Detailed Hydrocarbon Analyses of Naphtha by On-Line NMR

Integration of Real-Time NMR Feed Analysis With Advanced Process Control and Optimization

Presented By
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Process NMR Associates, LLC
Danbury, Connecticut

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Presentation Overview

- Process NMR Associates, LLC – Business Profile
- NMR Basics – Very Briefly
- Advantages/Disadvantages of NMR as a Process Spectroscopy
- Applications
    1. Naphtha Steam Cracking Control and Optimization
    2. Reformer Unit Control
- Conclusion

Company: Process NMR Associates, LLC

Founded : 1997

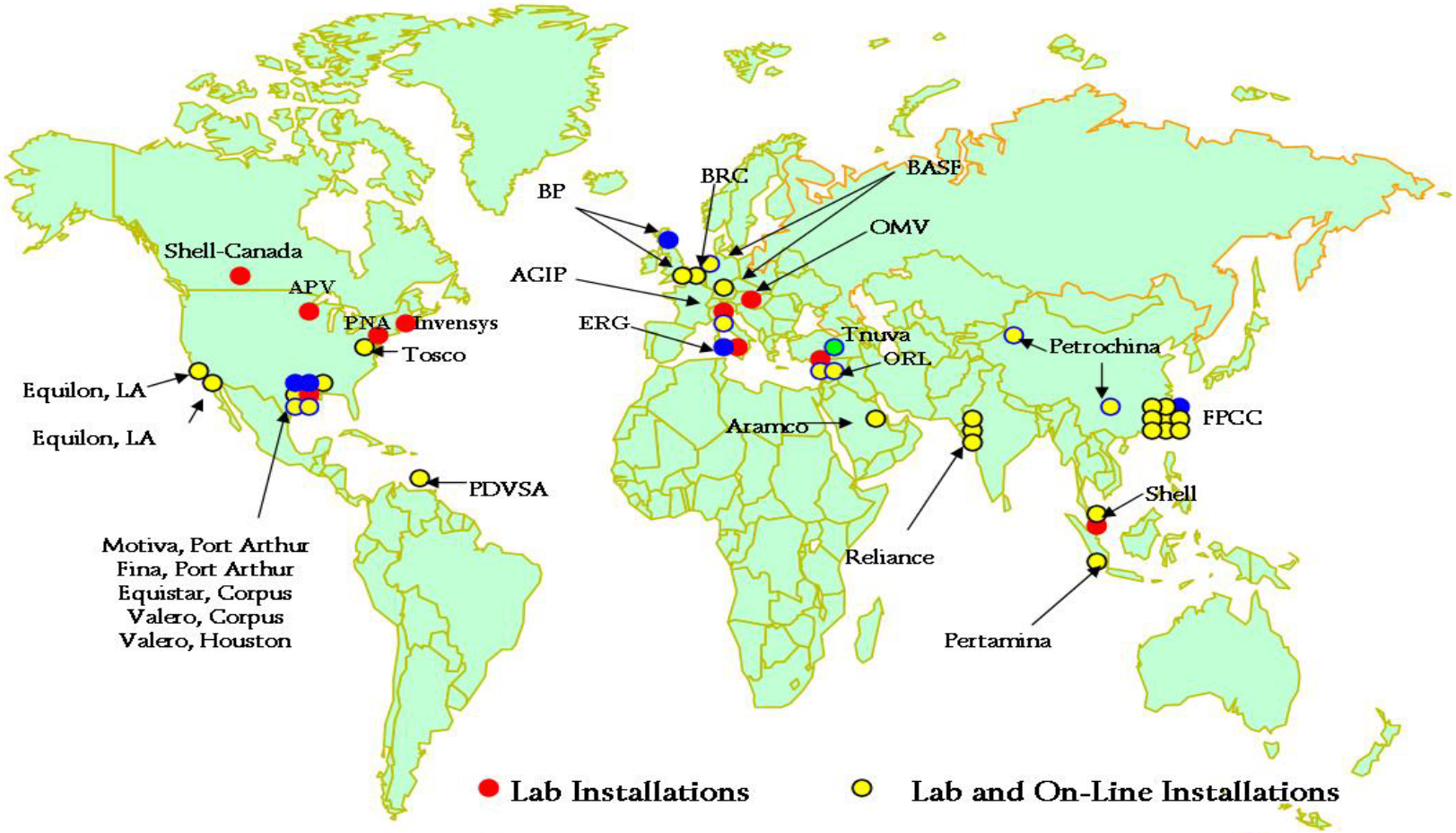
Personnel: 2 Ph.D. Chemists

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 MRA Installations



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PROCESS NMR ASSOCIATES

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.

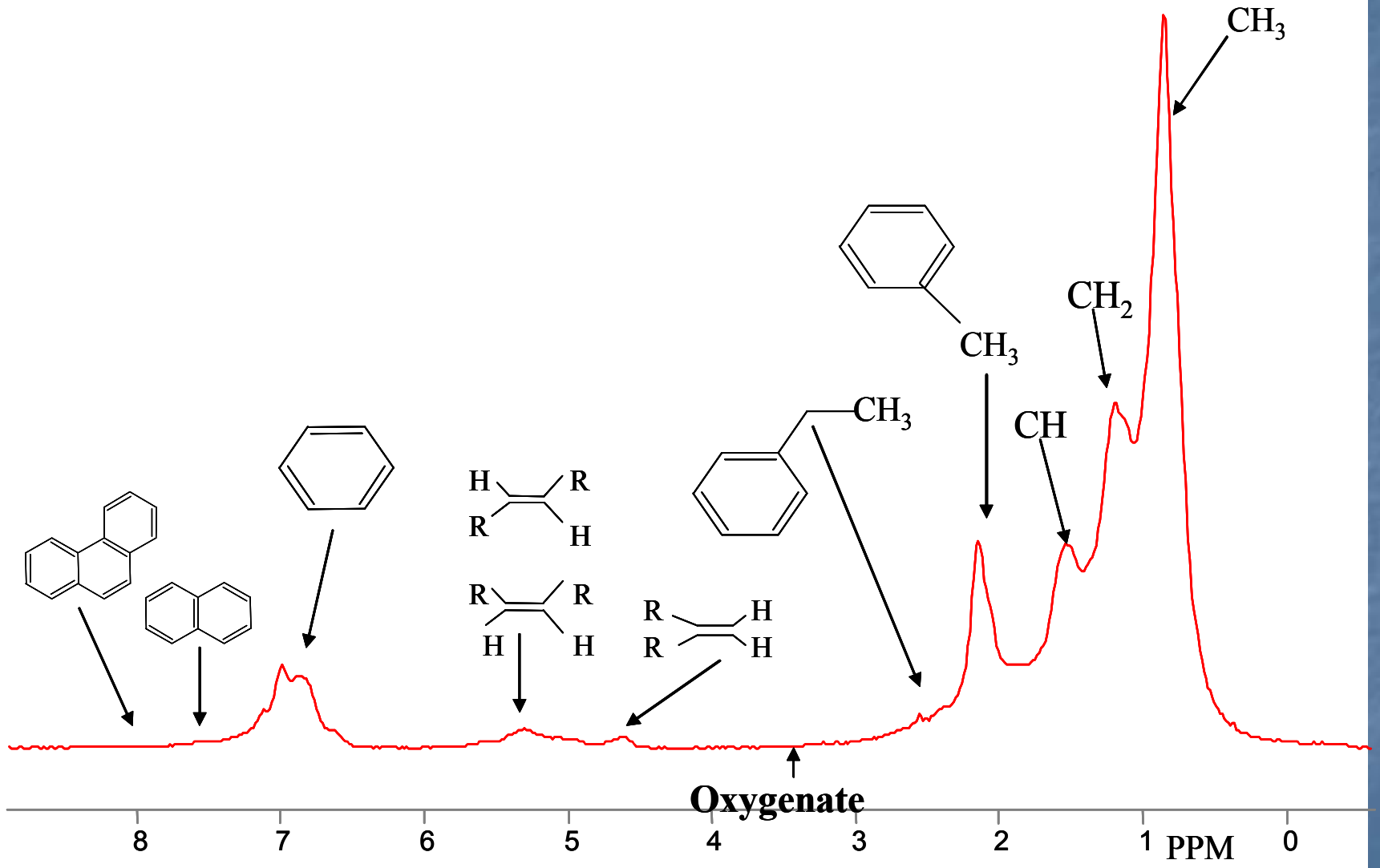
Advantages and Disadvantages of NMR Applied to Process

Advantages:

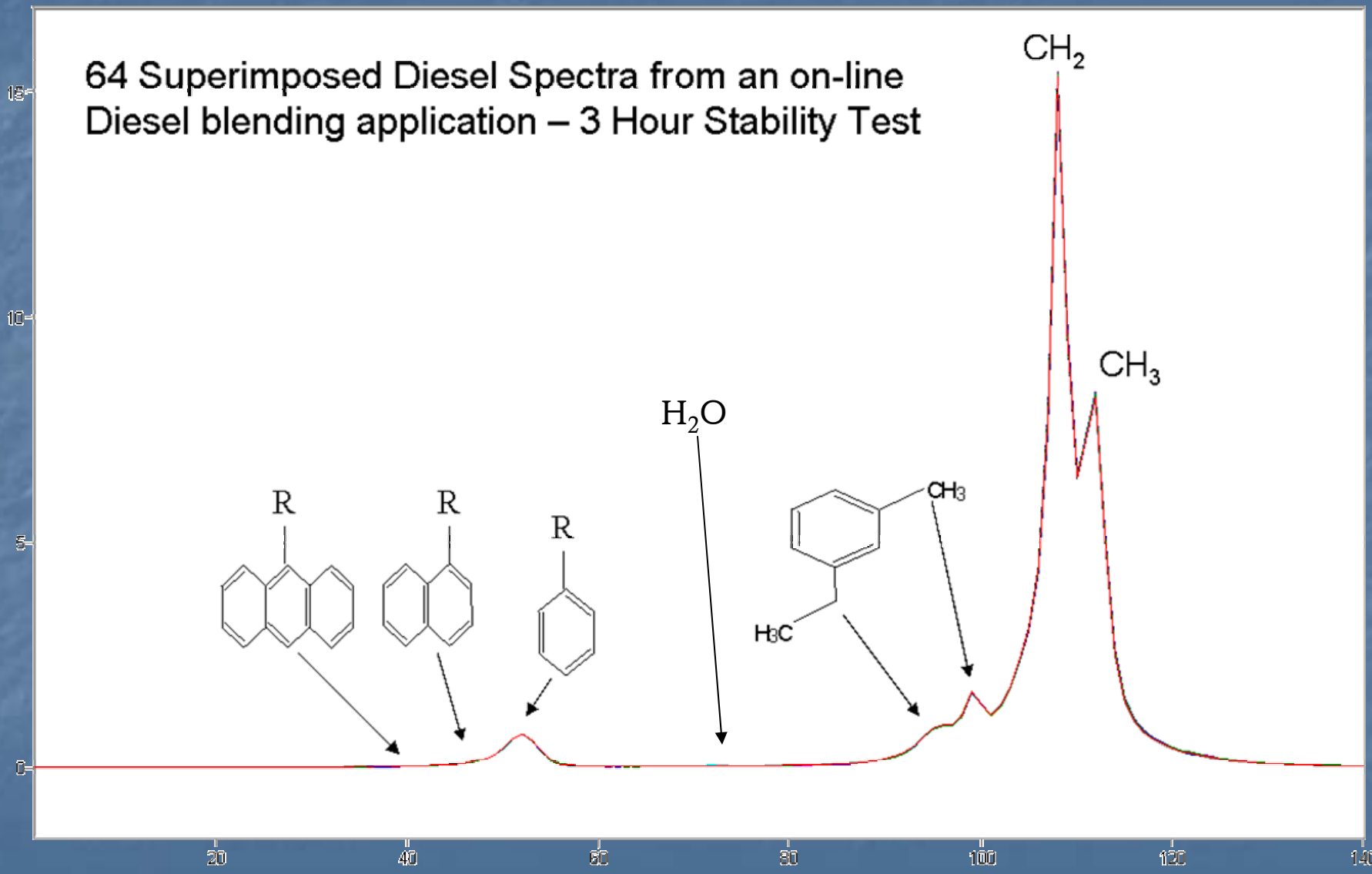
Non-optical spectroscopy
No spectral temperature dependence under optimal conditions
Minimal sampling requirements
Spectral response to sample chemistry is linear
Chemical regions of NMR spectra are orthogonal
Entire volume is sampled by the NMR experiment
Water is in distinct region and can be digitally removed
Detailed hydrocarbon information is readily observed.
Fundamental chemical information can be derived directly from spectrum.
Colored or black samples are readily observed

Disadvantages:

Solids cannot be observed
Individual molecular components 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

Application: Steam Cracking Optimization

Cracker Facility Capacity: 600,000 Tonnes per Year

Control Strategy: Feed Forward Detailed Hydrocarbon Analysis to SPYRO Optimization Package (Technip/KTI) and APC

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

NMR PLS Outputs: Naphtha – Detailed PIONA
c4-c10 n-paraffin, c4-C11 i-paraffin,
c6-c10 aromatics, c5-c10naphthenes
Other Projects require D86 and D2887 Distillation and Density

Value Added: Unit Optimization - $150K /year
4 Units Now Being Optimized ($600K/year)
ROI 6-8 Months

Performance : NMR Available 99%+ Since May 2000
Models Updated in a Limited Manner

Plant Issues :

Crackers produce 600,000 tonnes of ethylene per year

365 Days of Production per year with turnaround every third year

Strategic Requirements : Naphtha purchased with widely varying feed specification

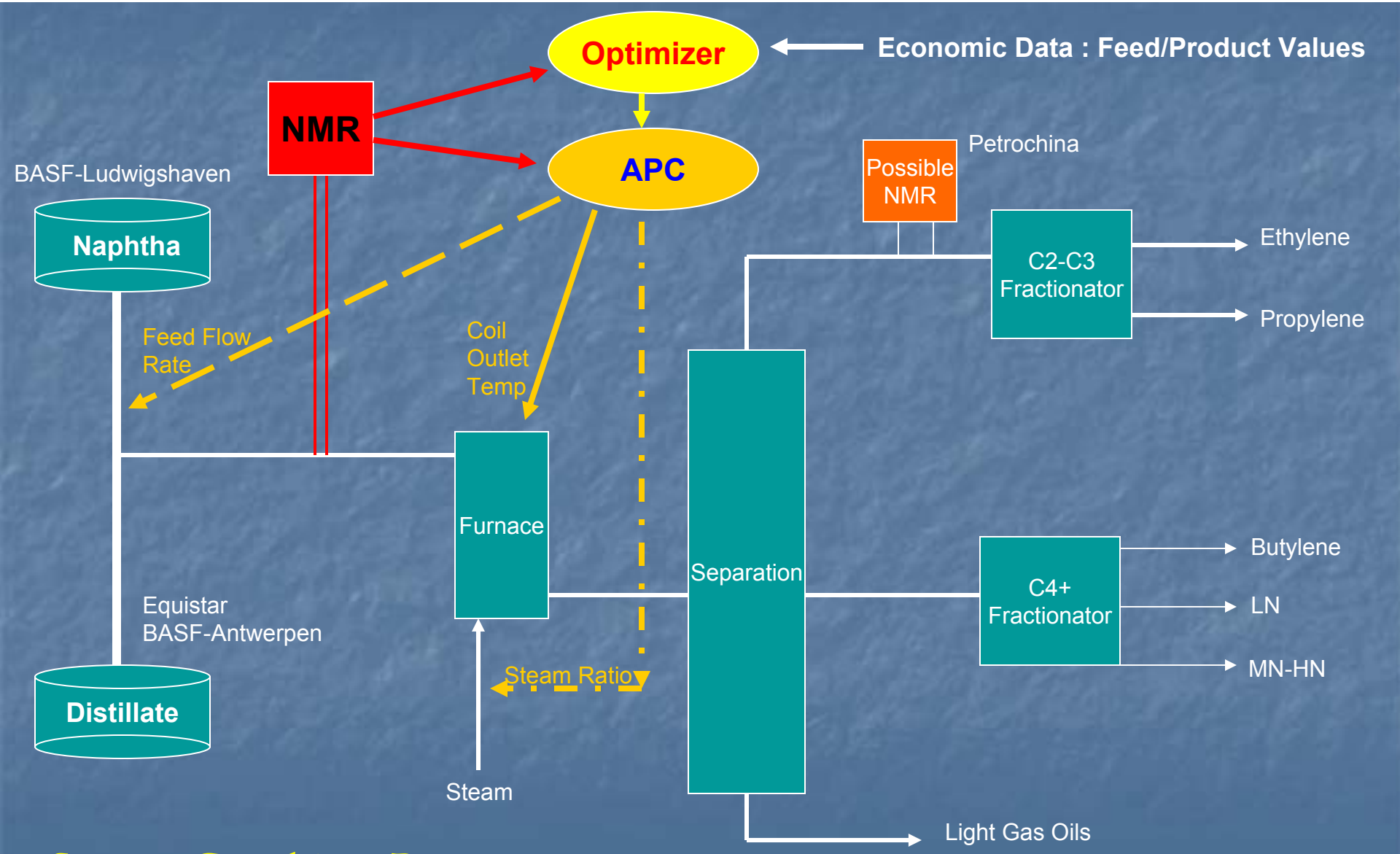
Need:

Cracker Feed Characterization for APC and Optimization

APC Requirements: Monitor feed characteristics to minimize lost production due to high number of feed transitions:

Simplistically:
1) Heavier naphtha can violate coil outlet temperatures leading to coking or tube wall damage
2) Lighter naphtha can exceed downstream compressor loading

Optimization Requirements: Detailed PIONA analysis allows conditions to be optimized for optimum ethylene/propylene/butylene production based on market conditions.



Steam Cracking Process

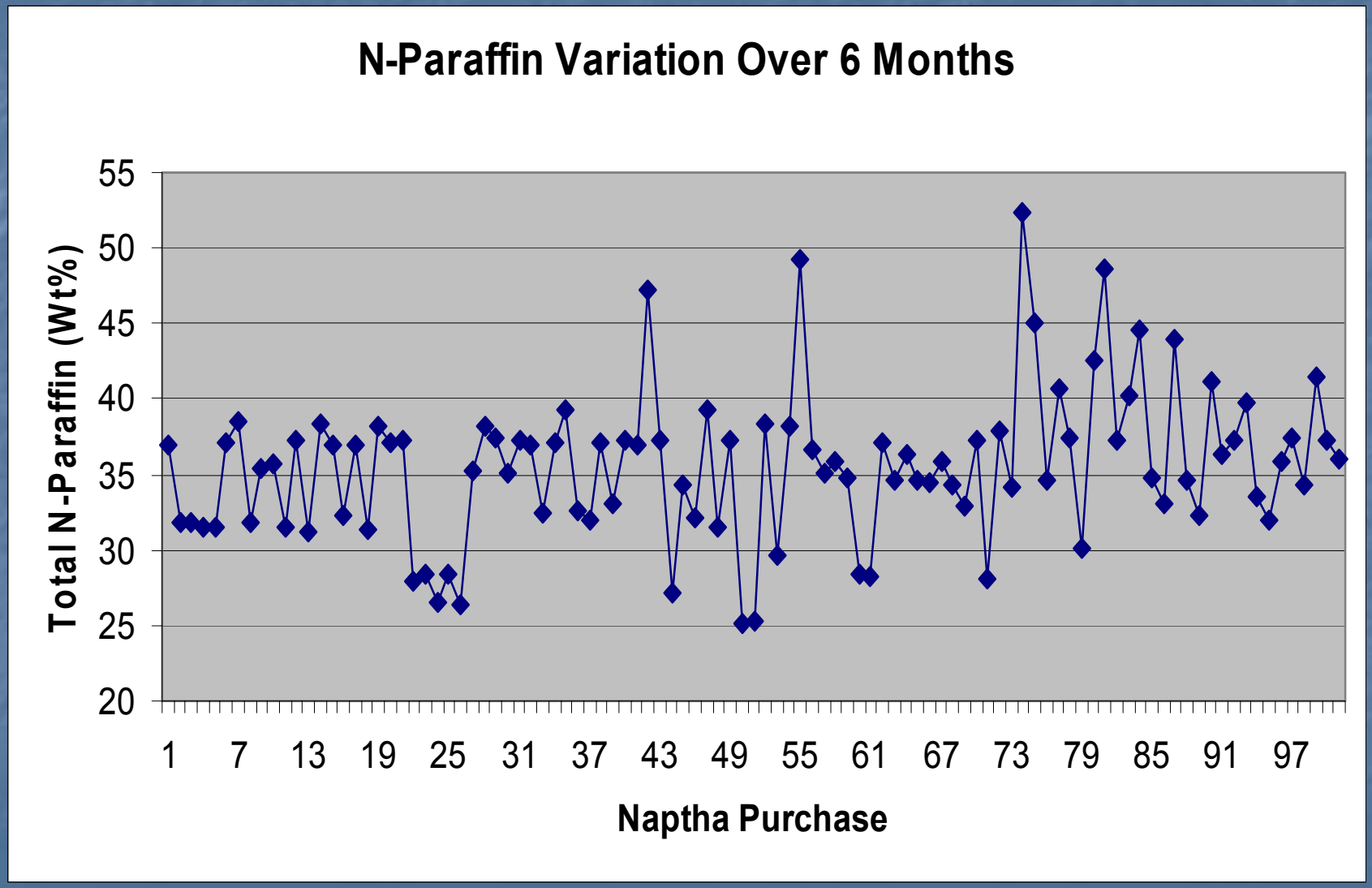
TYPICAL NAPHTHA

Component	Naphtha A	Naphtha B	Naphtha C
n-C4	3.46	4.53	3.28
n-C5	11.73	19.37	15.96
n-C6	7.97	10.5	10.92
n-C7	4.7	3.49	4.44
n-C8	2.9	0.95	2.03
n-C9	1.7	0.19	1.00
n-C10	0.46	0.02	0.14
Total n-Paraffin	33.08	39.08	37.77
iso-C4	0.4	0.38	0.42
iso-C5	9.86	15.51	11.05
iso-C6	9.05	13.49	13.48
iso-C7	5.8	5.33	7.10
iso-C8	4.03	2.15	3.60
iso-C9	2.45	0.5	1.84
iso-C10	1.47	0.1	0.65
iso-C11	0.2	0	0.05
Total iso-Paraffin	33.26	37.46	38.19

Component	Naphtha A	Naphtha B	Naphtha C
Cyclopentane	1.13	2.2	1.14
Methylcyclopentane	3.82	5.15	4.01
Cyclohexane	3.77	3.82	3.13
Methylcyclohexane	4.98	3.06	3.23
Other Nap-C7	3.26	3.36	2.78
Nap-C8	3.44	1.82	2.34
Nap-C9	2.92	0.61	1.73
Nap-C10	0.04	0	0.02
Total Naphthenes	23.36	20.02	18.38
Benzene	2.25	1.36	1.77
Toluene	3.15	1.23	1.79
Ethyl-Benzene	0.55	0.07	0.21
Xylenes	2.87	0.62	1.33
Arom-C9	1.07	0.04	0.36
Arom-C10	0.11	0	0.04
Total Aromatics	10	3.32	5.50
Total Olefins	0.3	0.12	0.03

Cracking Process Products

	Naphtha 1	Naphtha 2	Naphtha 3
Conversion (%)	81.5	94.2	92.0
Outlet Temperature (K)	1053	1073	1073
Steam/Feed Ratio	0.5	0.5	0.75
Yields (Wt%)			
Hydrogen	0.5	0.7	0.7
Methane	12.0	15.3	14.2
Ethyne	0.1	0.3	0.3
Ethene	19.5	23.5	24.0
Ethane	4.0	4.0	3.4
Propene	16.2	16.2	15.5
Propane	0.5	0.5	0.5
Butadiene	3.7	4.0	4.3
Butenes	7.9	5.4	6.0
Butane	2.6	1.4	1.7
C5+	30.2	26.0	25.8
Fuel Oil	2.5	3.4	3.0


N-Paraffin Variation Over 6 Months
Total N-Paraffin (Wt%)
55
50
45
40
35
30
25
20
1
7
13
19
25
31
37
43
49
55
61
67
73
79
85
91
97
Naptha Purchase

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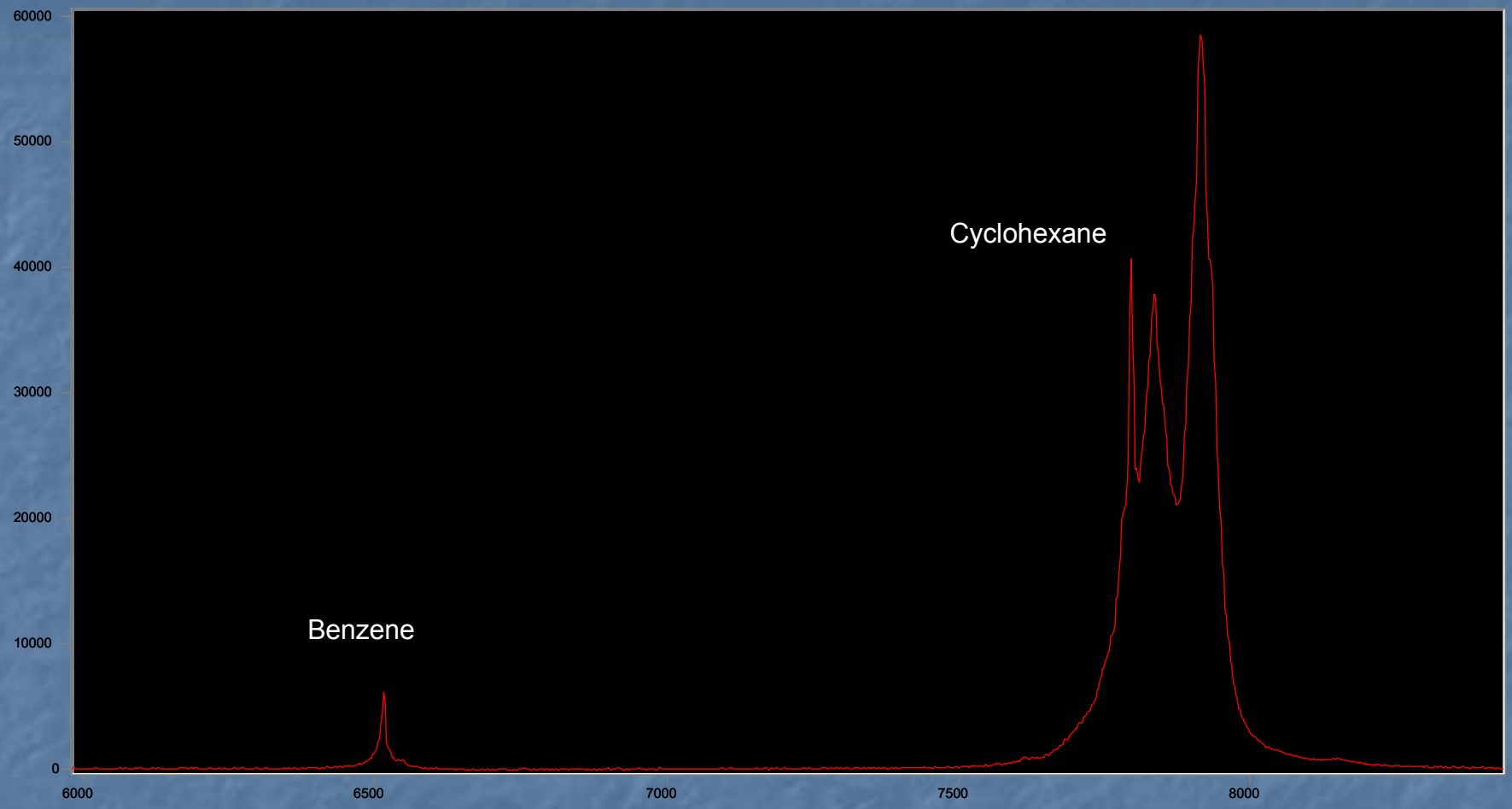

Arbitrary / Arbitrary

Paged Y-Zoom CURSOR

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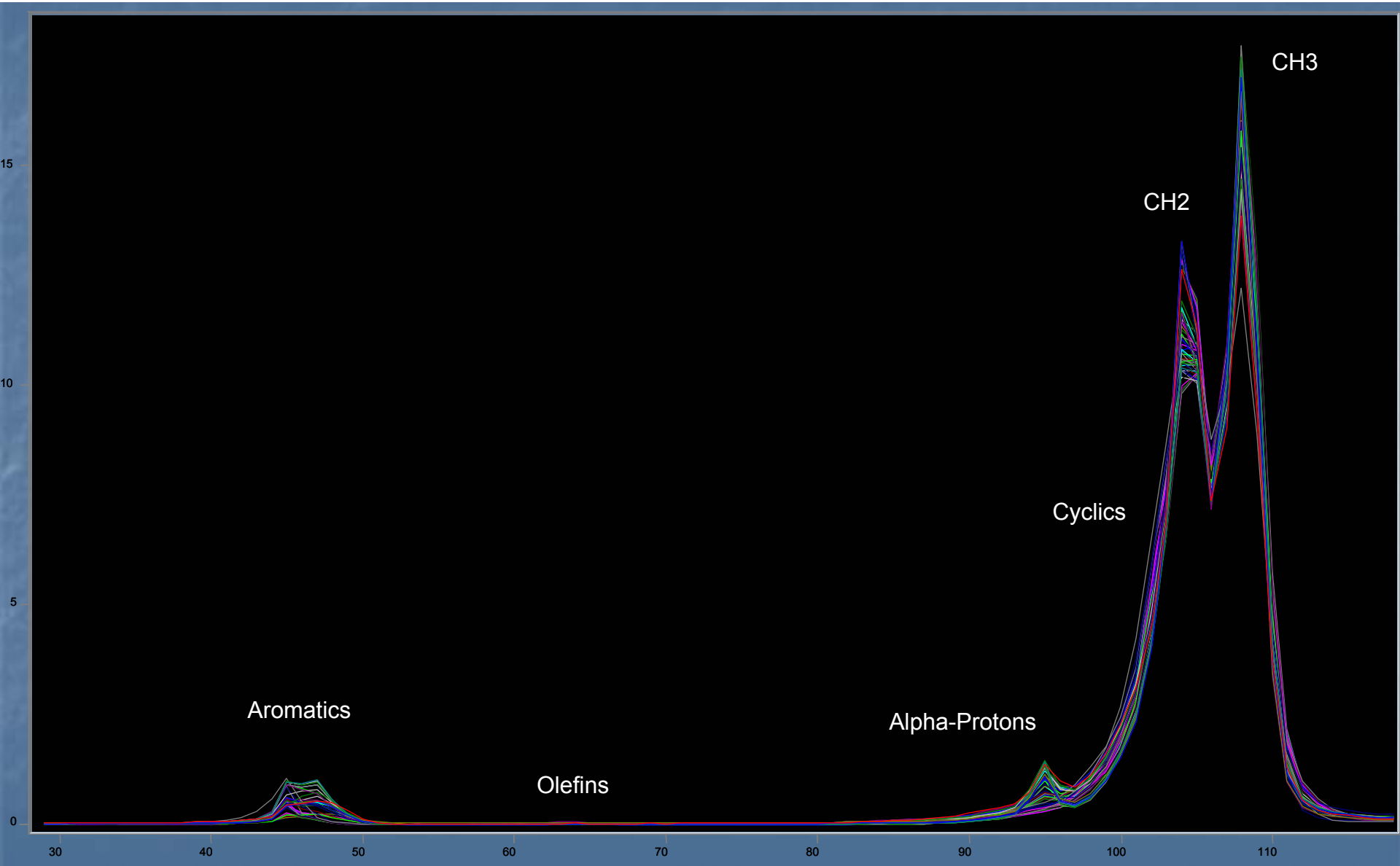
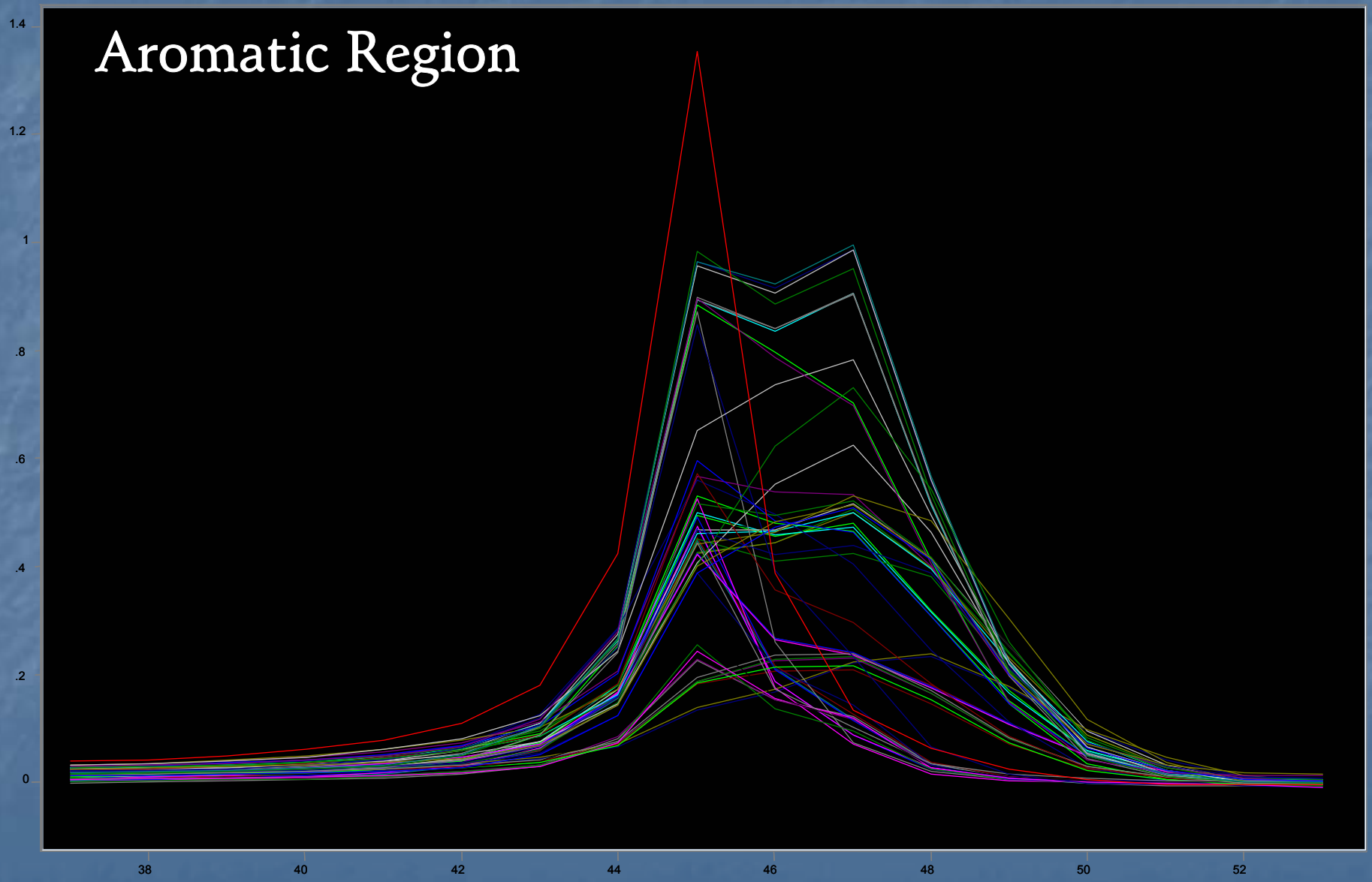
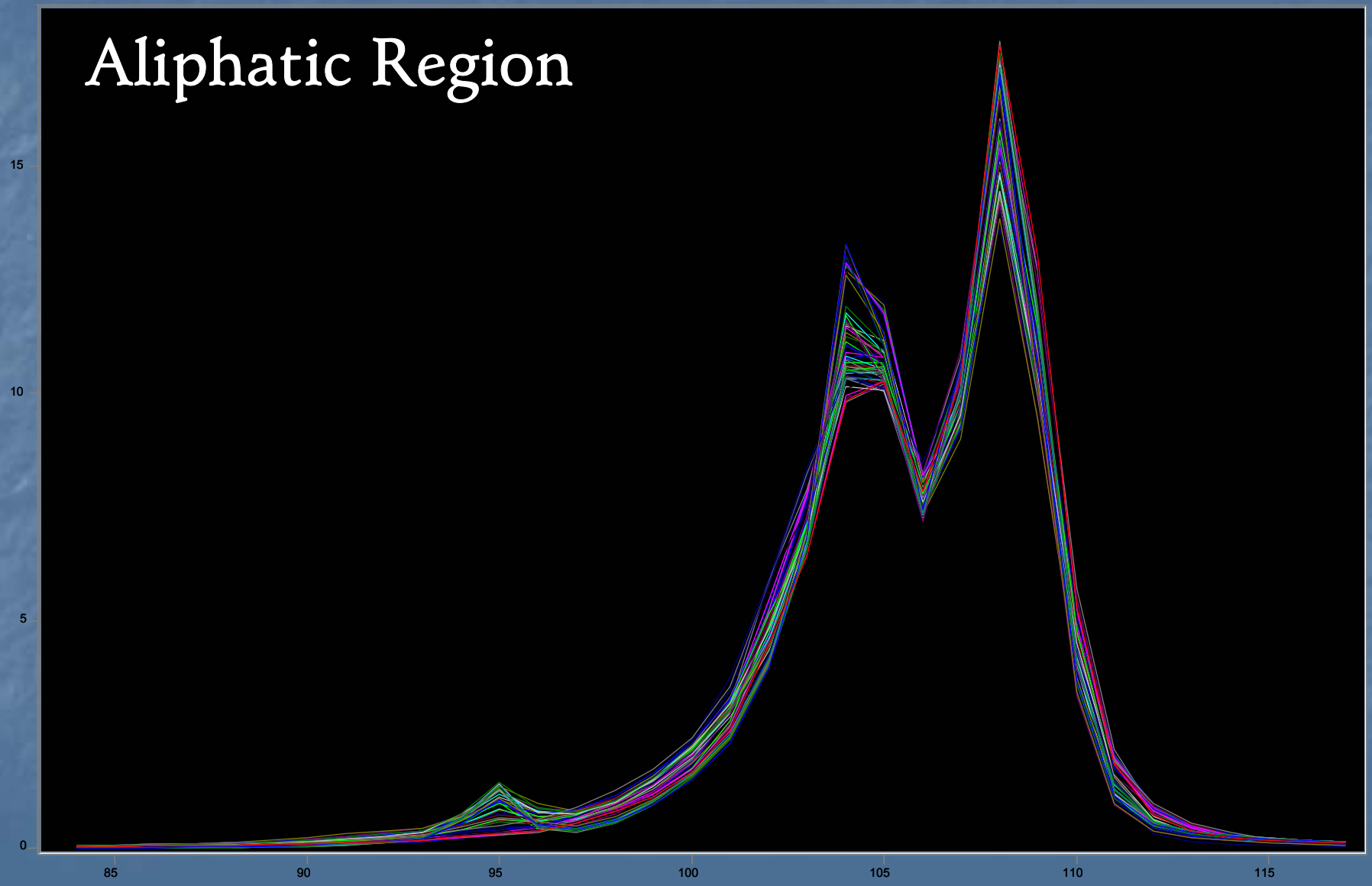
Foxboro NMR SPC File.

PROCESS NMR ASSOCIATES




Aromatic Region
1.4
1.2
1
.8
.6
.4
.2
0
38
40
42
44
46
48
50
52

Aliphatic Region



Steam Cracker Optimization - Project Timeline

Feasibility Performed (30 Samples) – December 1999

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

Online System Installed – April 2000

On-Line Localization and Further Model Expansion (65 Samples)– 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)

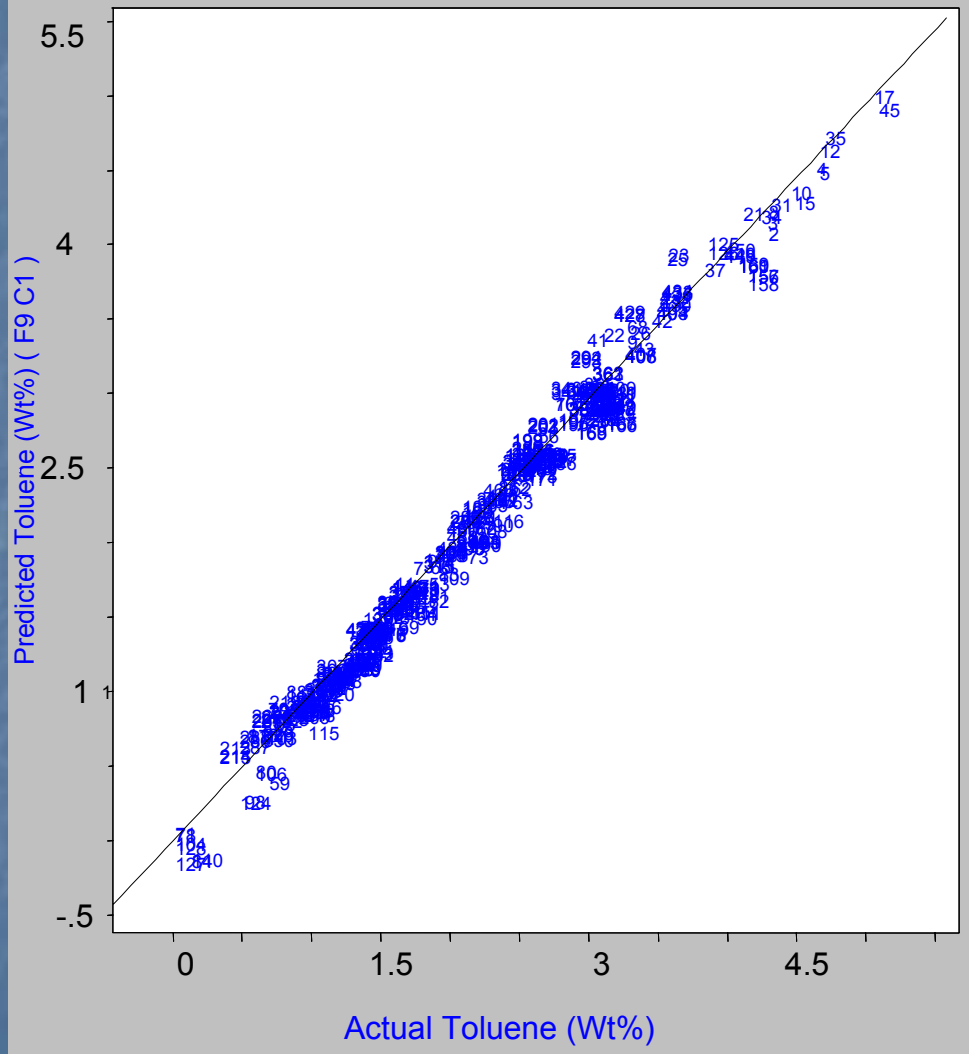
NMR Put on Control (Detailed PIONA into SPYRO Model for Unit Optimization) Oct 2000

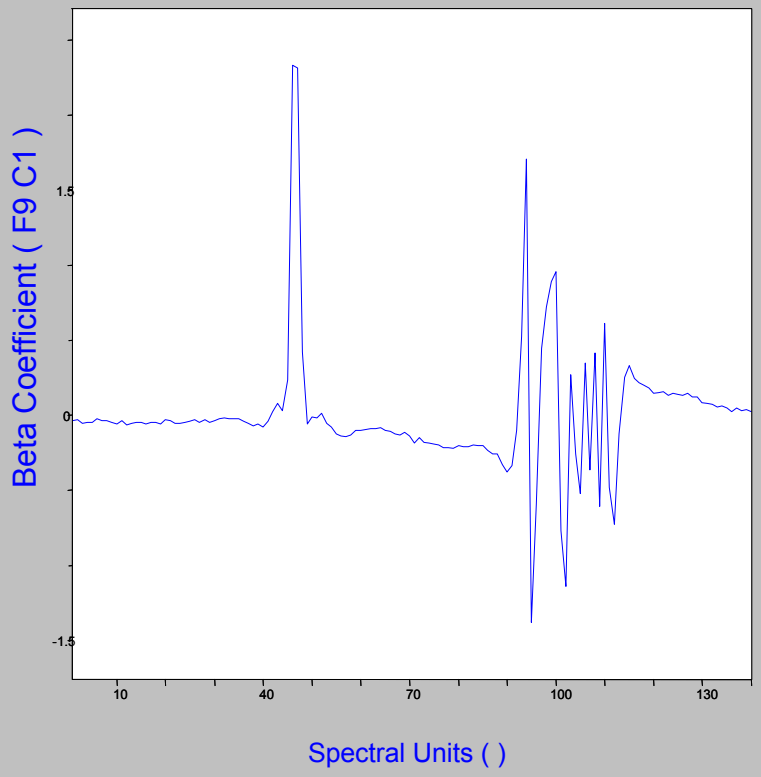
Models have been performing relatively untouched (6 parameters of 32 updated on 4 occasions) since end of validation period. Models updated in limited manner 5 times in 2 years.

99+% Availability September 2000 – May 2002

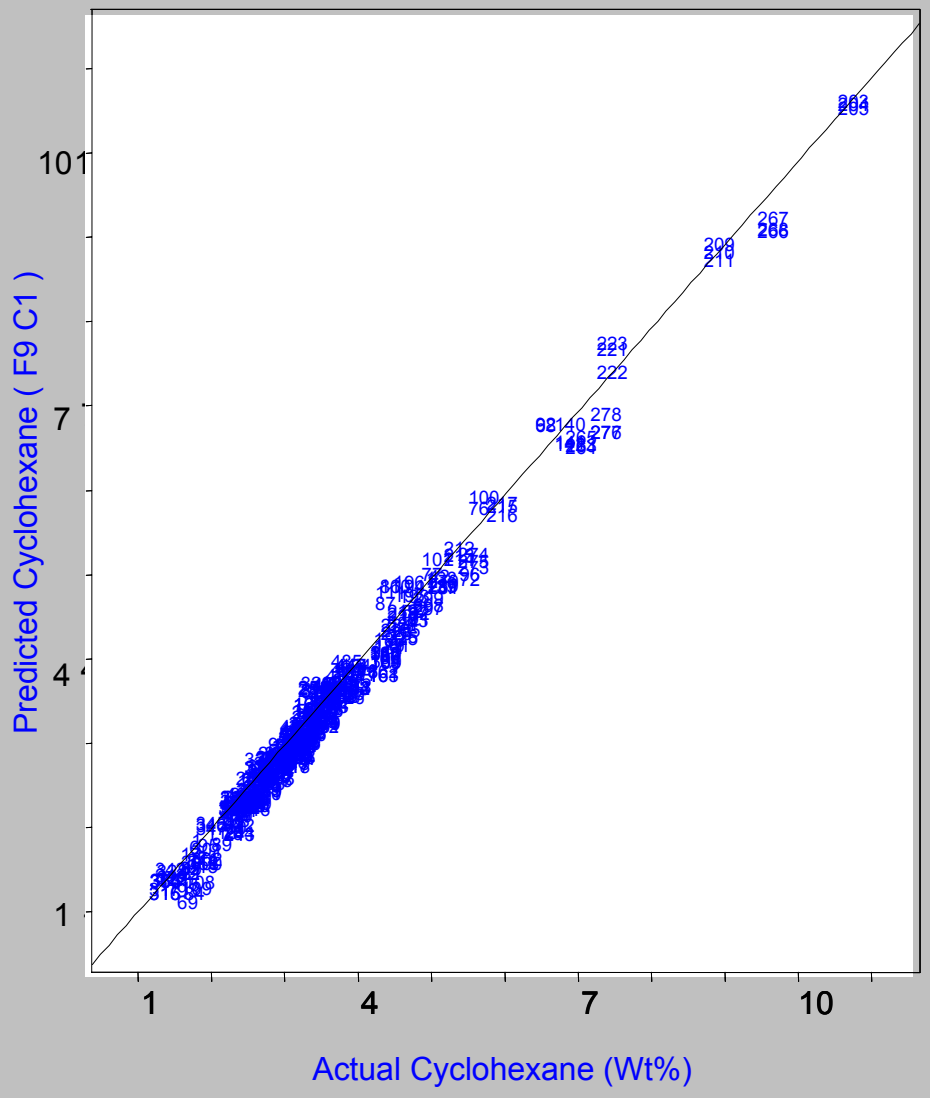
March 2002 – Three Further Feed-Streams Added to NMR – No model updates required.

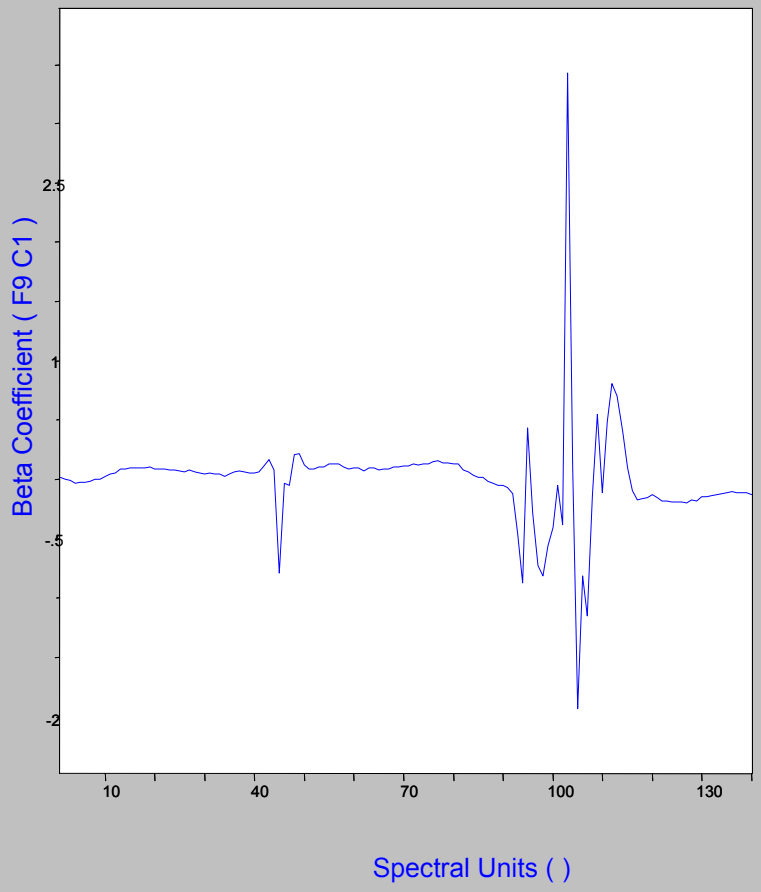
Toluene


Predicted Toluene (Wt%) (F9 C1)
Actual Toluene (Wt%)
5.5
4
2.5
1
-.5
0
1.5
3
4.5

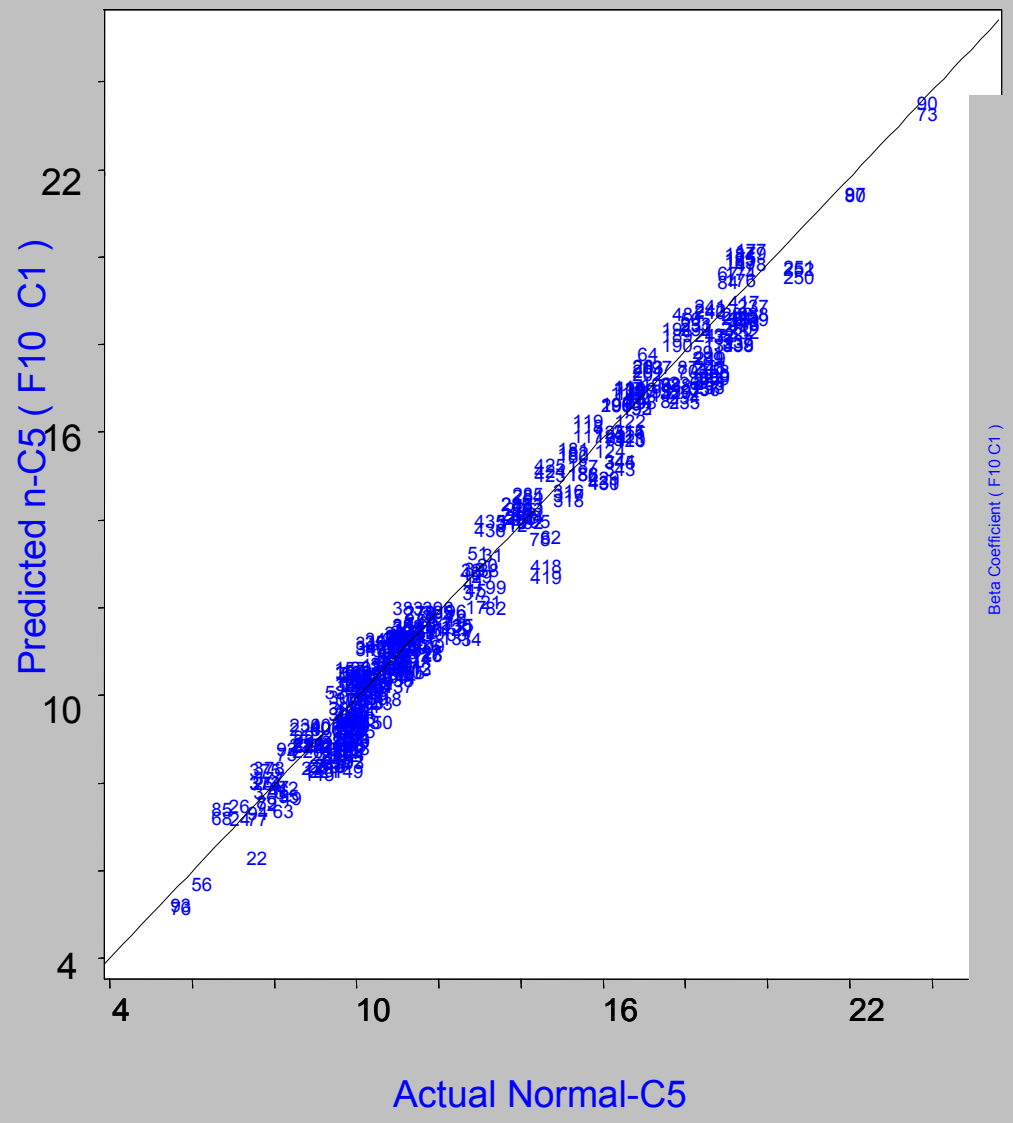

Beta Coefficient (F9 C1)
Spectral Units ( )
1.5
0
-1.5
10
40
70
100
130

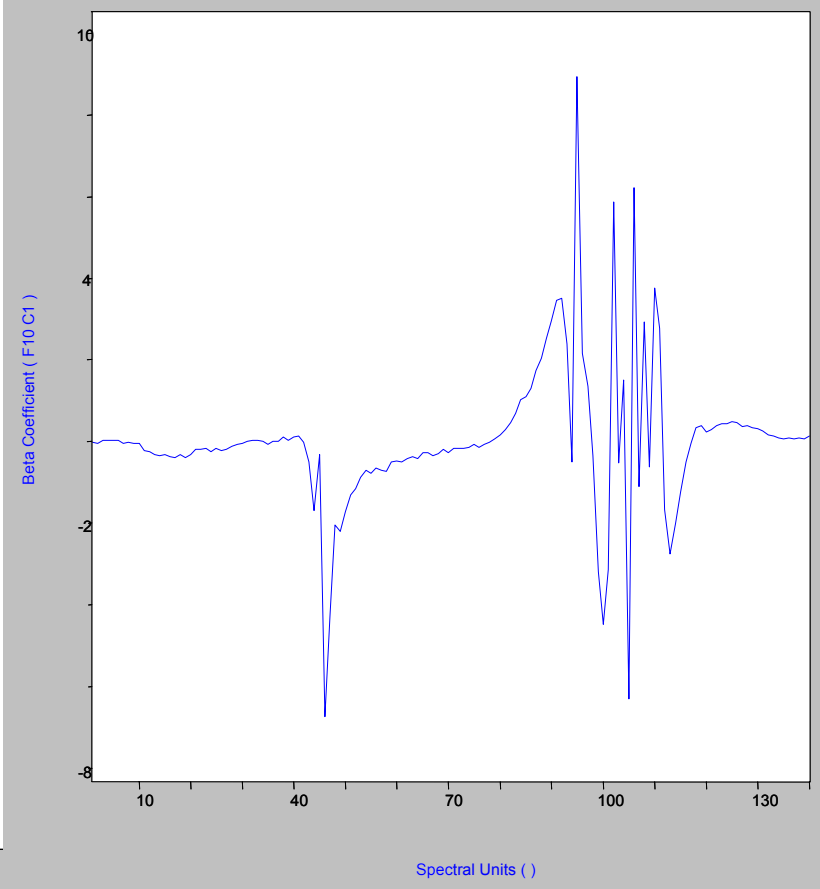
Cyclohexane



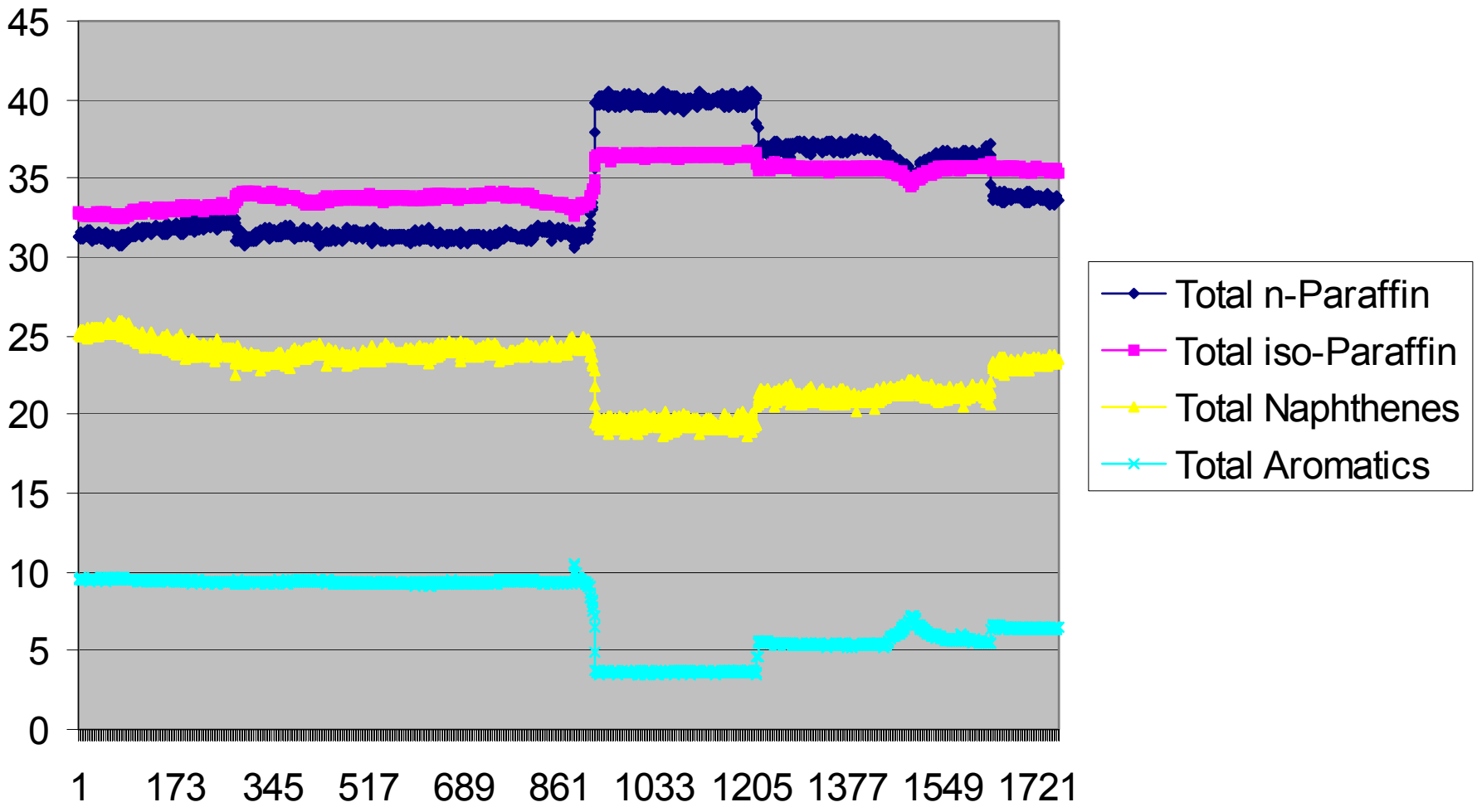


Normal-C5

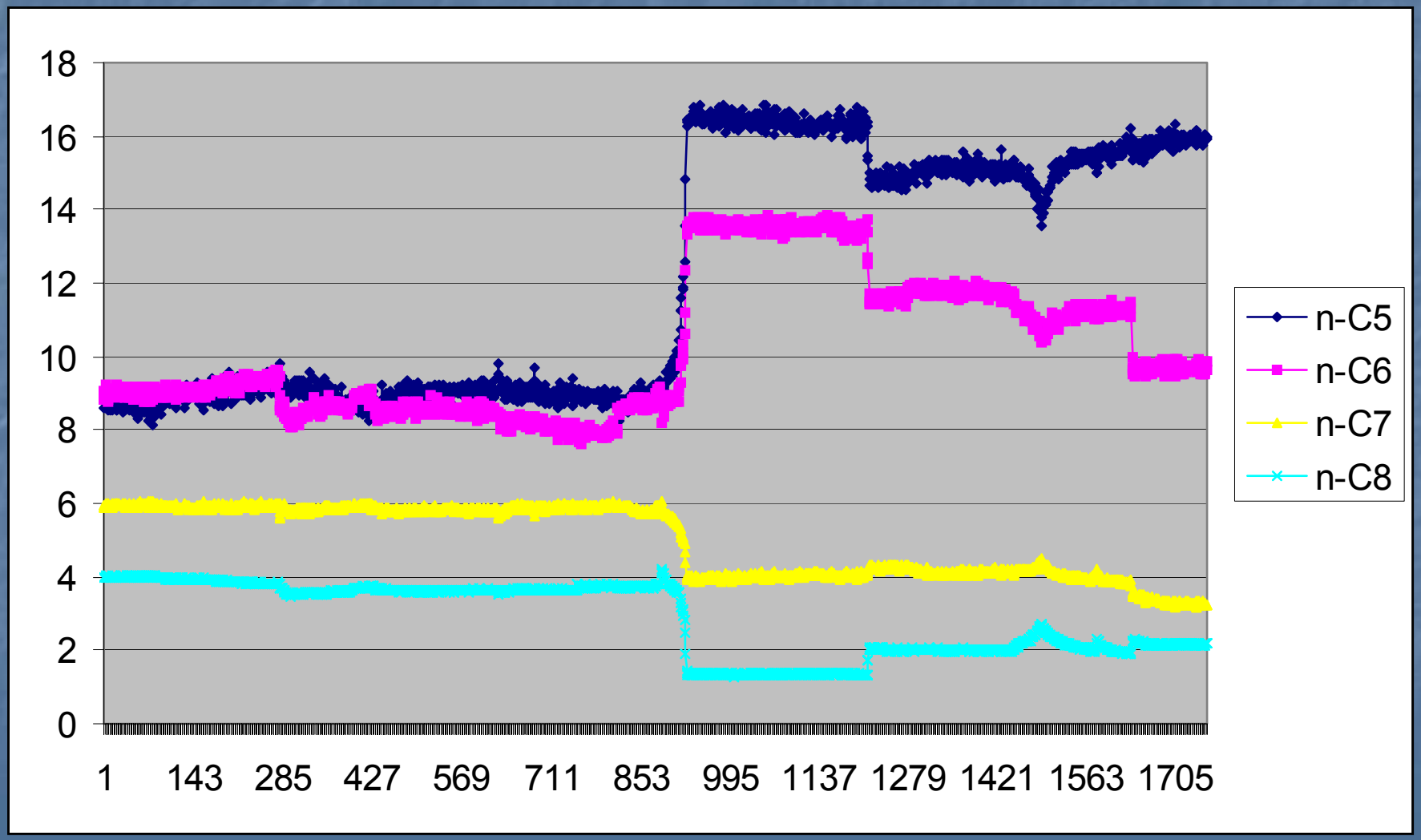

Predicted n-C5 (F10 C1)
Actual Normal-C5
4
10
16
22


Beta Coefficient (F10 C1)
Spectral Units ( )
10
40
70
100
130

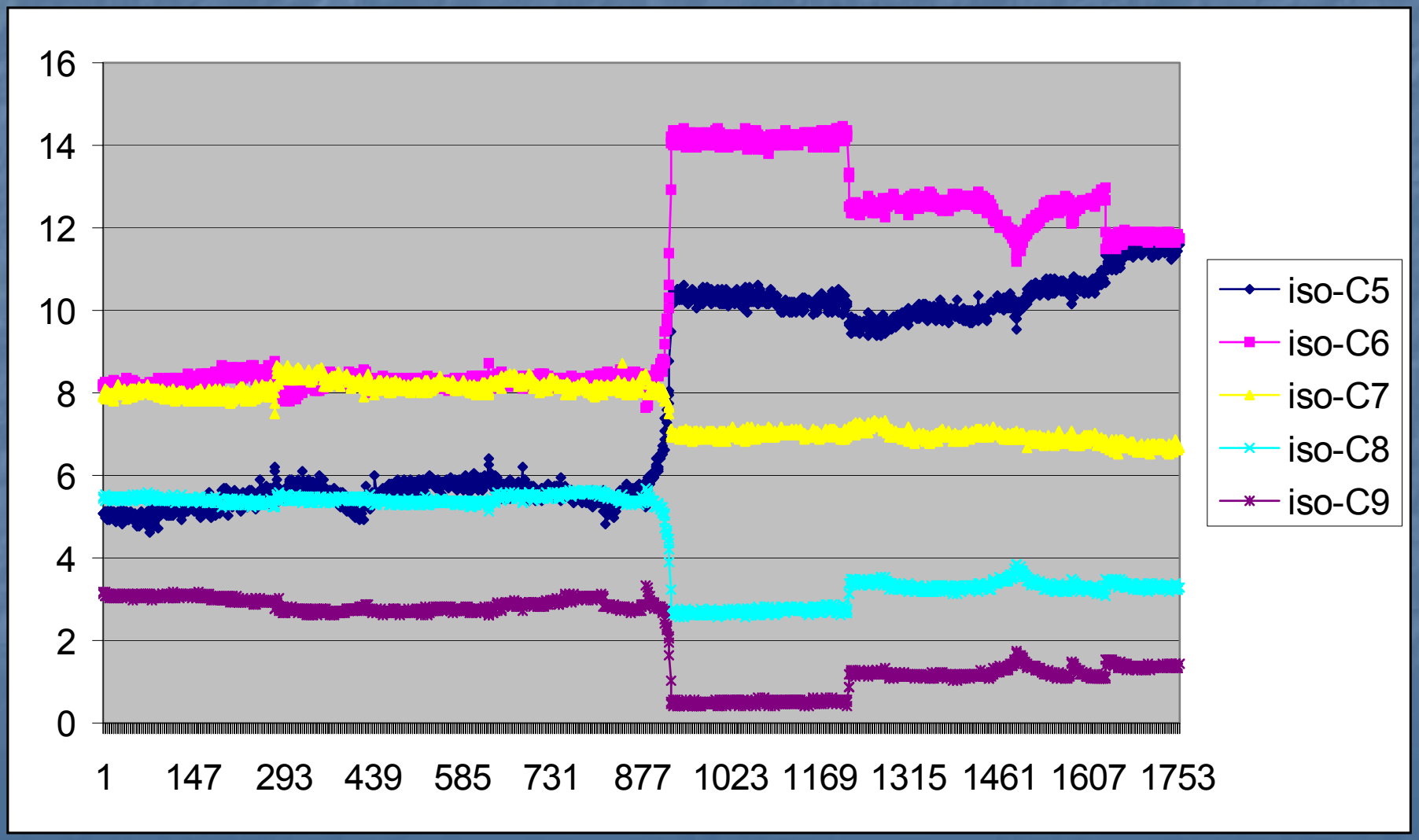
96 Hours of NMR Process Output - PINA



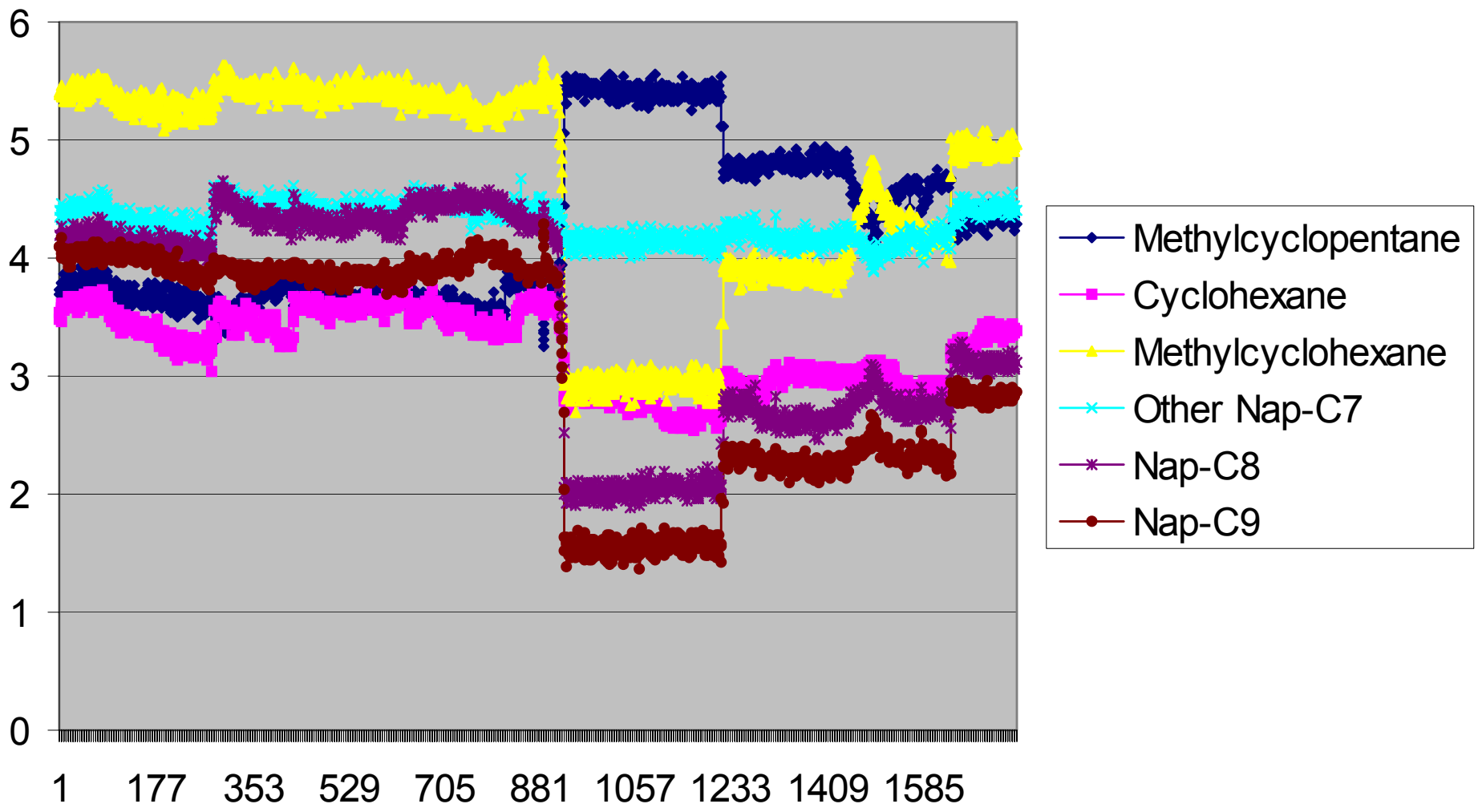
96 Hours of NMR Process Output – n-Paraffin Components



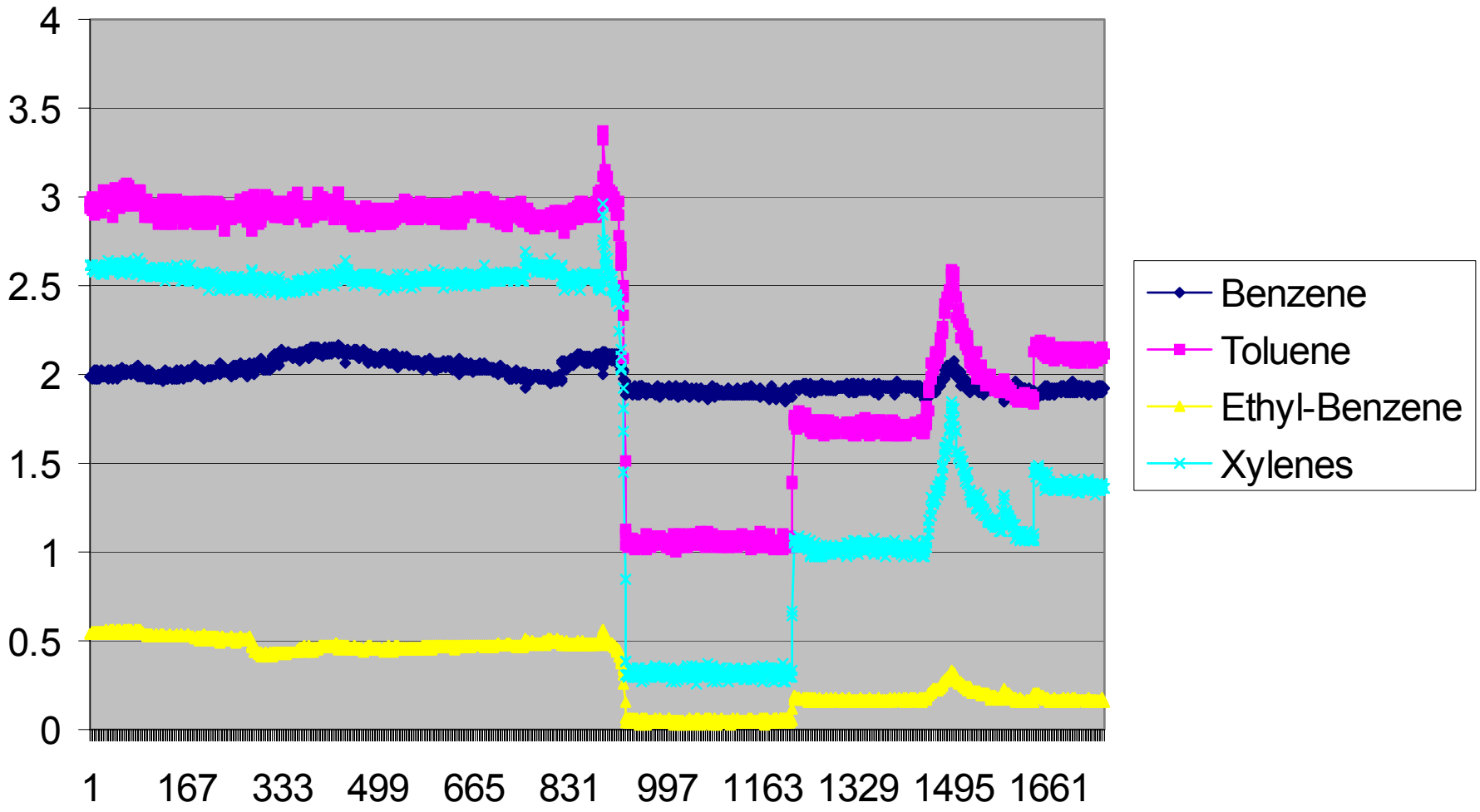
96 Hours of NMR Process Output – iso-Paraffin Components

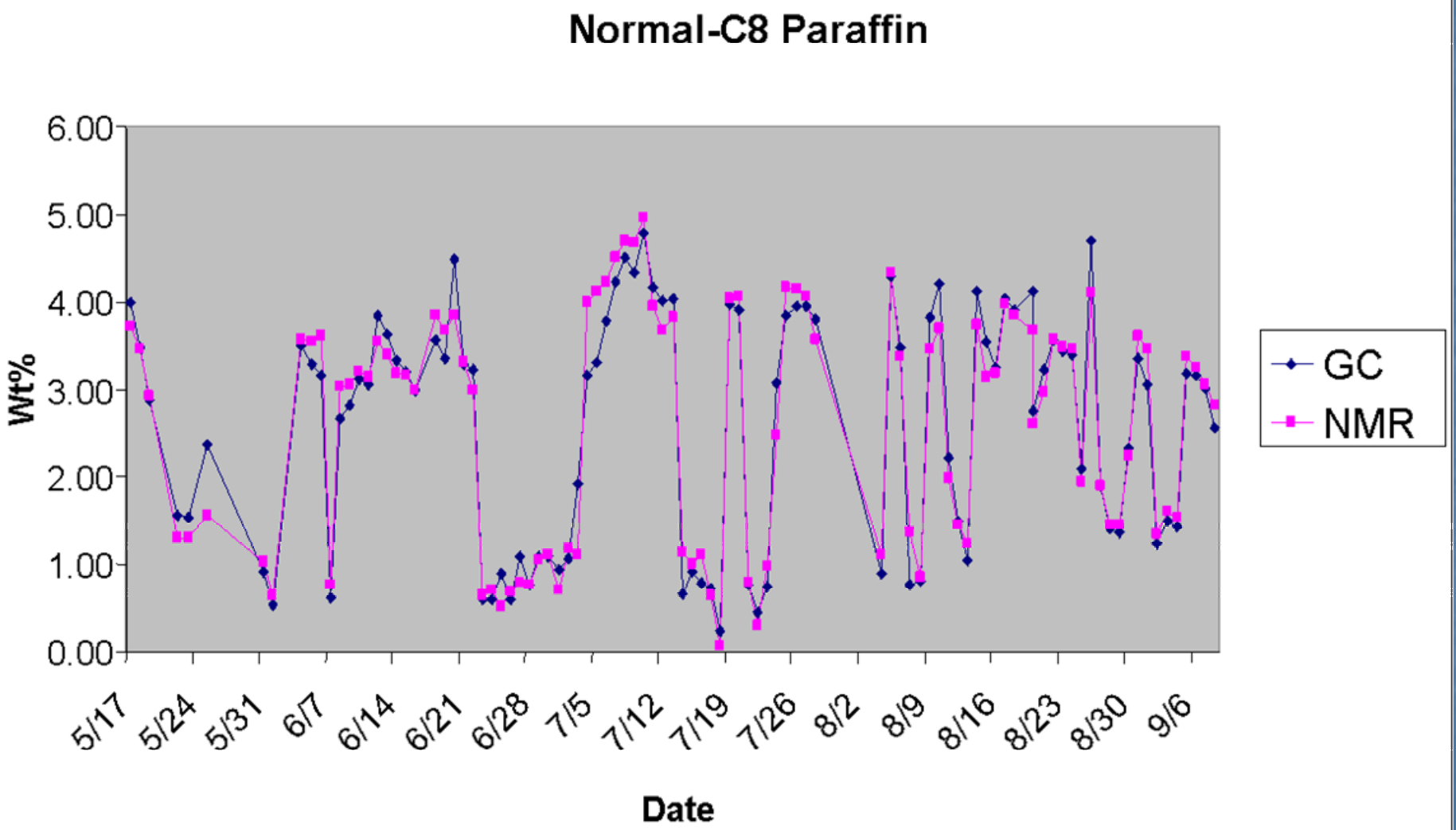


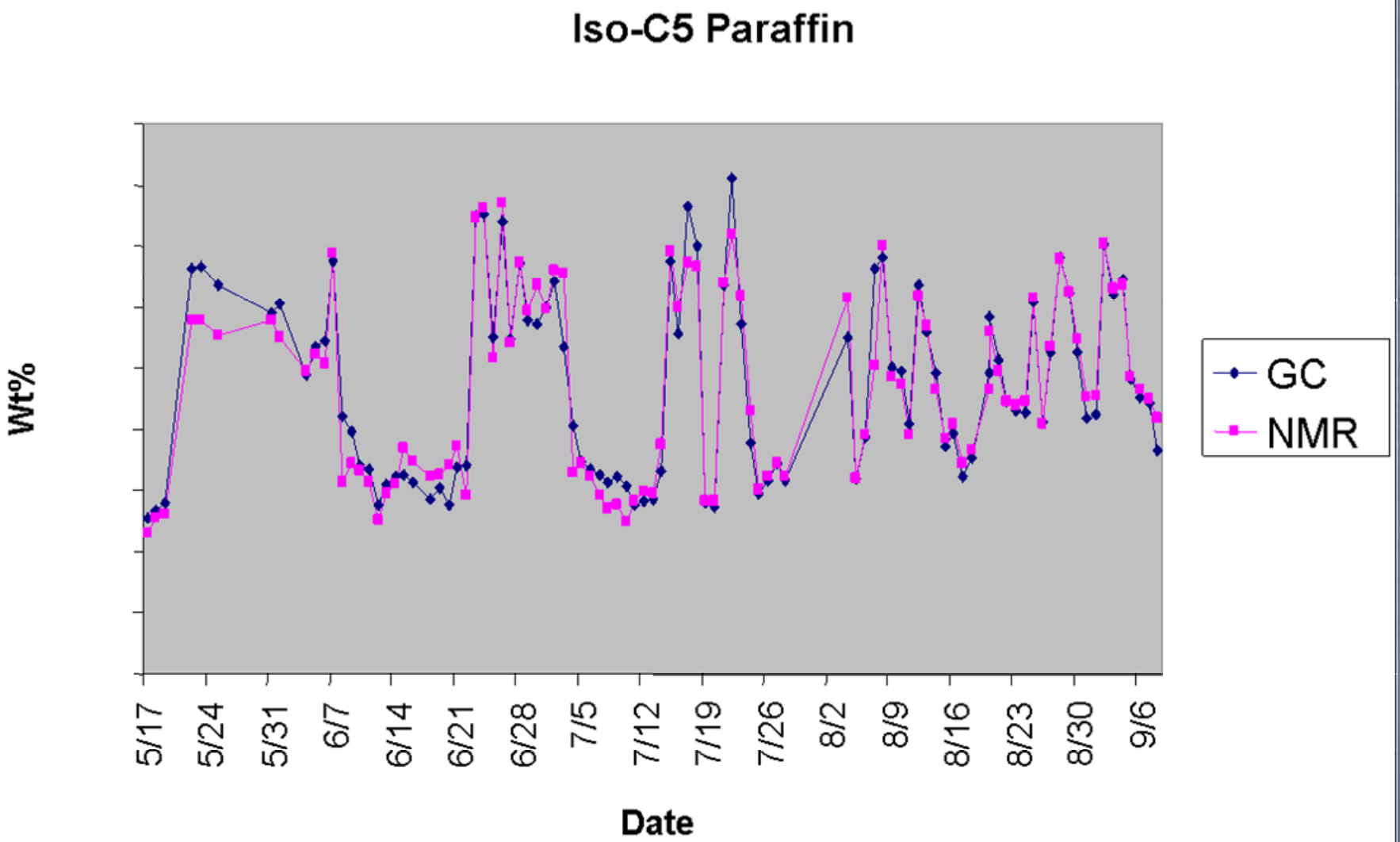
96 Hours of NMR Process Output – Naphthene Components

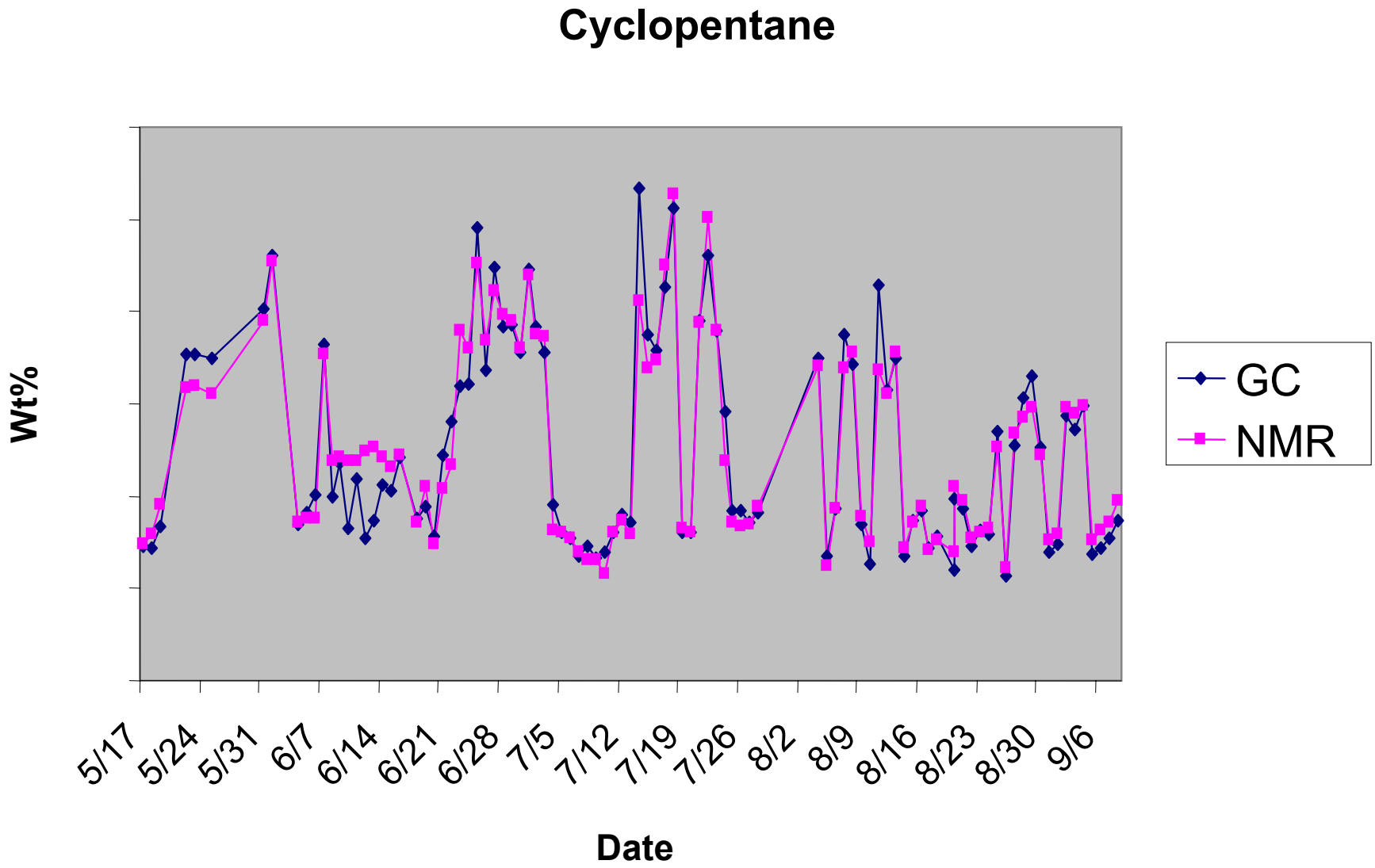


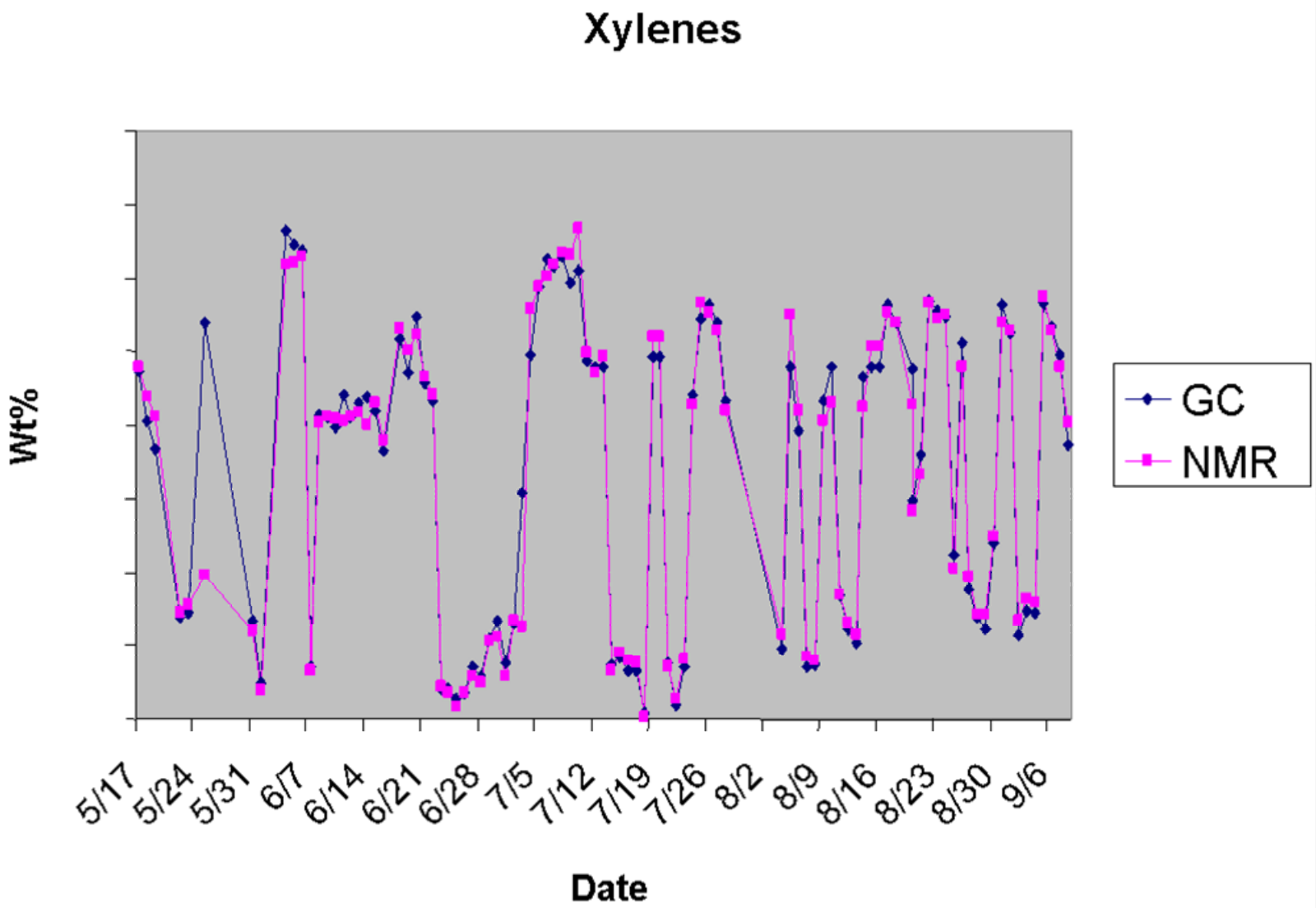
96 Hours of NMR Process Output – Aromatic Components




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%
GC
NMR
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


Xylenes
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

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 (12) GC Analyzers Replaced Yielding Reduced Maintenance

Reduced Laboratory Requirements

Other Installations:
Expanding Model Base to Cover Gas Oils and Mixed Naphtha/Gas Oil Blend Operation
Model base to be developed for NMR analyzer on gaseous products of naphtha cracker.

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

Conclusion

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

See Further Information at http://www.process-nmr.com

Acknowledgements

Paul Giammatteo – PNA

Tal Cohen – Foxboro NMR Israel

Tony Van Poyenbroeck – Cardoen Technology, Belgium

Invensys

Our NMR Customers