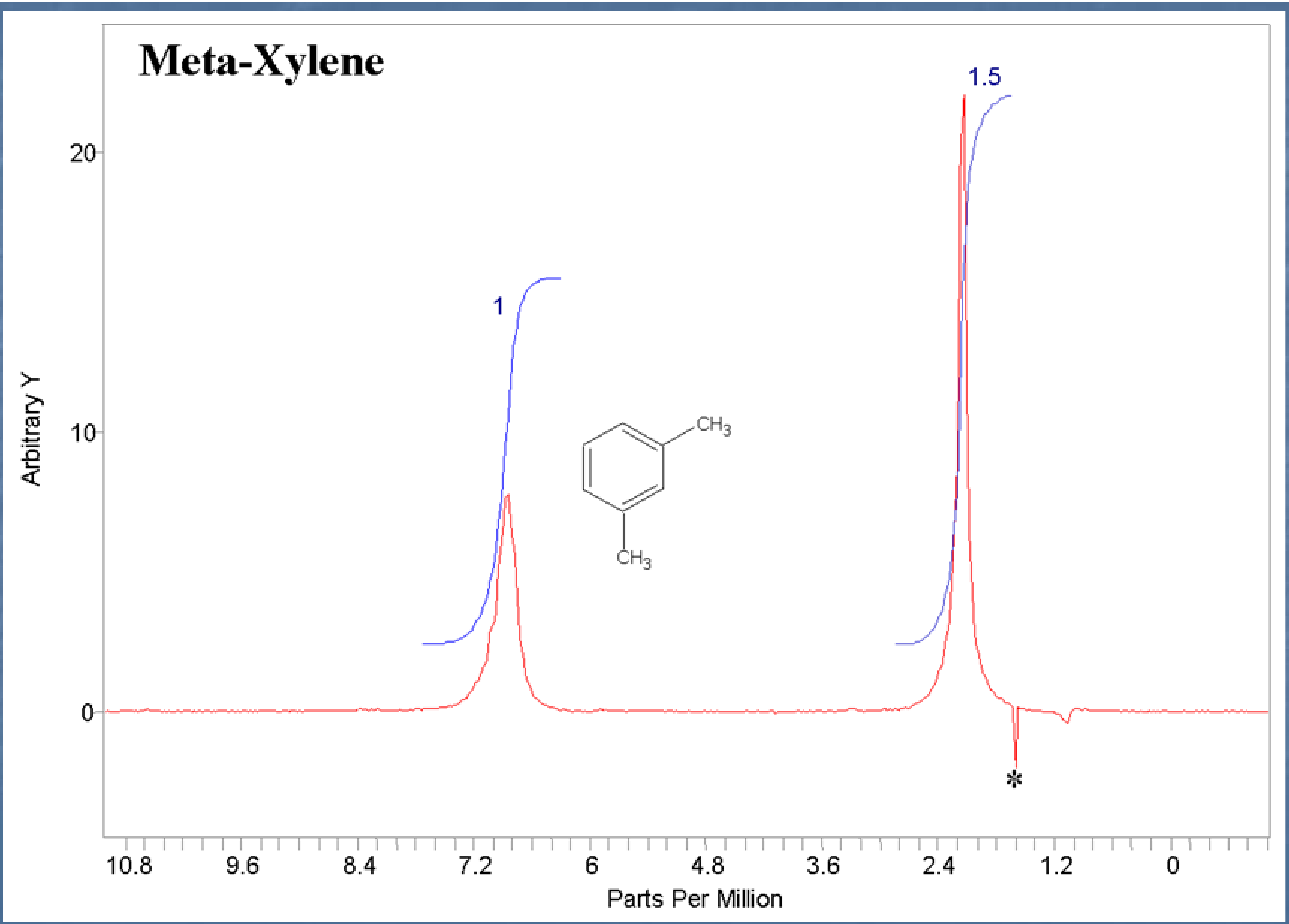
Figure 3 : Chemistry of Poly(styrene-co-butadiene)

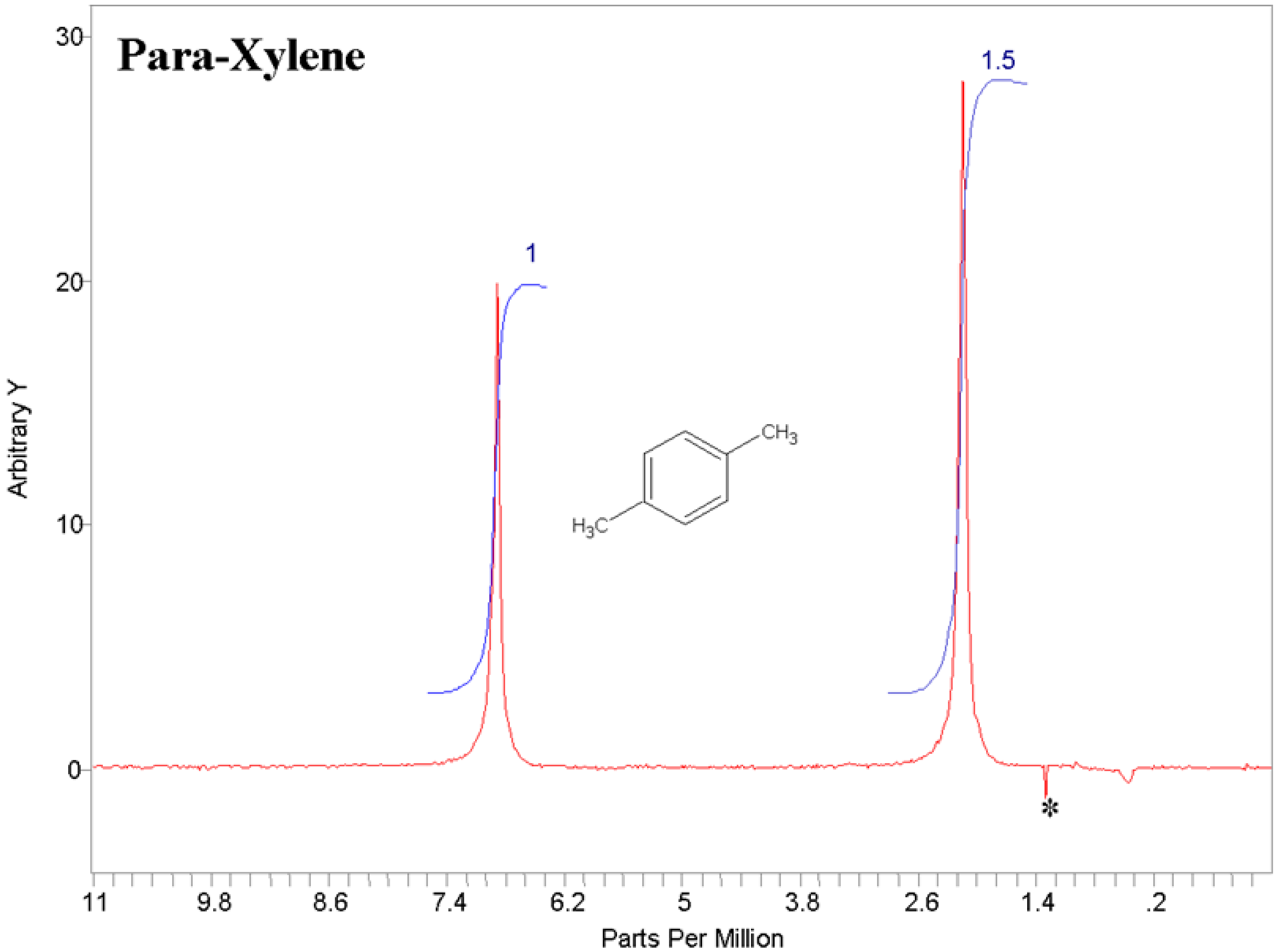


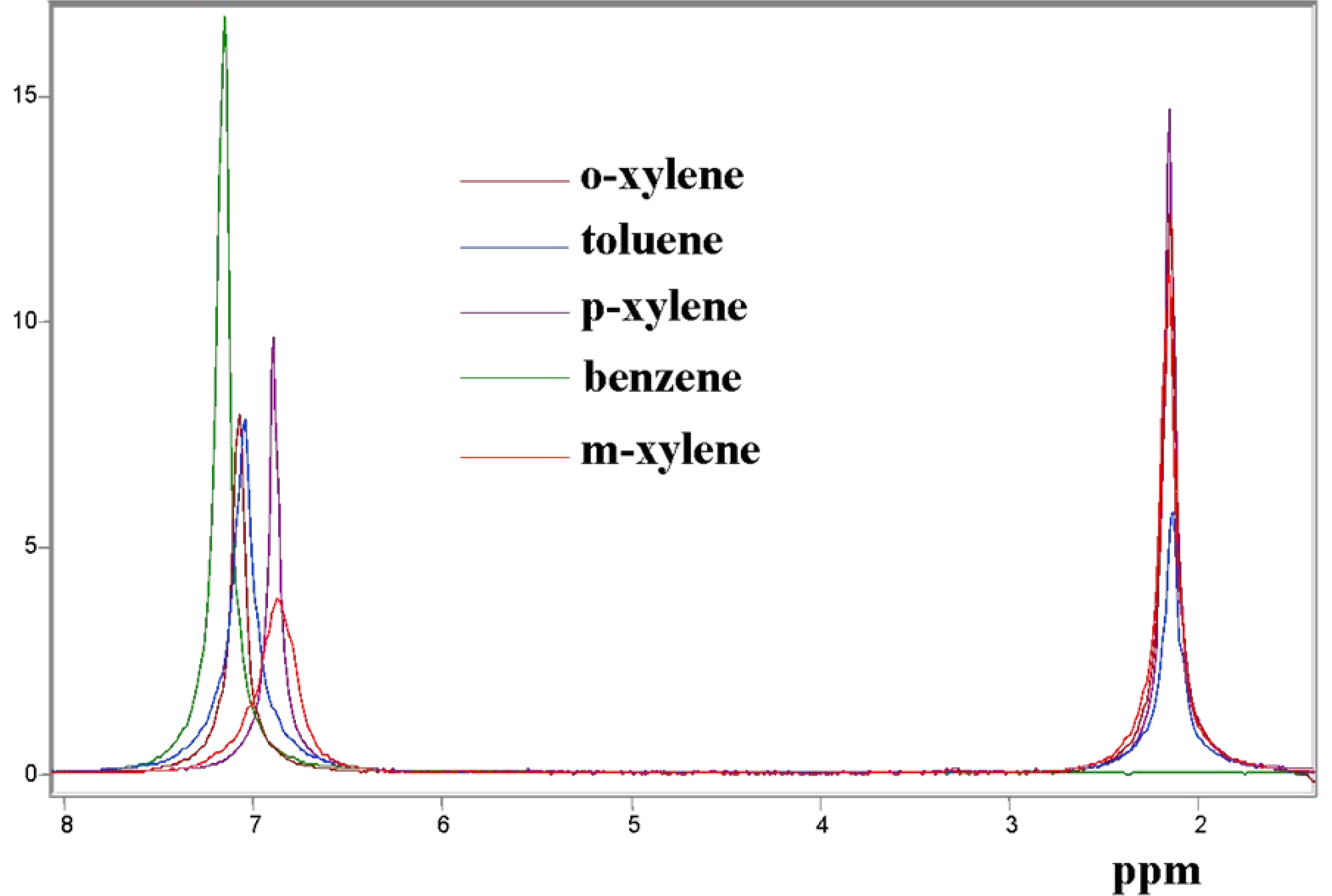
Aromatic/Olefinic Region Showing Change From Block to Random

Ortho-Xylene

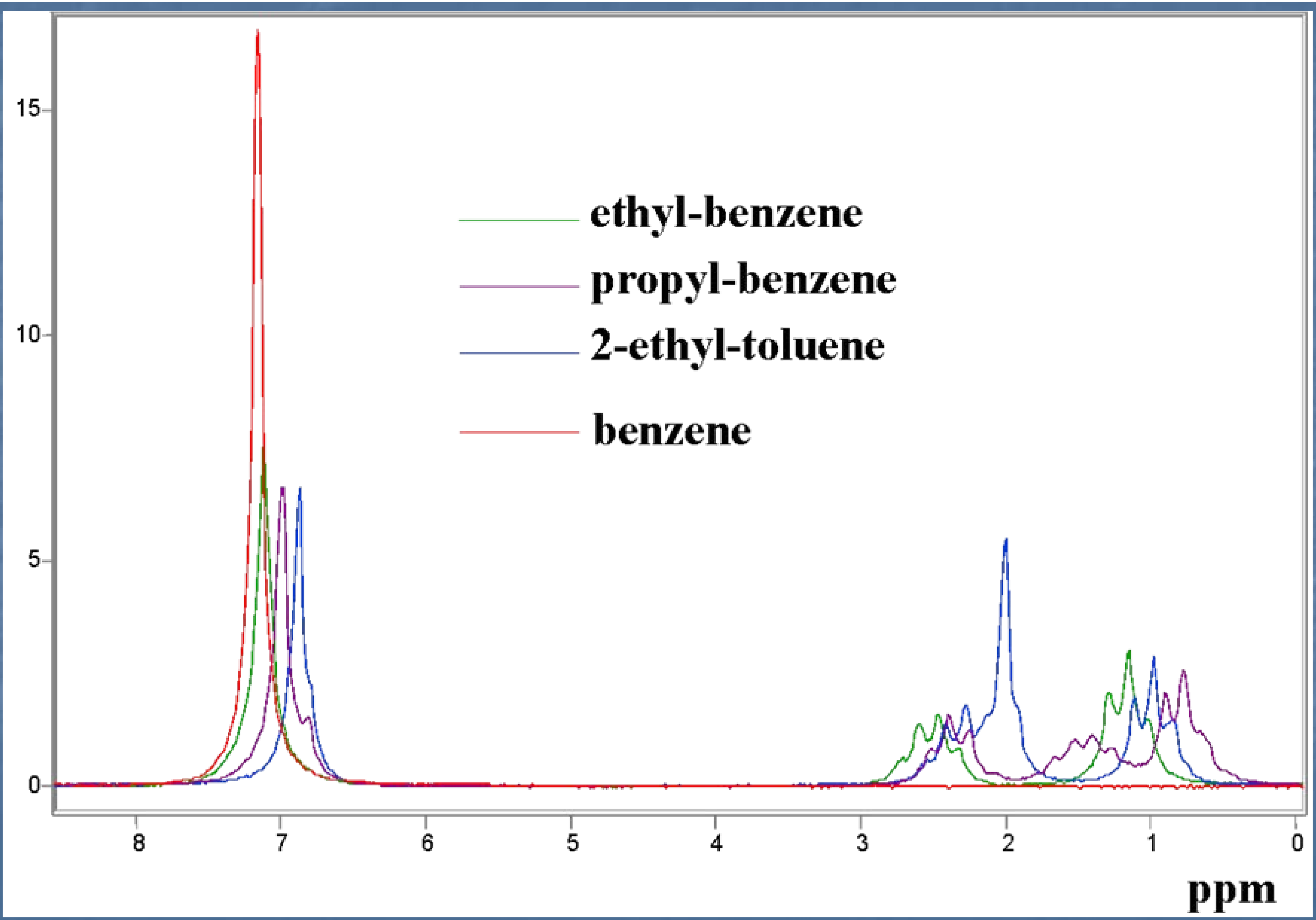



Meta-Xylene
1
1.5
CH3
CH3
*
20
10
0
Arbitrary Y
10.8
9.6
8.4
7.2
6
4.8
3.6
2.4
1.2
0
Parts Per Million


Para-Xylene
30
20
10
0
Arbitrary Y
1
1.5
CH3
H3C
*
11
9.8
8.6
7.4
6.2
5
3.8
2.6
1.4
.2
Parts Per Million



15
10
5
0
8
7
6
5
4
3
2
ppm
o-xylene
toluene
p-xylene
benzene
m-xylene


ethyl-benzene
propyl-benzene
2-ethyl-toluene
benzene
15
10
5
0
8
7
6
5
4
3
2
1
0
ppm

Conclusion

High Resolution FT-NMR has Left the Research Laboratory…. and is Arriving in a Process Near You!

Acknowledgements

Paul Giammatteo – PNA

Tal Cohen – Foxboro NMR Israel

Tony Van Poyenbroeck – Cardoen Technology, Belgium

Invensys

Our NMR Customers