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

Presented By

John Edwards, Ph.D.

Process NMR Associates, LLC
Danbury, Connecticut

March 22, 2011
RSC Reaction Monitoring Symposium, Sandwich, Kent, UK

PROCESS NMR ASSOCIATES

300+ Analytical NMR Customers

smiths detection
bringing technology to life

MODCON

COSA INSTRUMENT

ACTIVE SPECTRUM

QUALION
NMR ANALYZERS

Swagelok

Process NMR Associates LLC
P N A

Engineering
N.M.R.
Process Systems LLC
Chemistry

TTC Labs, Inc.
Process Engineering Excellence

TopNIR Systems

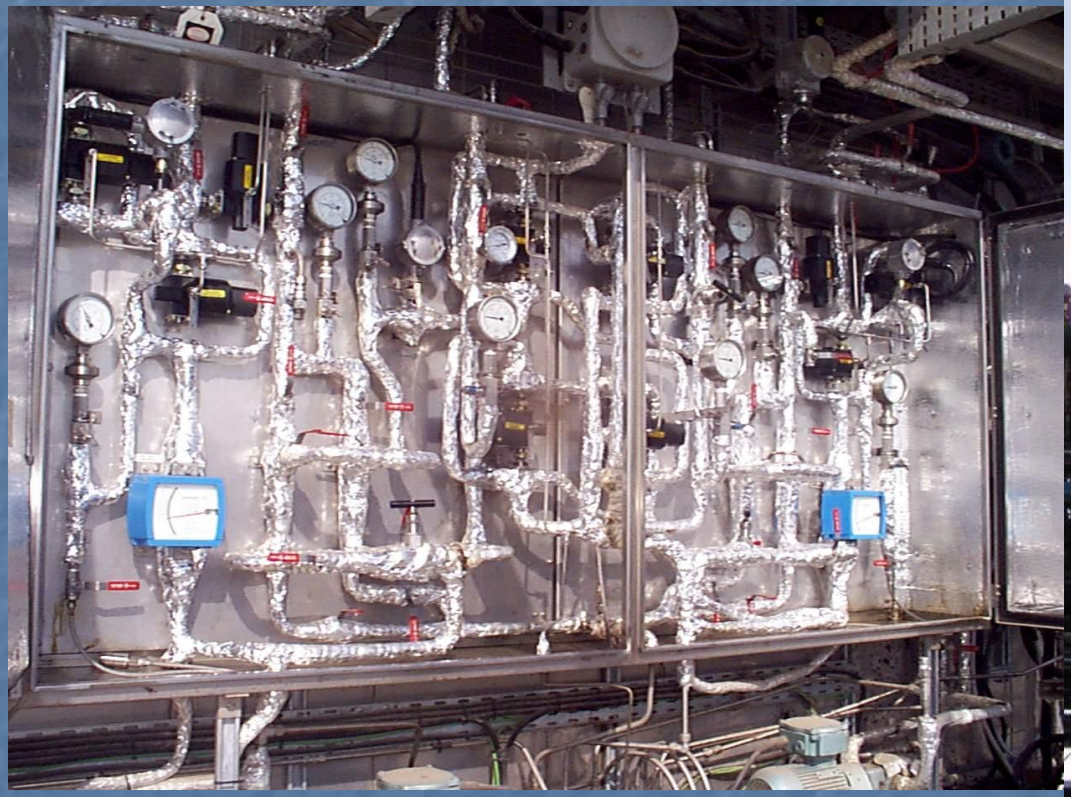
RESONANCE SYSTEMS

ASPECT

Triangle Analytical, Inc.

High Resolution FT-NMR – Online / in Process

NMR Sample System and Placement



NMR Lock - External ^{7}Li Lock @ 22.5 MHz

Matrix Shimming Performed
by Optimizing FID RMS

Shim DACs Built into the Magnet Enclosure

PROCESS NMR ASSOCIATES

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 stabilit
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.

PROCESS NMR ASSOCIATES

New Magnet System

New magnet design solves the problem of:

- Long term and short term Stability
- Temperature sensitivity

State of the Art electronics:

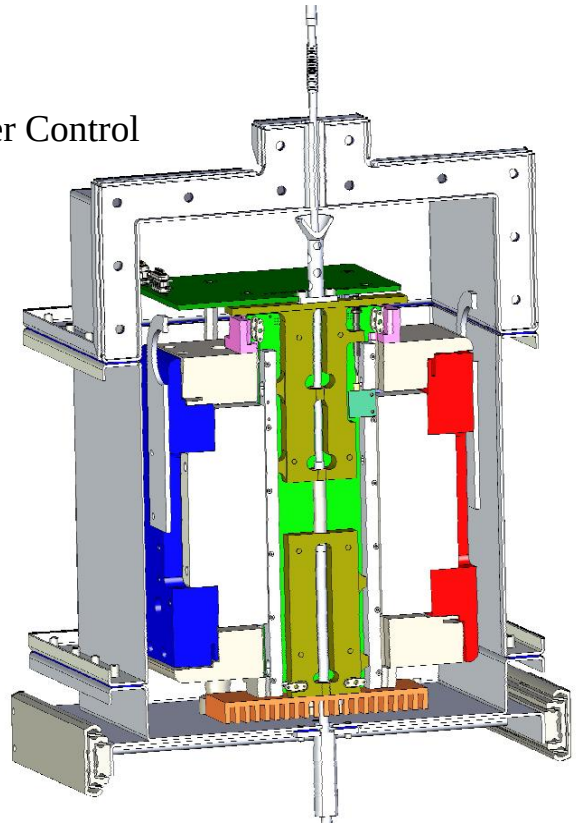
- Smaller foot-print
- 40 Shim coils on 2 single PCB
- Integrated PCB for Shim & Heater Control
- Digital RF & Acquisition – improve SNR

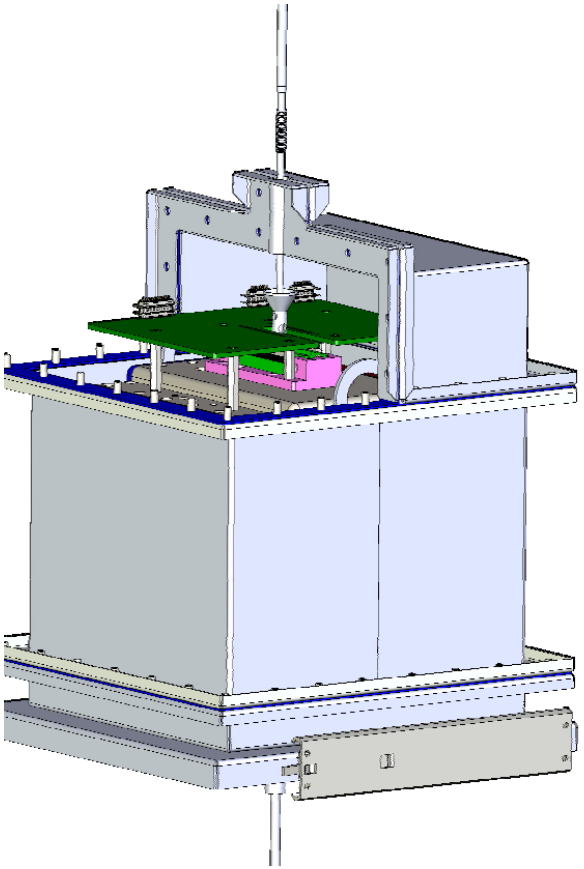
New concept of Process Probe:

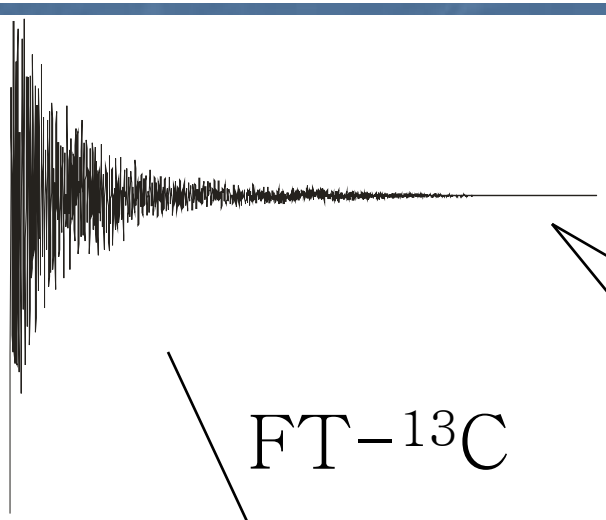
- Entire sample pipe through without contact with the system
- Much better temperature insulation
- Higher Q (better sensitivity)

New Software:

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

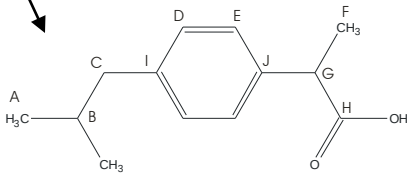


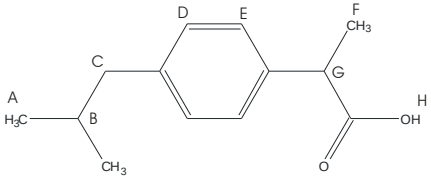




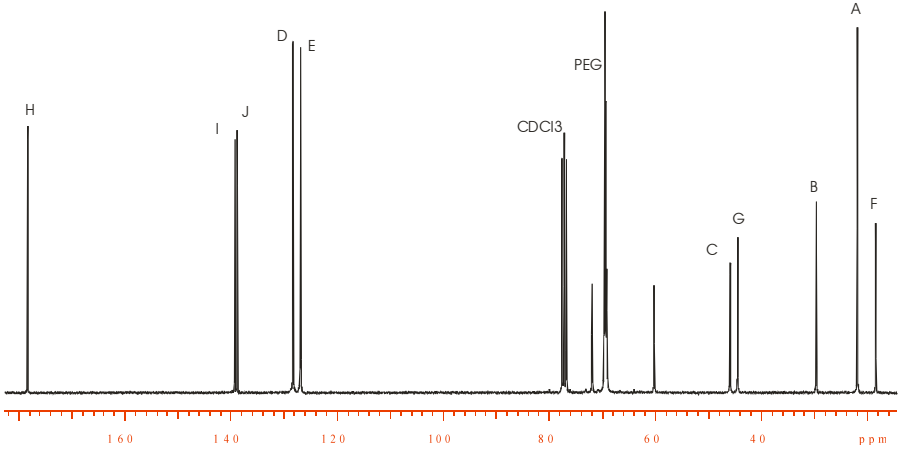
FT–^{13}C

FT–^{1}H

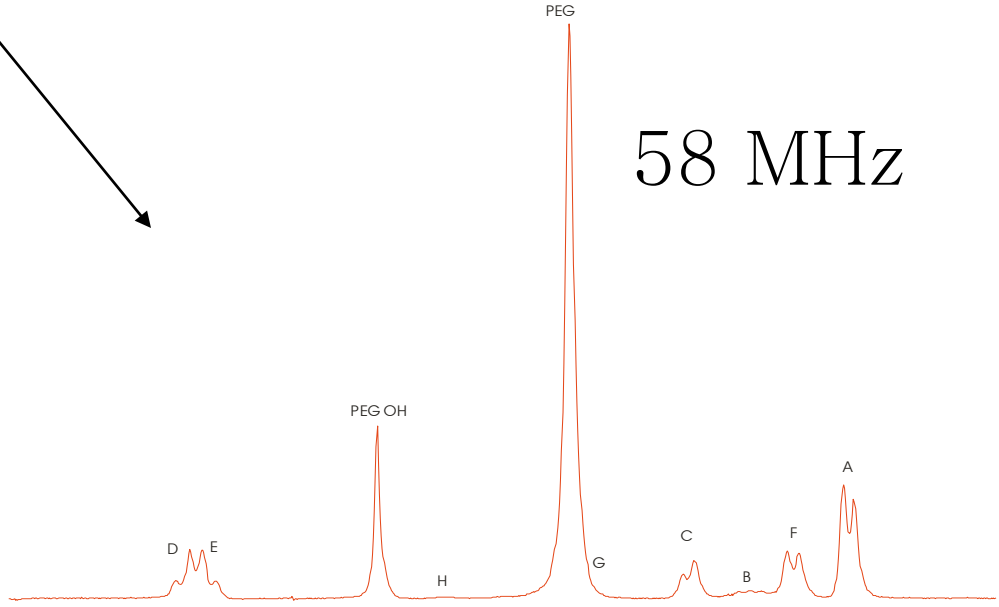




300 MHz



58 MHz



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: Steam Cracking Optimization Installed 2000

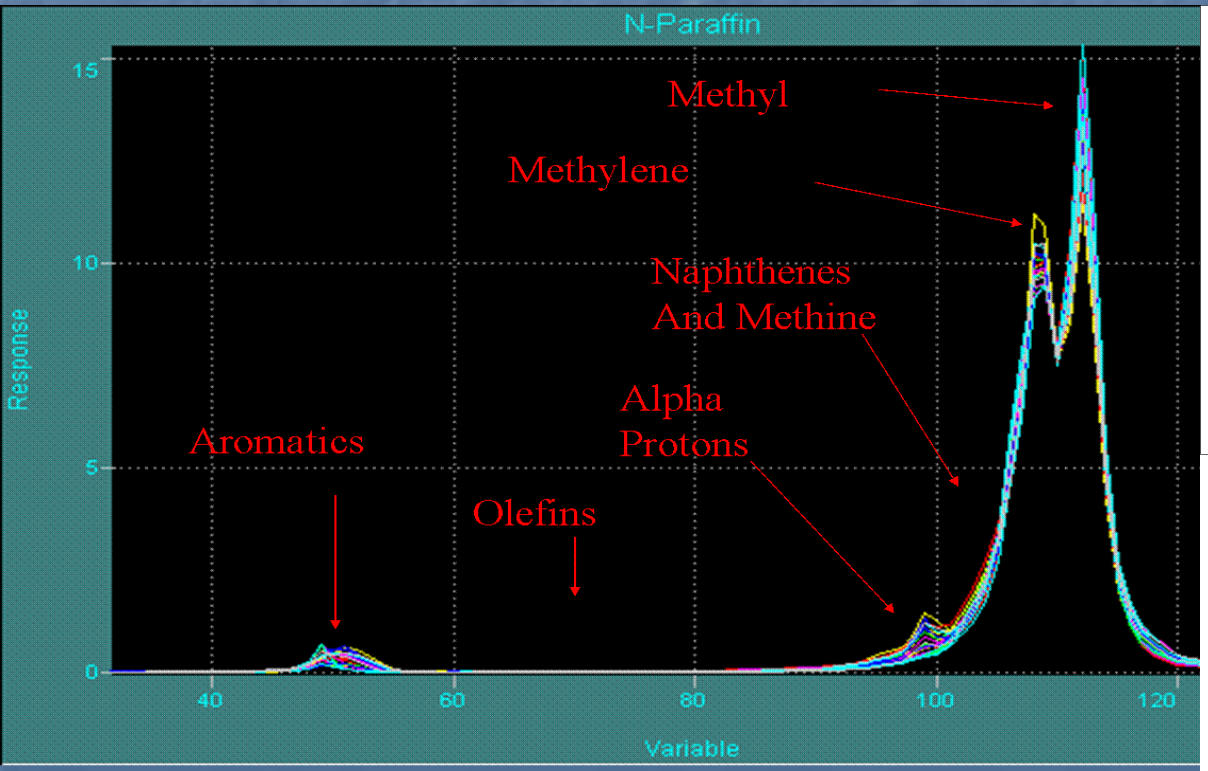
Cracker Facility Capacity: 600,000 Tonnes per Year

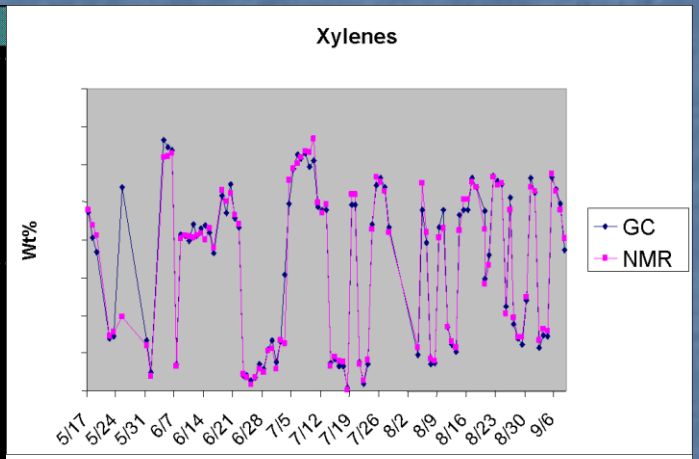
Control Strategy: Feed Forward Detailed Hydrocarbon Analysis to SPYRO Optimization

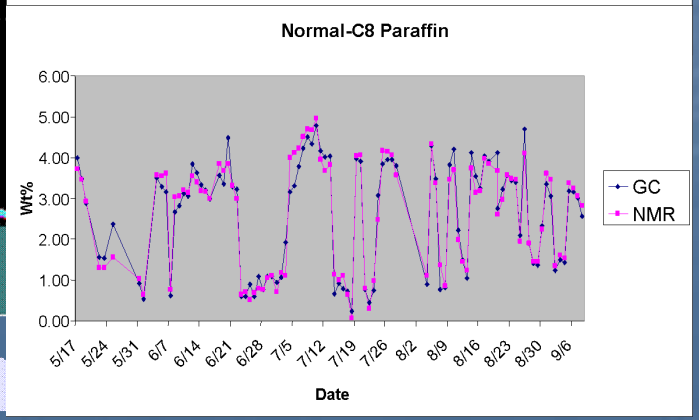
NMR Analysis: 3-4 Minute Cycle (Single Stream)

NMR PLS Outputs: Naphtha – Detailed PIONA

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

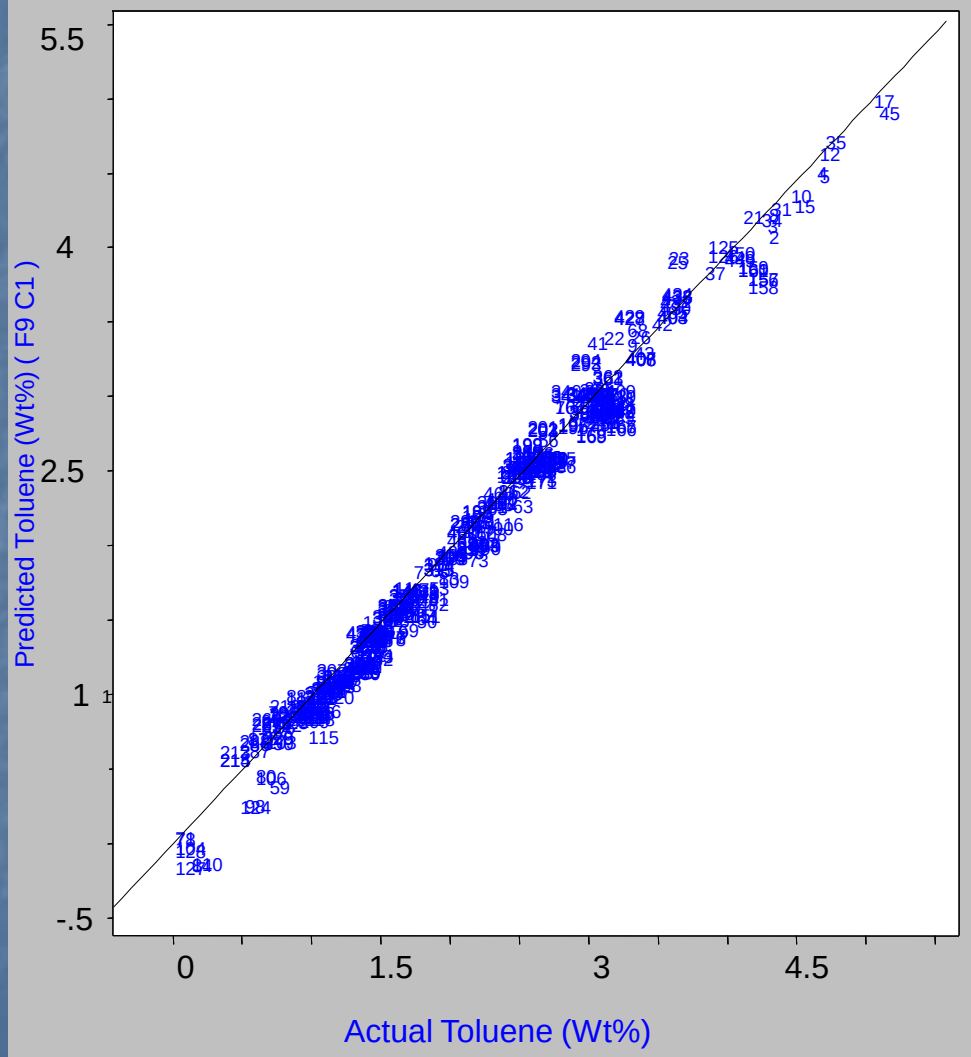


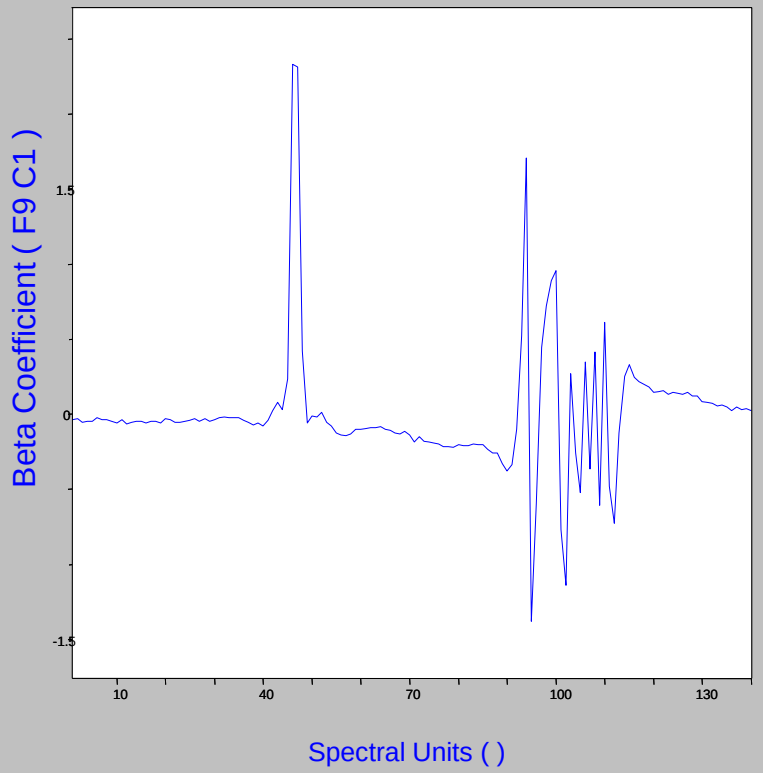




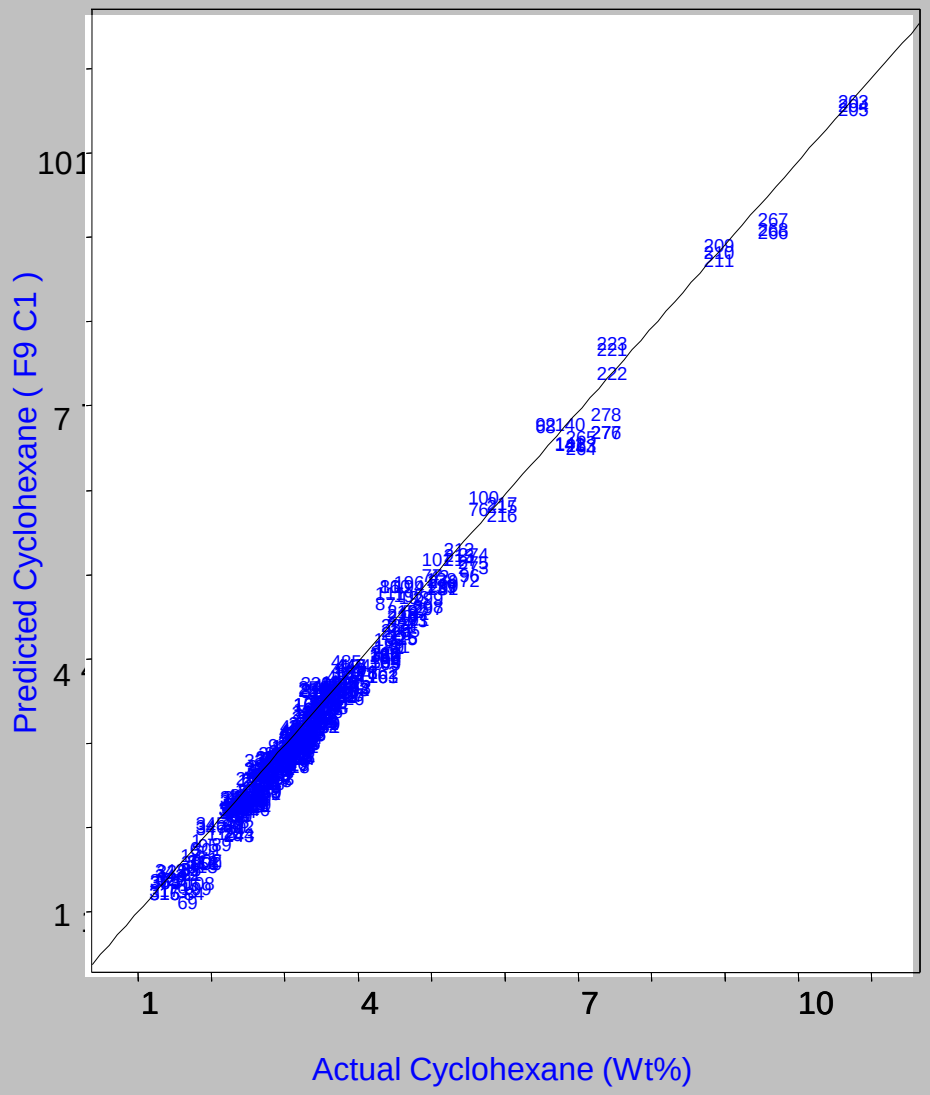
Spectral Variability Observed in Naphtha Samples

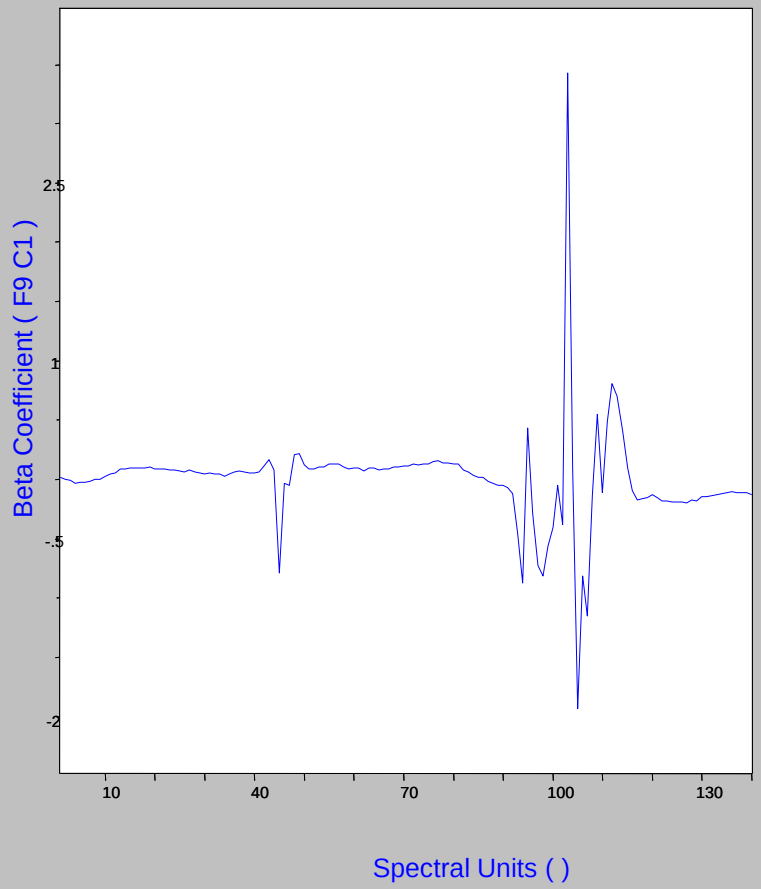
Toluene

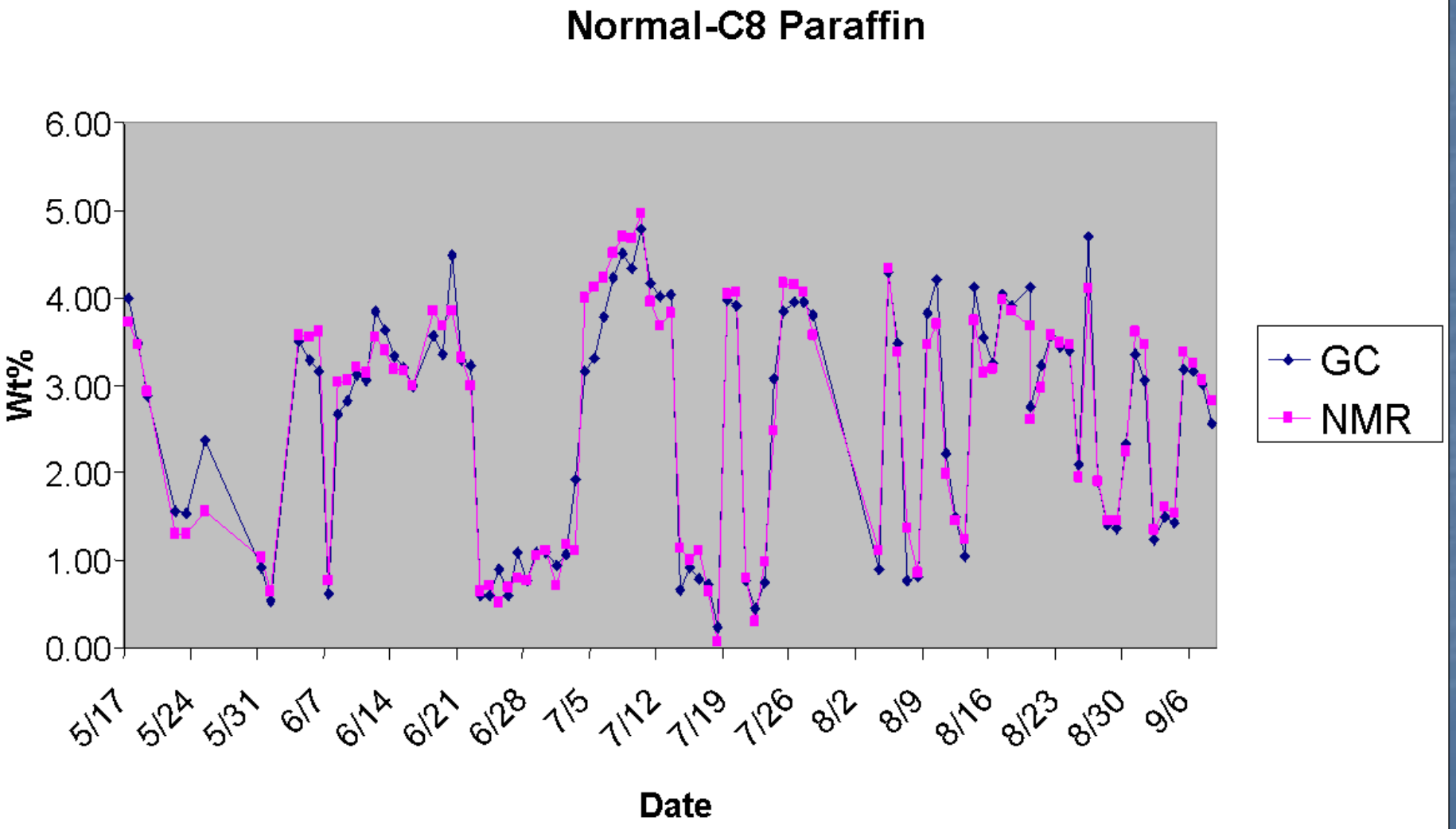

5.5
4
2.5
1
-.5
0
1.5
3
4.5
Predicted Toluene (Wt%) (F9 C1)
Actual Toluene (Wt%)

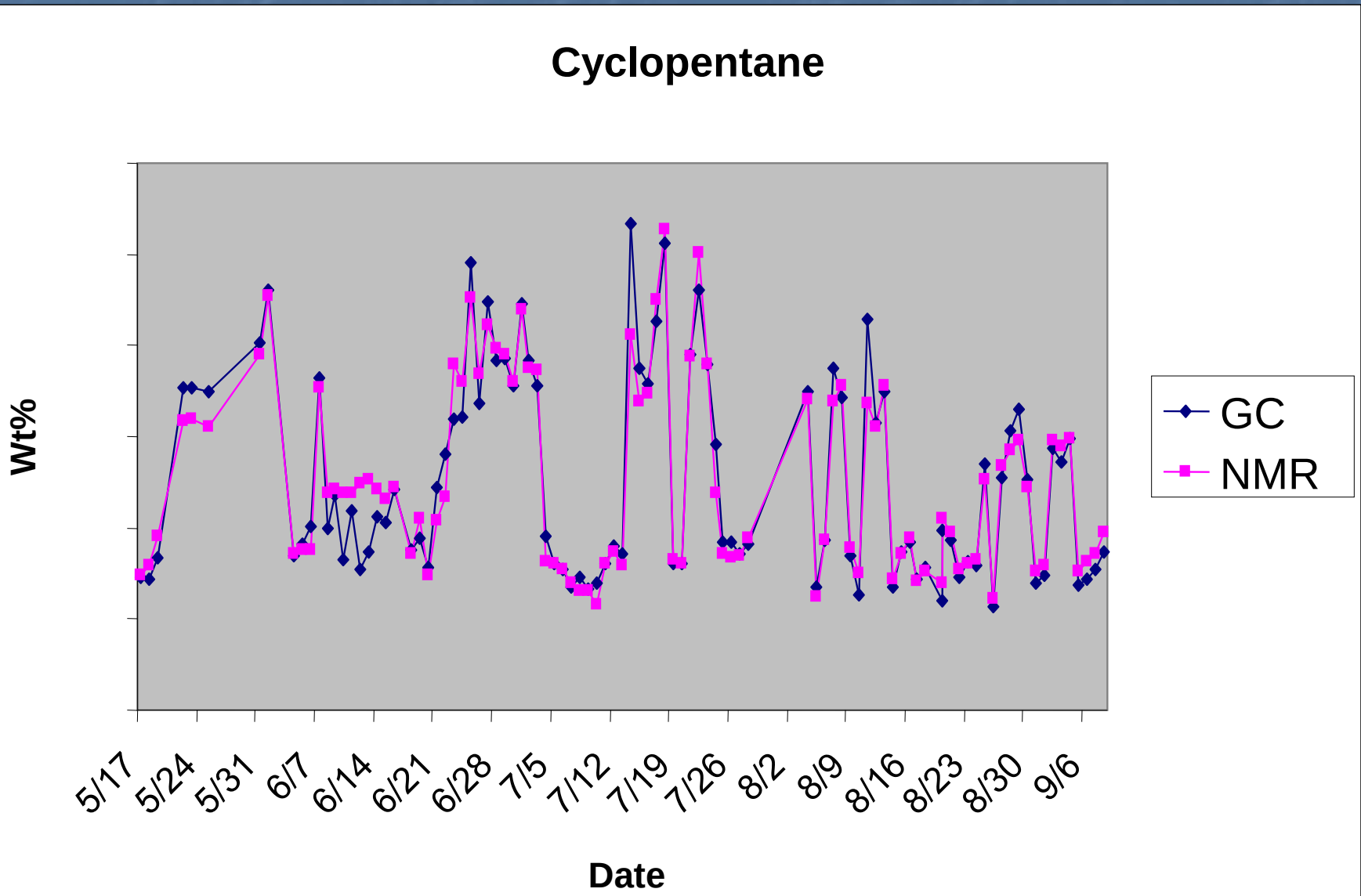

1.5
0
-1.5
10
40
70
100
130
Beta Coefficient (F9 C1)
Spectral Units ( )

Cyclohexane

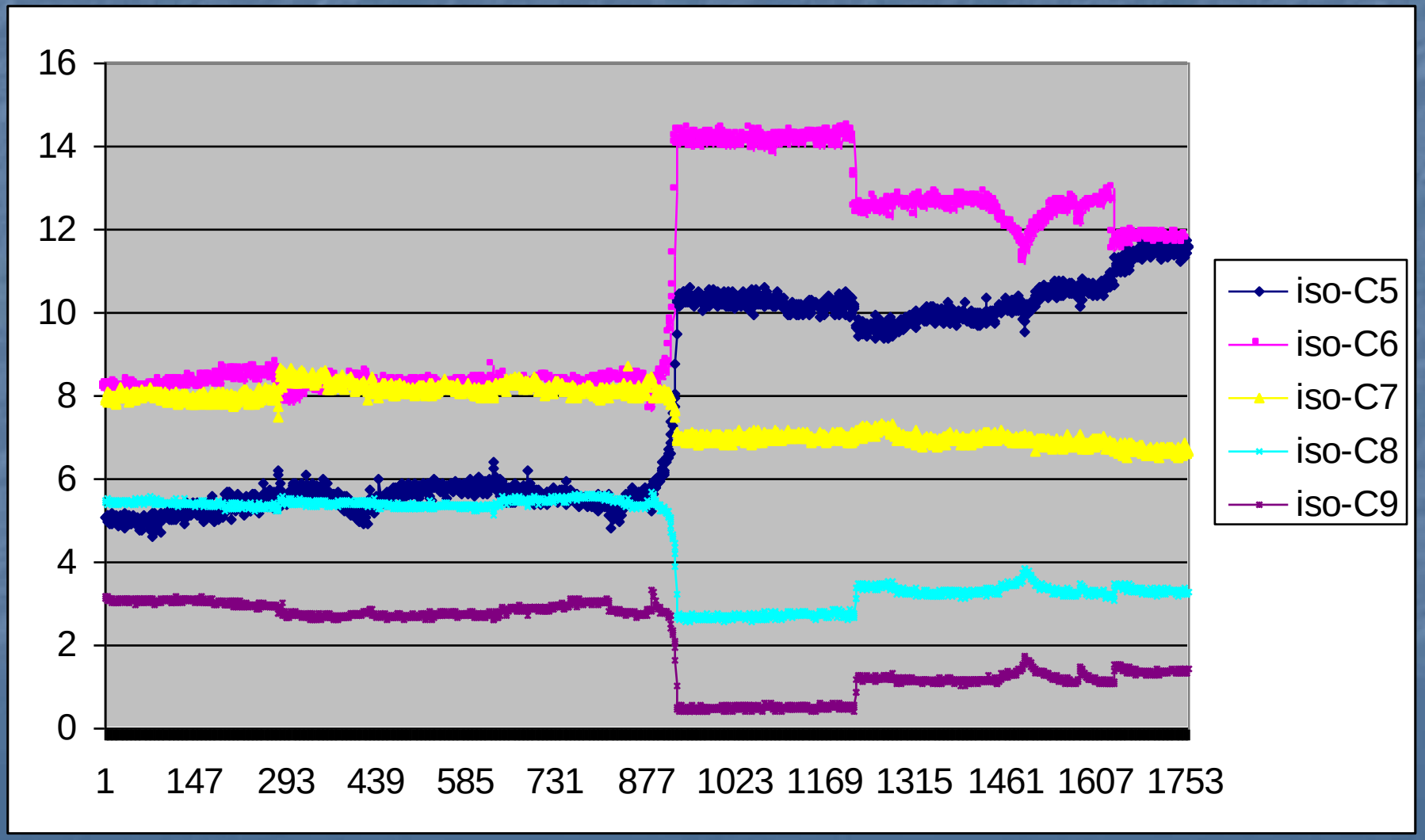





Normal-C8 Paraffin
Wt%
6.00
5.00
4.00
3.00
2.00
1.00
0.00
5/17
5/24
5/31
6/7
6/14
6/21
6/28
7/5
7/12
7/19
7/26
8/2
8/9
8/16
8/23
8/30
9/6
Date
GC
NMR


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

96 Hours of NMR Process Output – iso-Paraffin 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

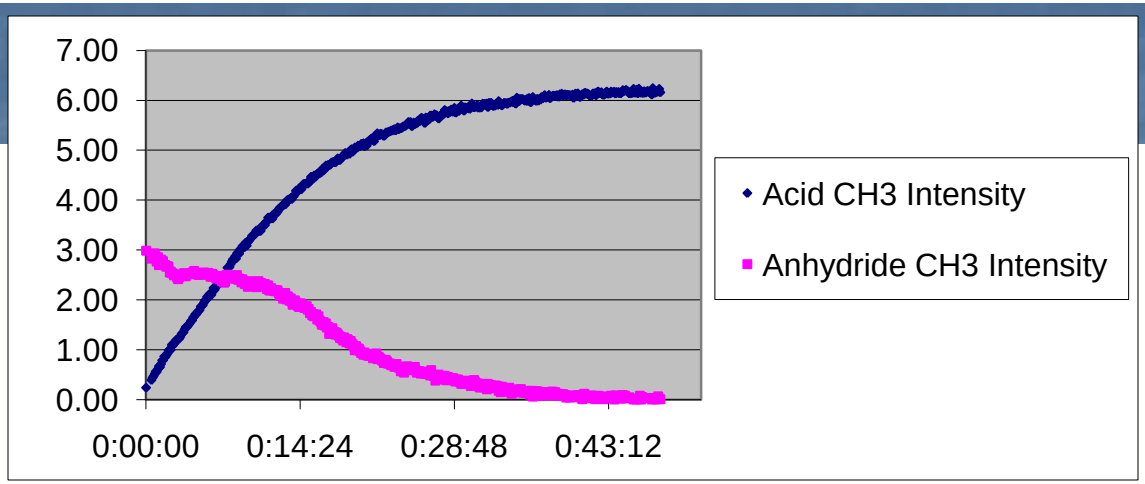
2000 - Crude Unit Analyzer

2000 - Crude Blending System

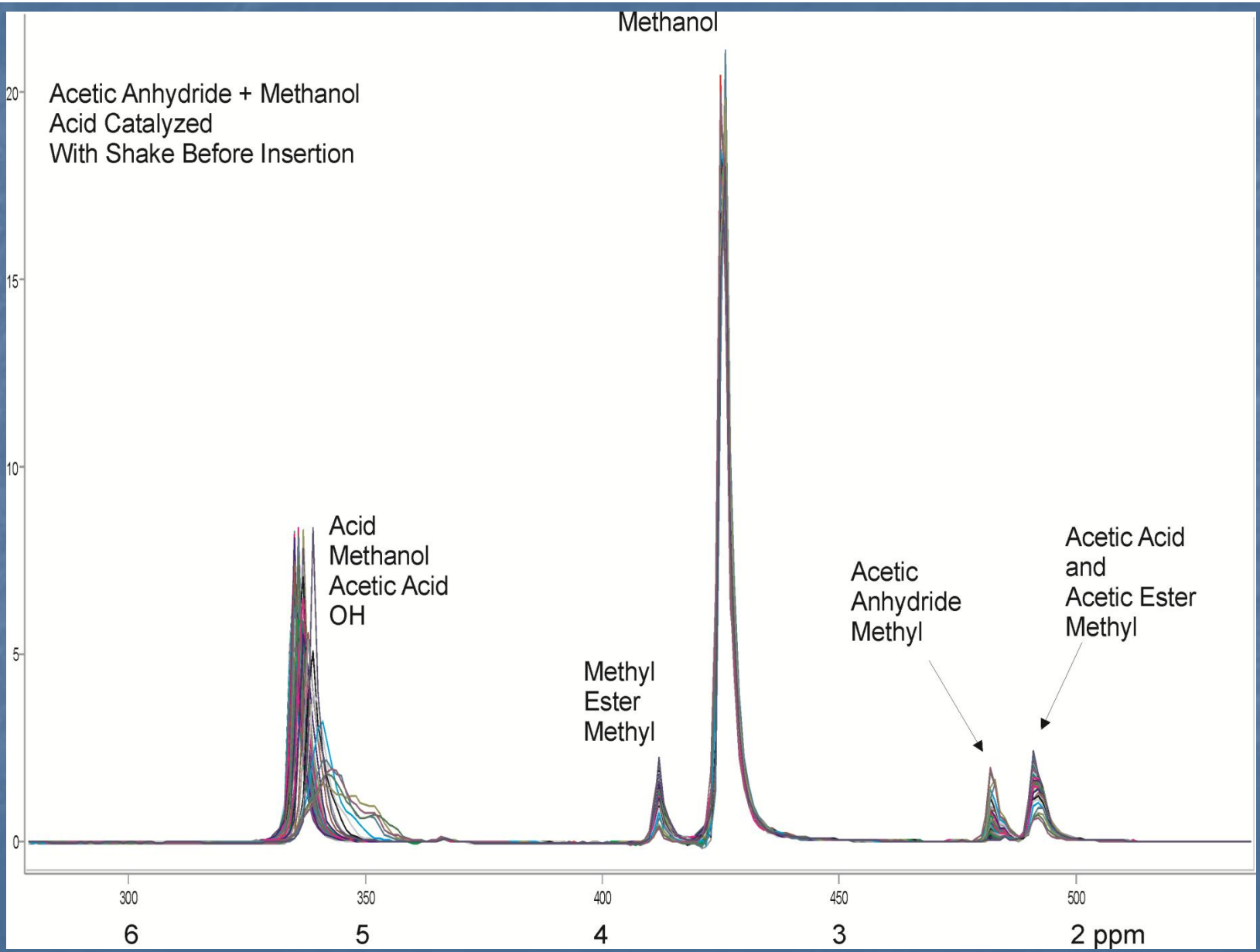
2001 - Gasoline Blending System,

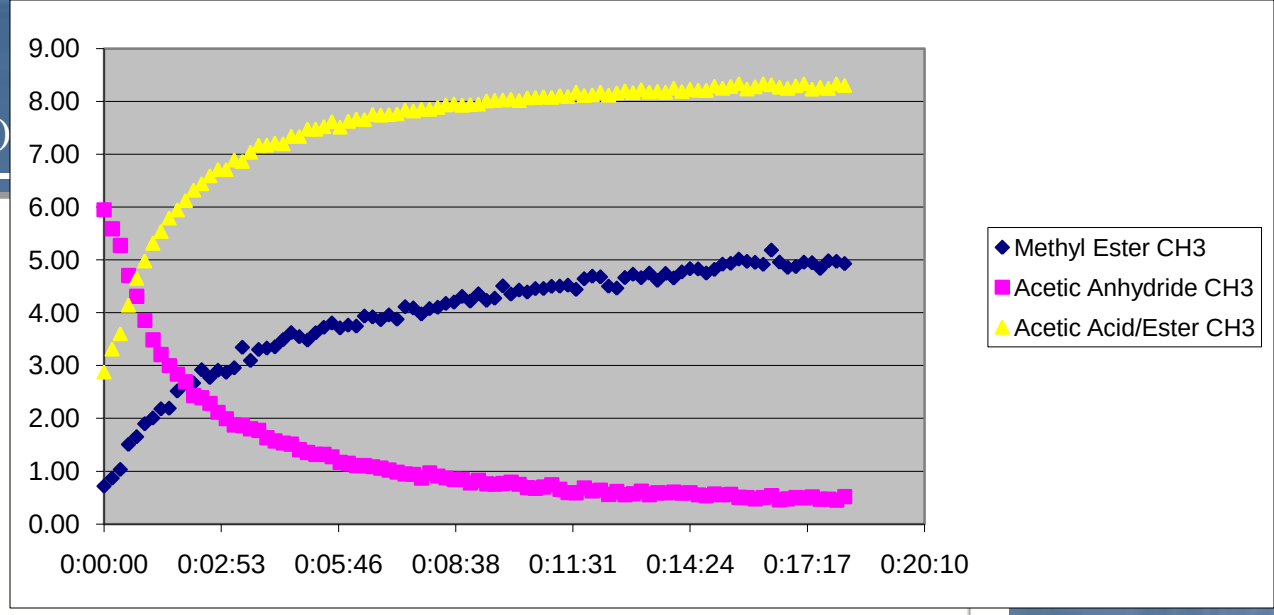
2001 - Base Oil Manufacturing Analyzer

2002 - FCC Unit Analyzer

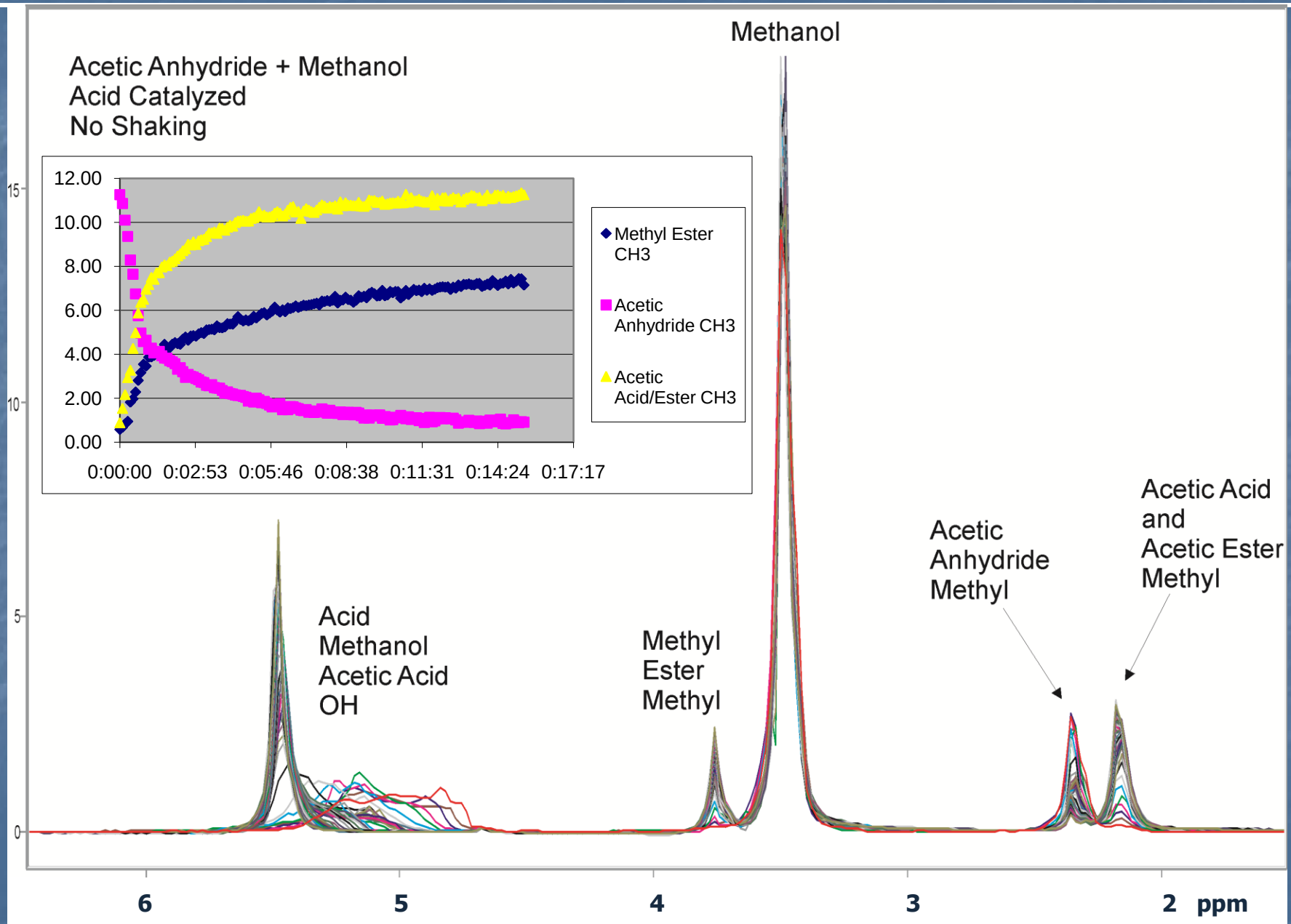

7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
0:00:00
0:14:24
0:28:48
0:43:12
Acid CH3 Intensity
Anhydride CH3 Intensity

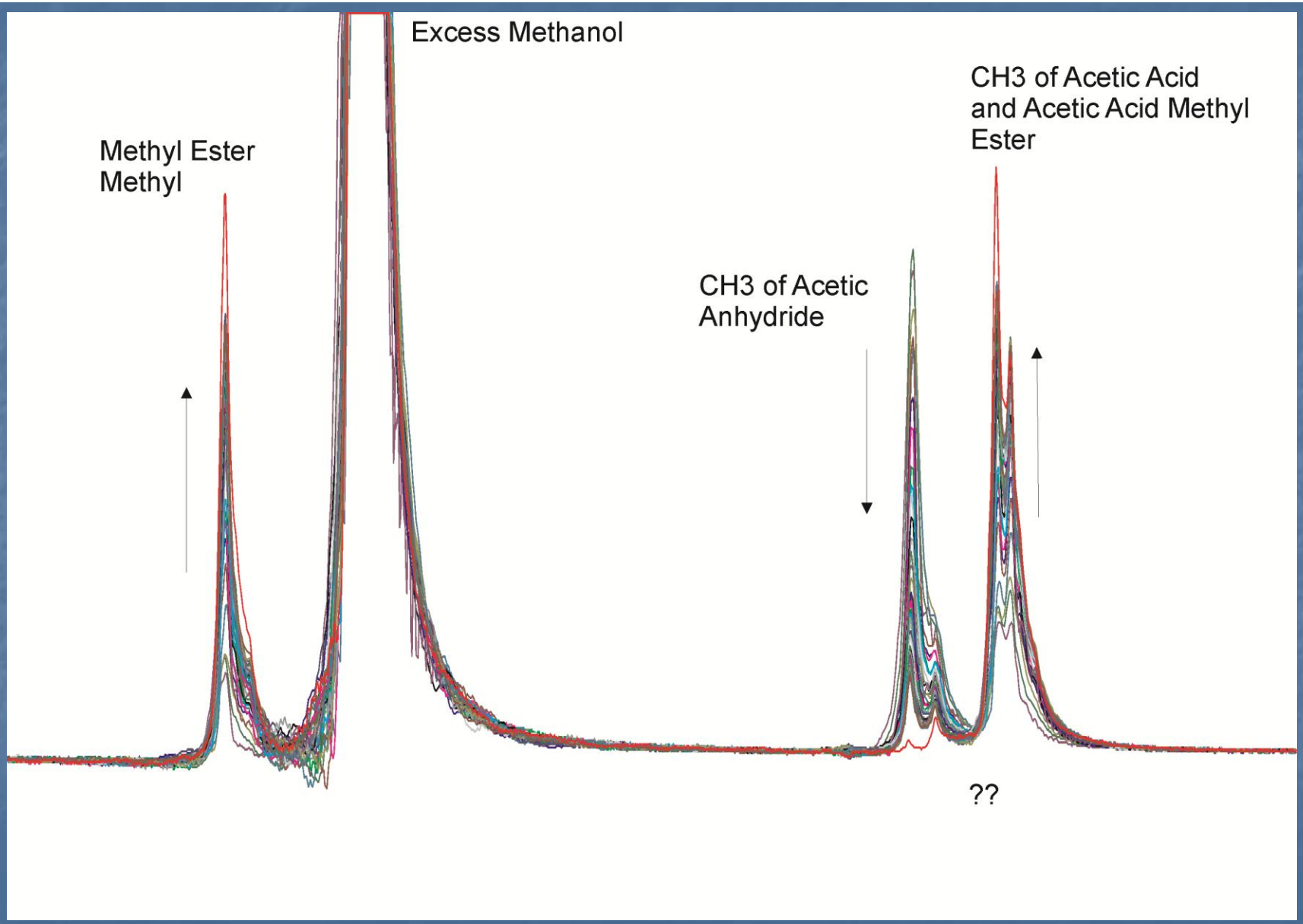
Water
Acetic Acid
Acetic Anhydride

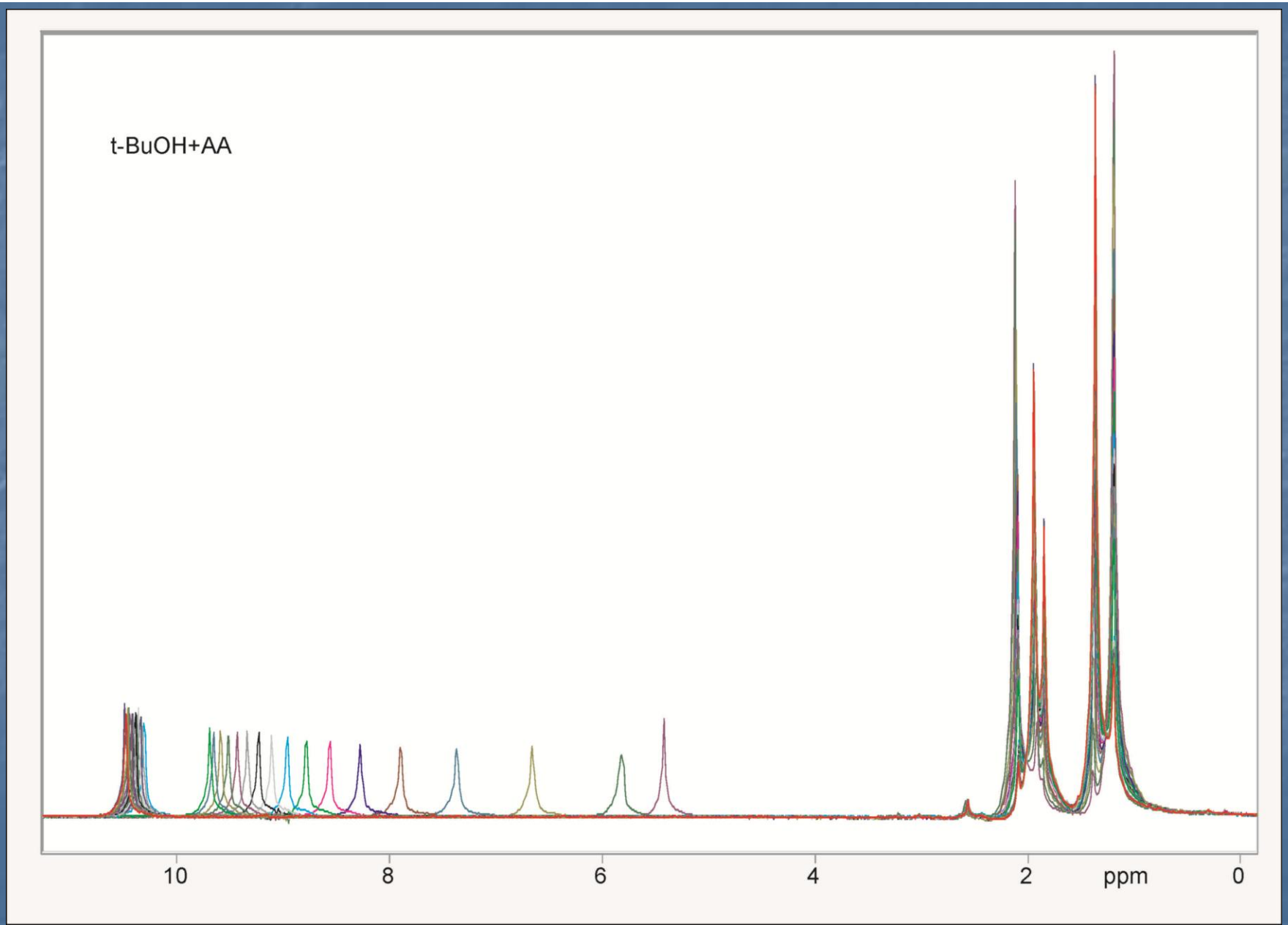

Methanol
Acetic Anhydride + Methanol
Acid Catalyzed
With Shake Before Insertion
20
15
10
5
0
Acid
Methanol
Acetic Acid
OH
Methyl
Ester
Methyl
Acetic
Anhydride
Methyl
Acetic Acid
and
Acetic Ester
Methyl
300
350
400
450
500
6
5
4
3
2 ppm

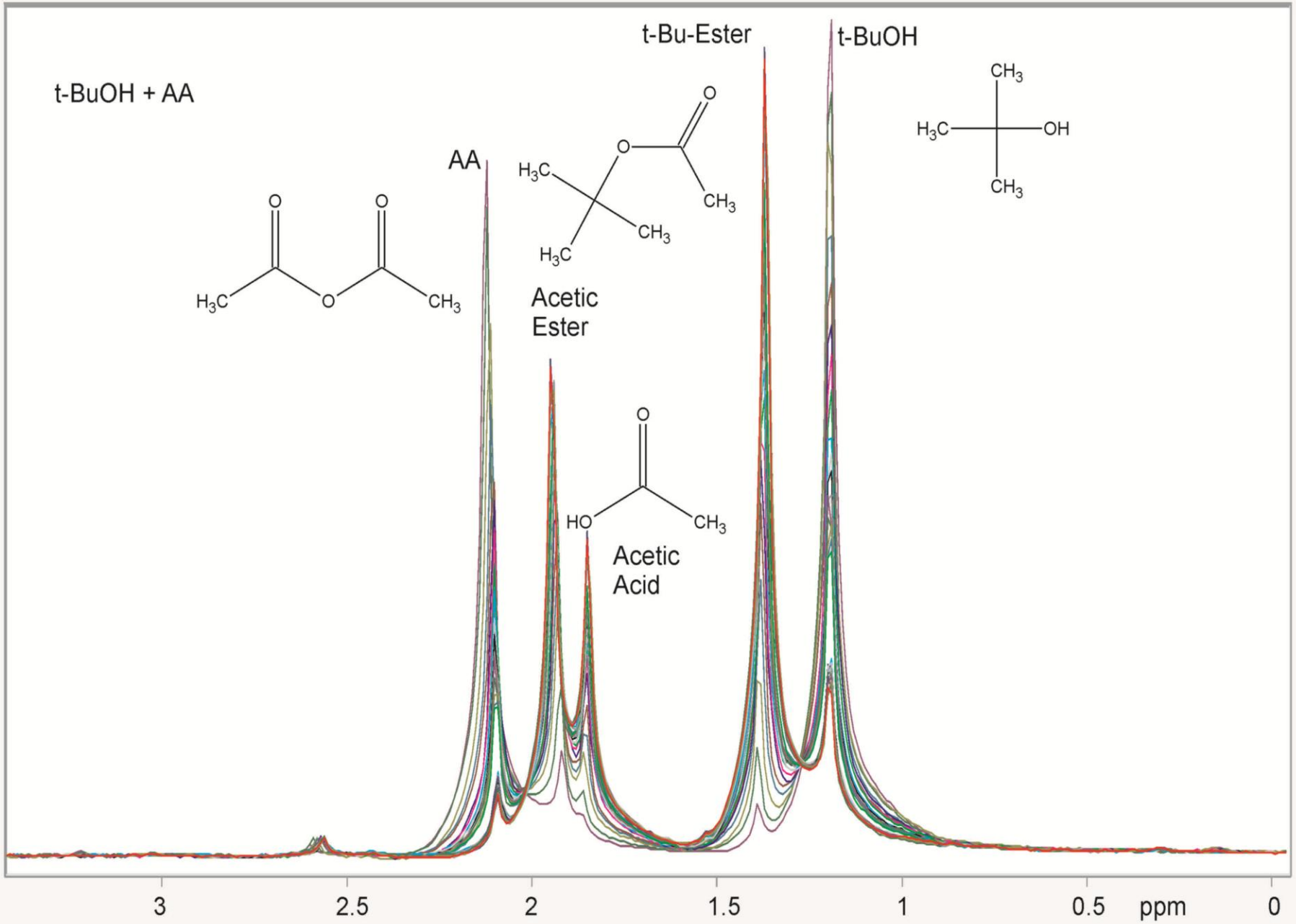

9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
0:00:00
0:02:53
0:05:46
0:08:38
0:11:31
0:14:24
0:17:17
0:20:10
Methyl Ester CH3
Acetic Anhydride CH3
Acetic Acid/Ester CH3

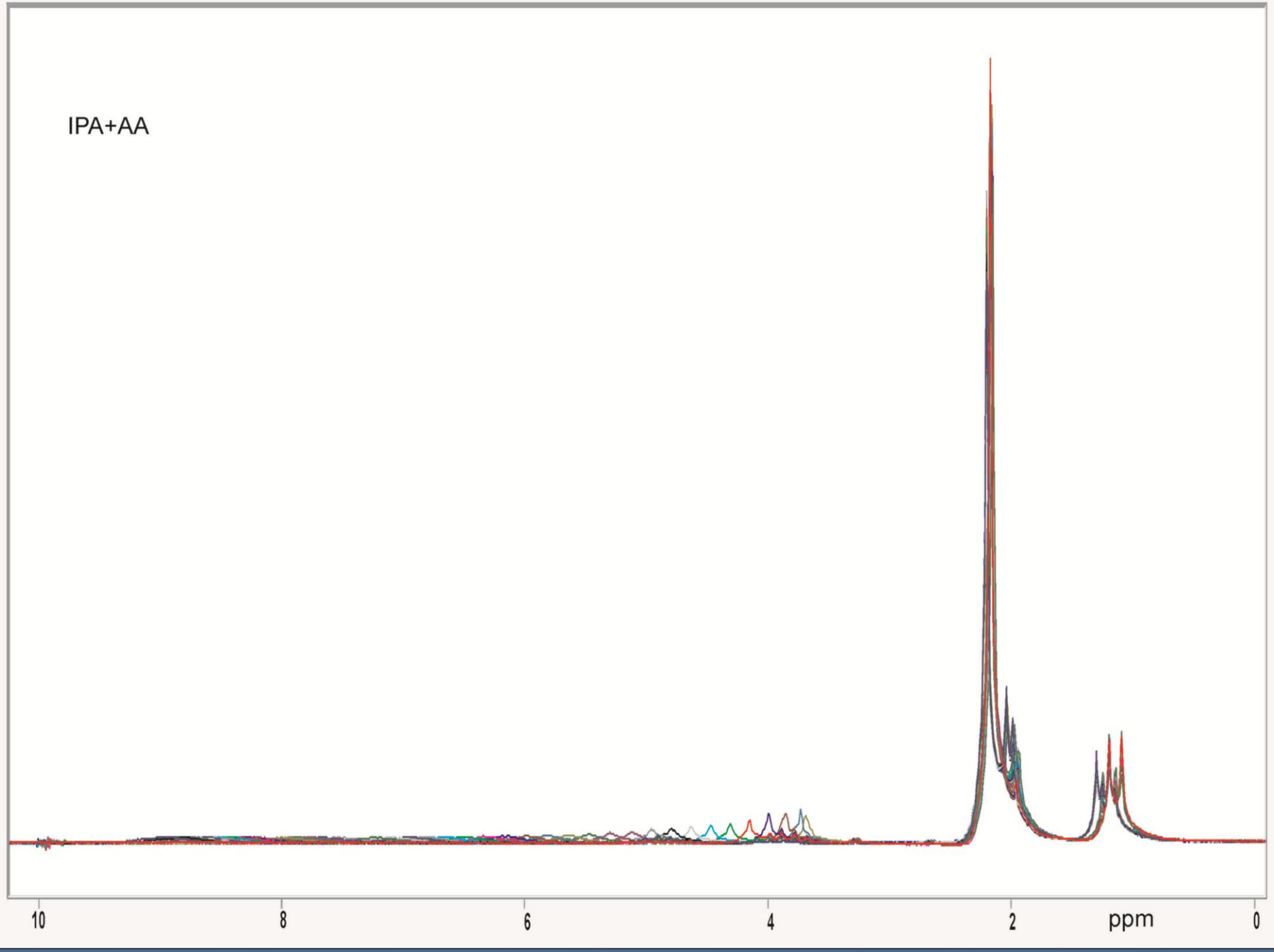
H2O
-O-CH3
Acetic Acid
and Acetic Acid
Ester - CH3-CO
Acetic
Anyhdride
400
420
440
460
480
500
4
3.6
3.2
2.8
2.4
2 ppm

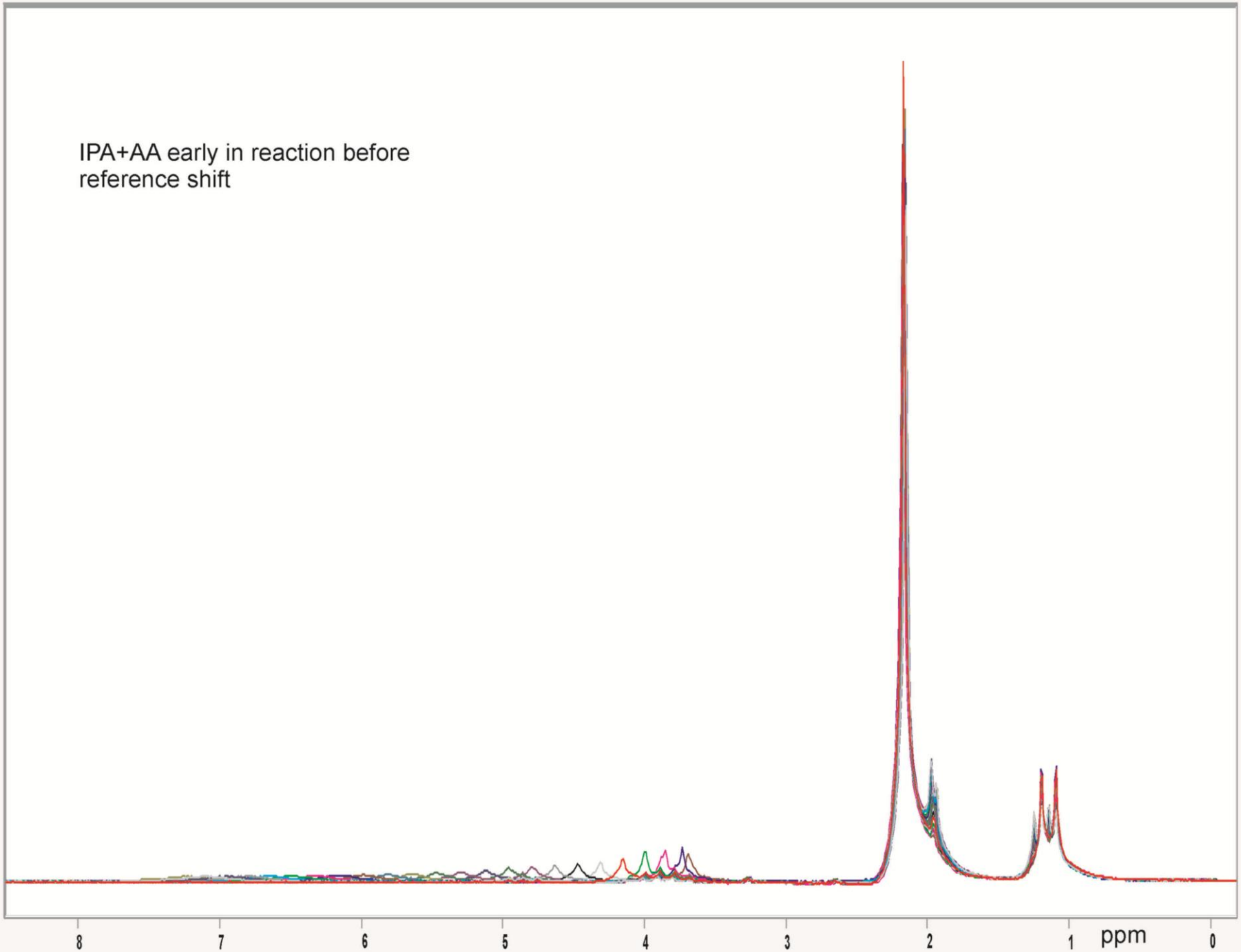

Acetic Anhydride + Methanol
Acid Catalyzed
No Shaking
12.00
10.00
8.00
6.00
4.00
2.00
0.00
0:00:00
0:02:53
0:05:46
0:08:38
0:11:31
0:14:24
0:17:17
Methyl Ester CH3
Acetic Anhydride CH3
Acetic Acid/Ester CH3
Methanol
Acid
Methanol
Acetic Acid
OH
Methyl
Ester
Methyl
Acetic
Anhydride
Methyl
Acetic Acid
and
Acetic Ester
Methyl
15
10
5
0
6
5
4
3
2
ppm

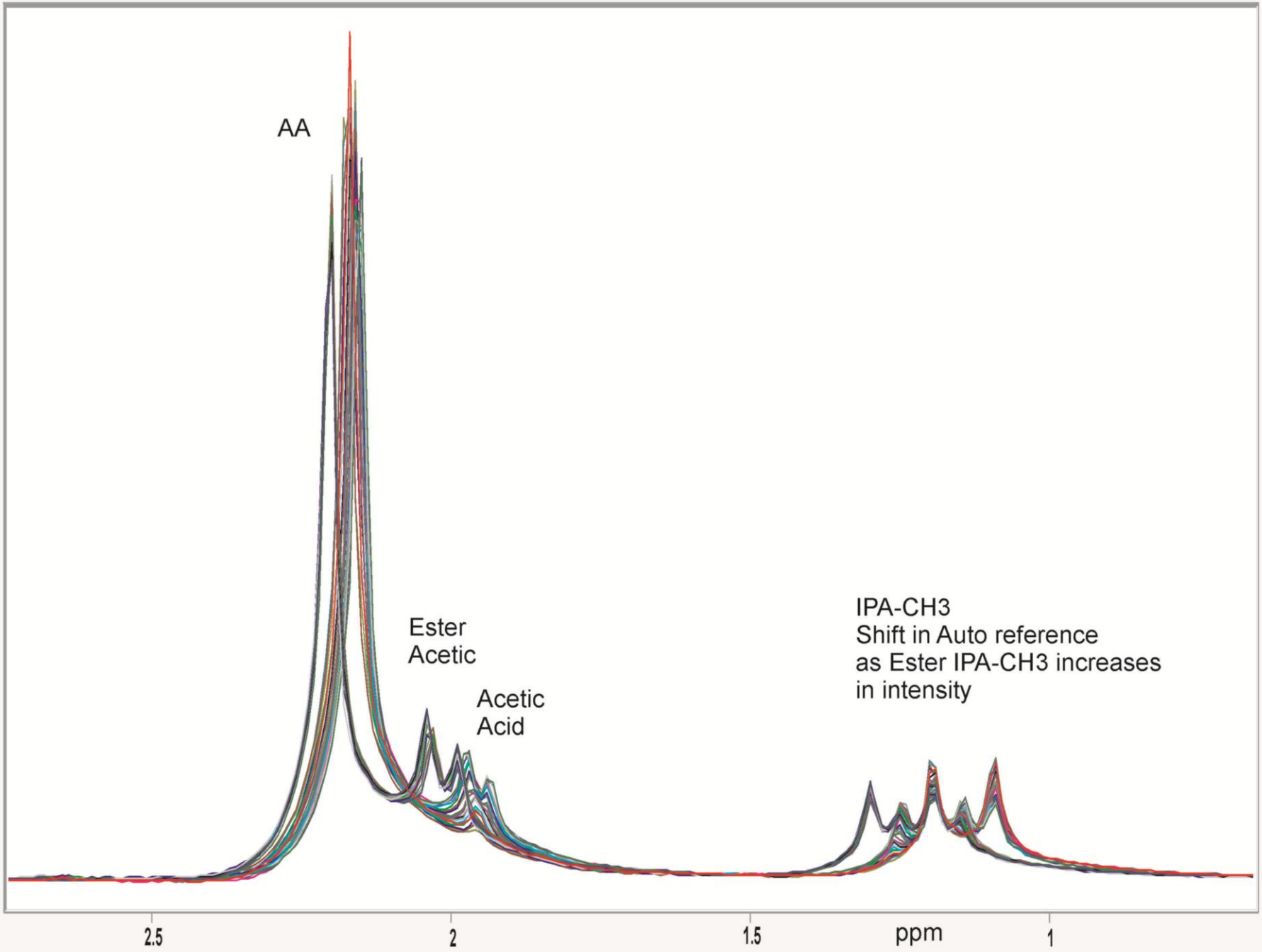

Excess Methanol
CH3 of Acetic Acid
and Acetic Acid Methyl
Ester
Methyl Ester
Methyl
CH3 of Acetic
Anhydride
??

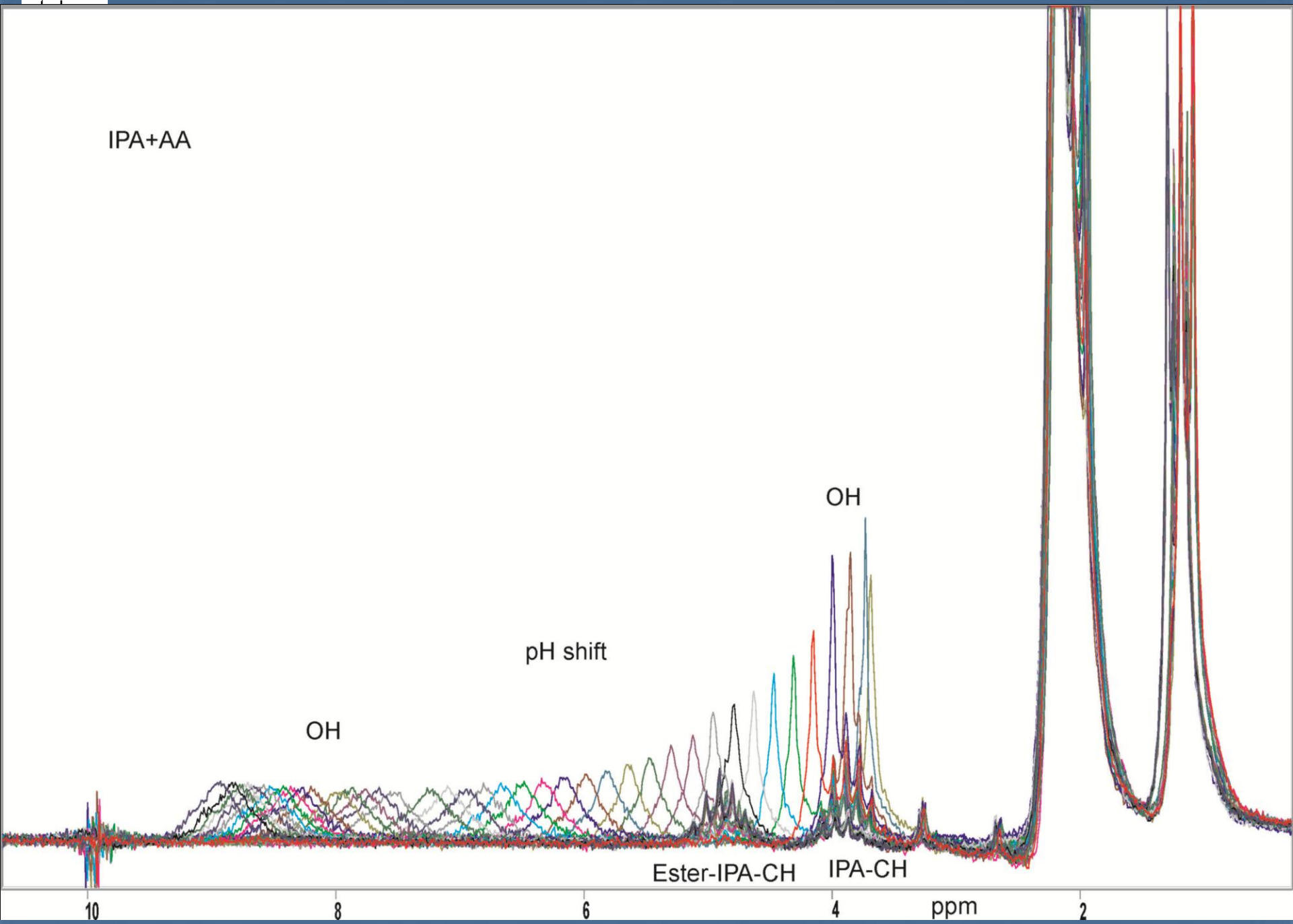

t-BuOH+AA
10
8
6
4
2
ppm
0


t-BuOH + AA
AA
t-Bu-Ester
t-BuOH
Acetic
Ester
Acetic
Acid
3
2.5
2
1.5
1
0.5
ppm
0


IPA+AA
10
8
6
4
2
ppm
0

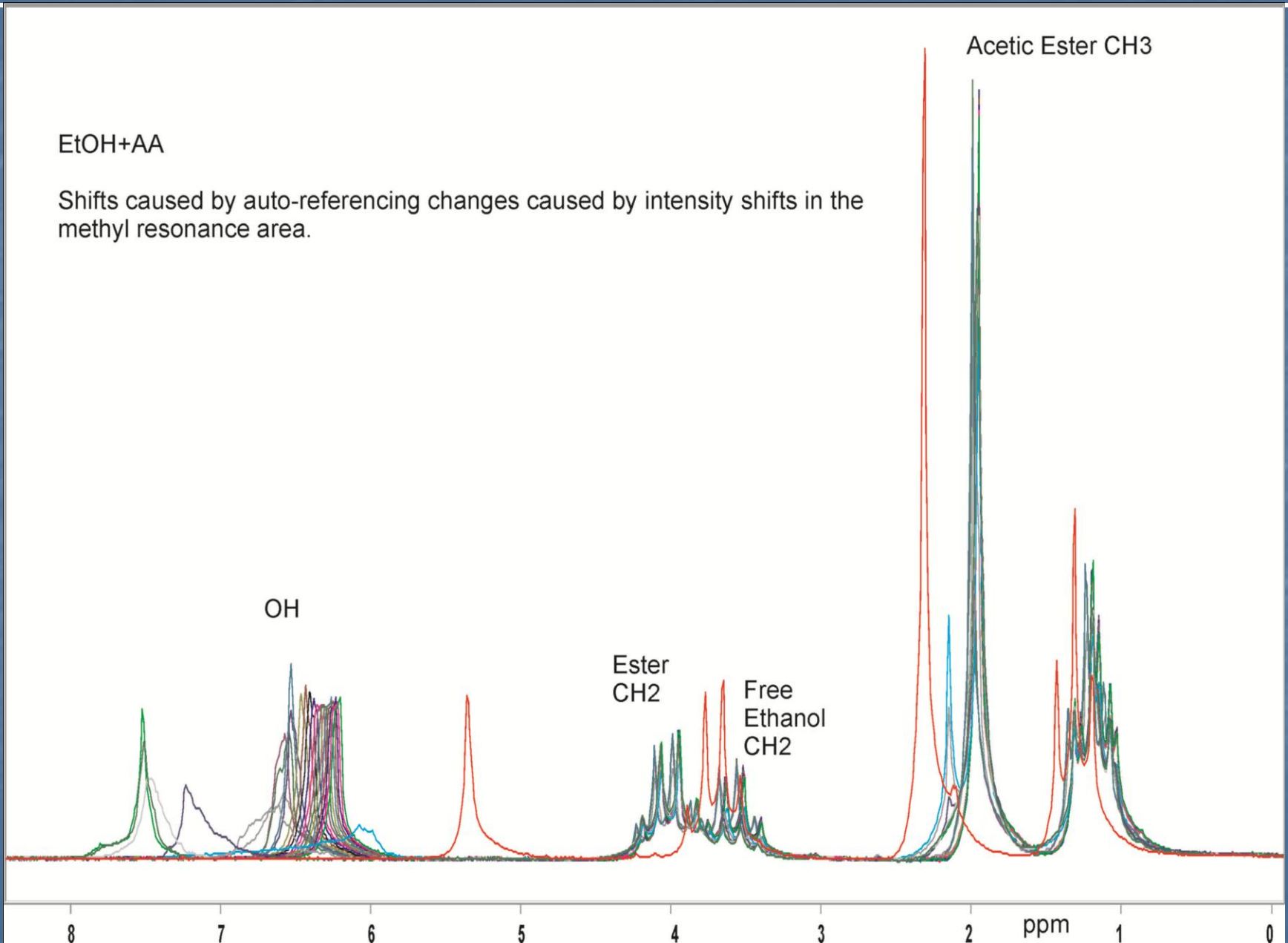

IPA+AA early in reaction before
reference shift
8
7
6
5
4
3
2
1
ppm
0

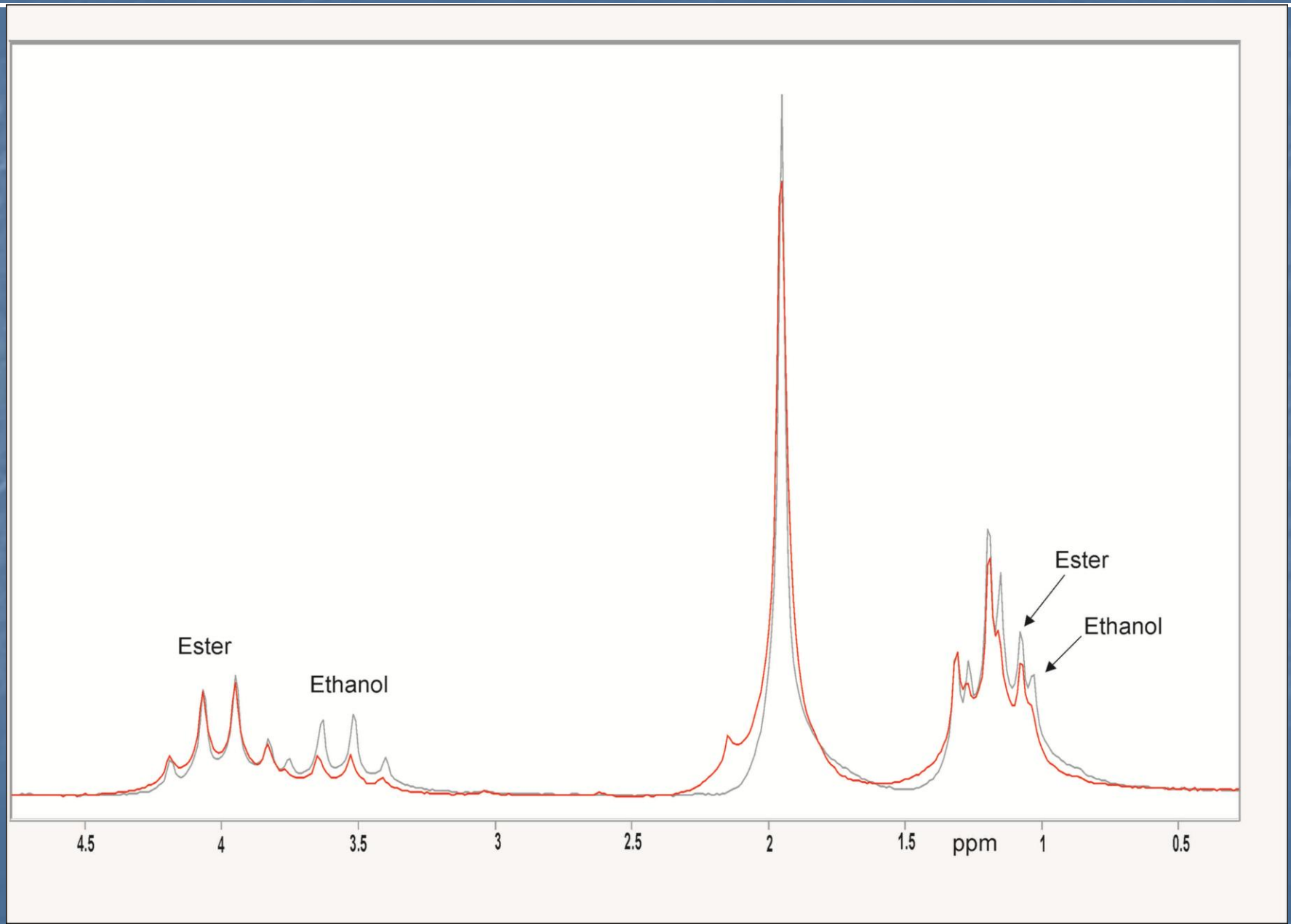

AA
Ester
Acetic
Acetic
Acid
IPA-CH3
Shift in Auto reference
as Ester IPA-CH3 increases
in intensity
2.5
2
1.5
ppm
1

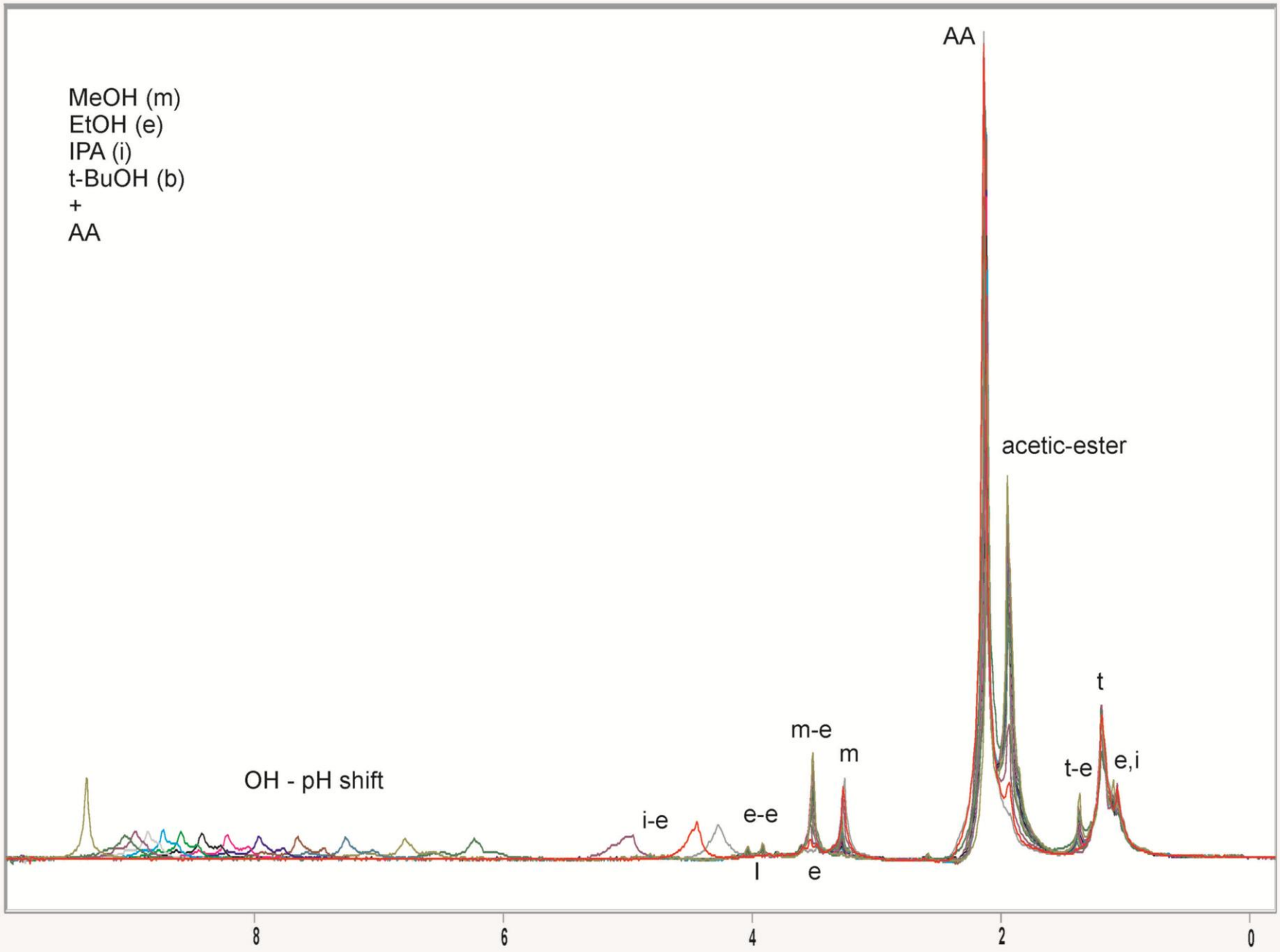

IPA+AA
OH
pH shift
OH
Ester-IPA-CH
IPA-CH
10
8
6
4
ppm
2

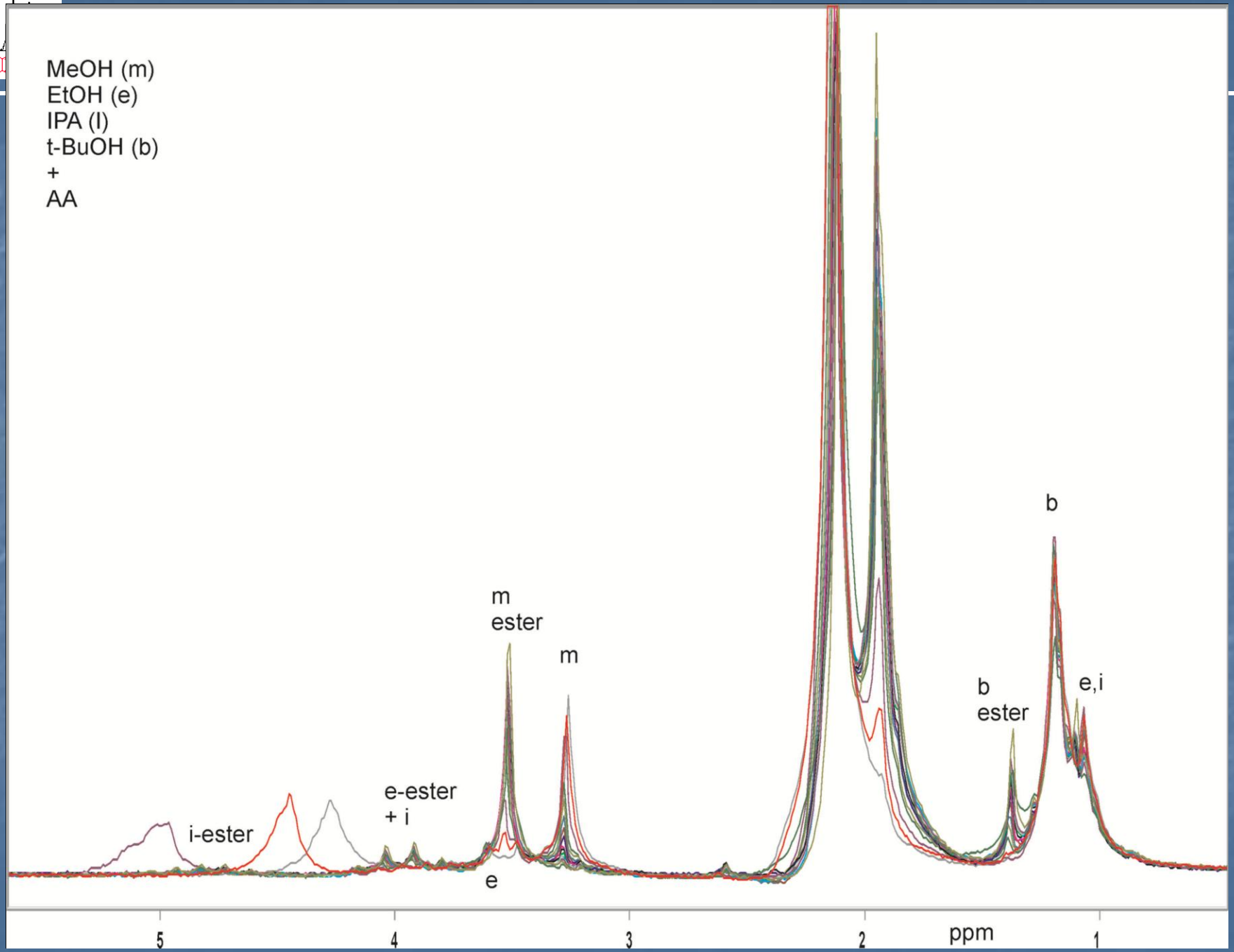
EtOH+AA

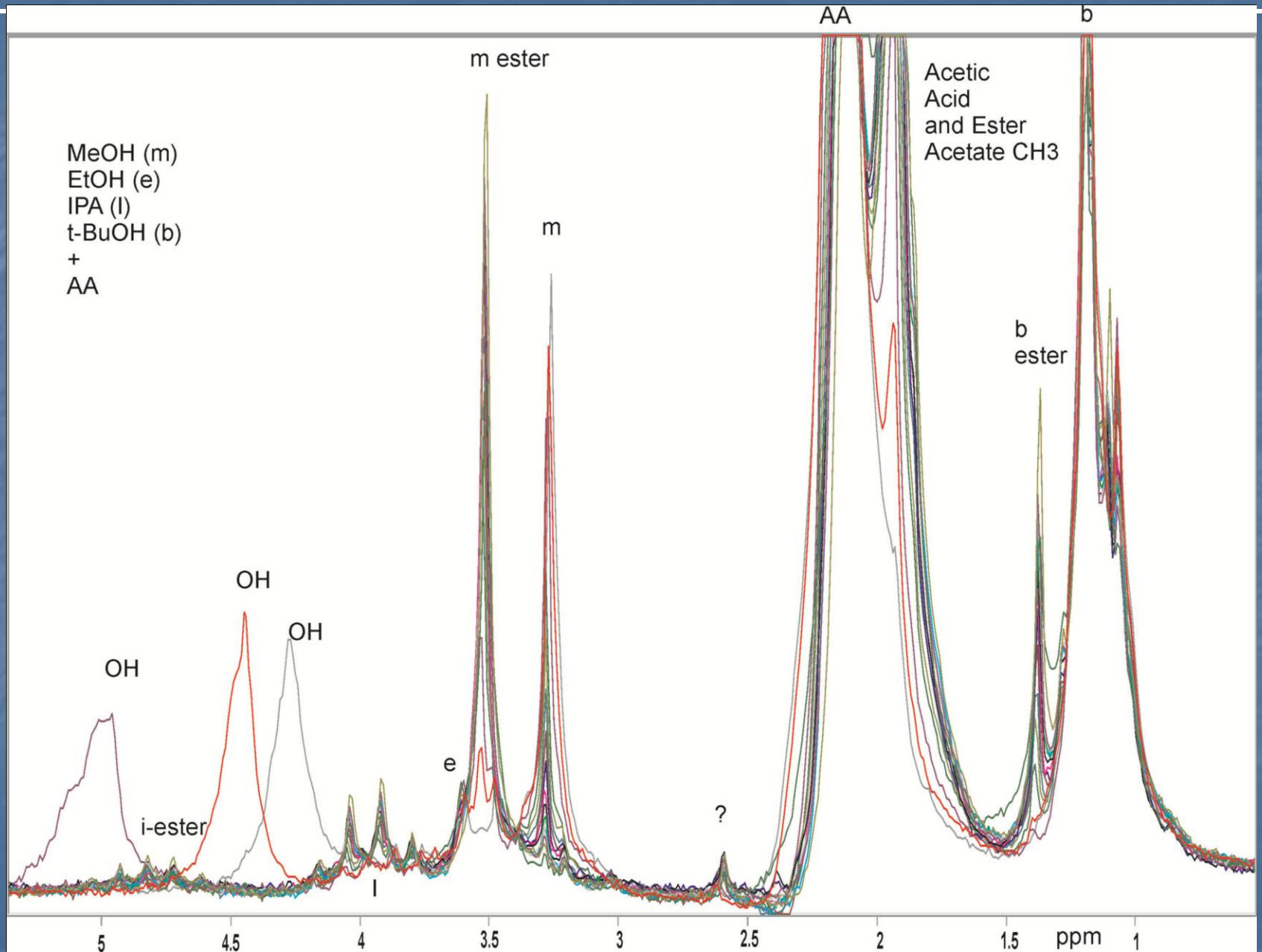
Shifts caused by auto-referencing changes caused by intensity shifts in the methyl resonance area.

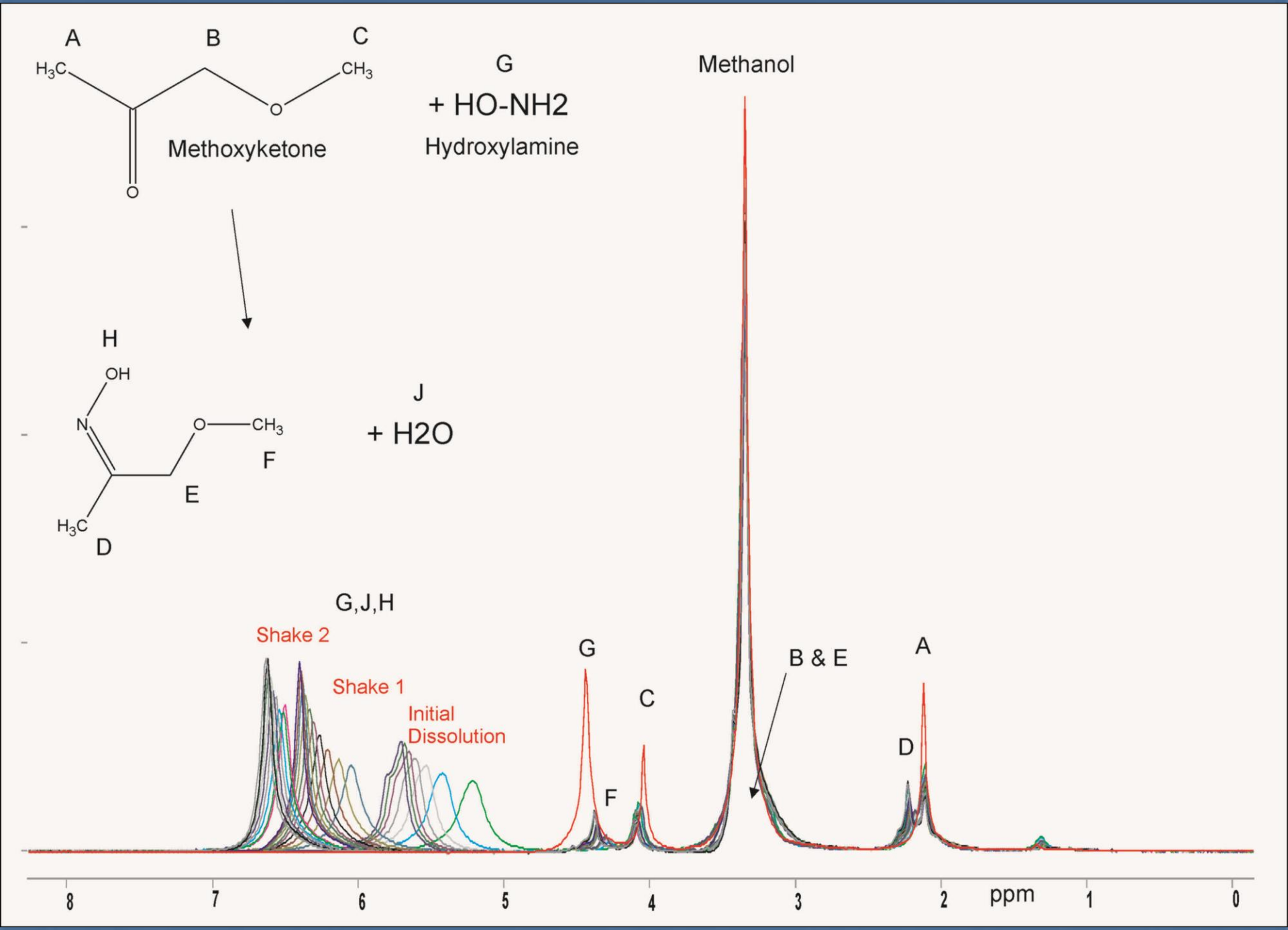


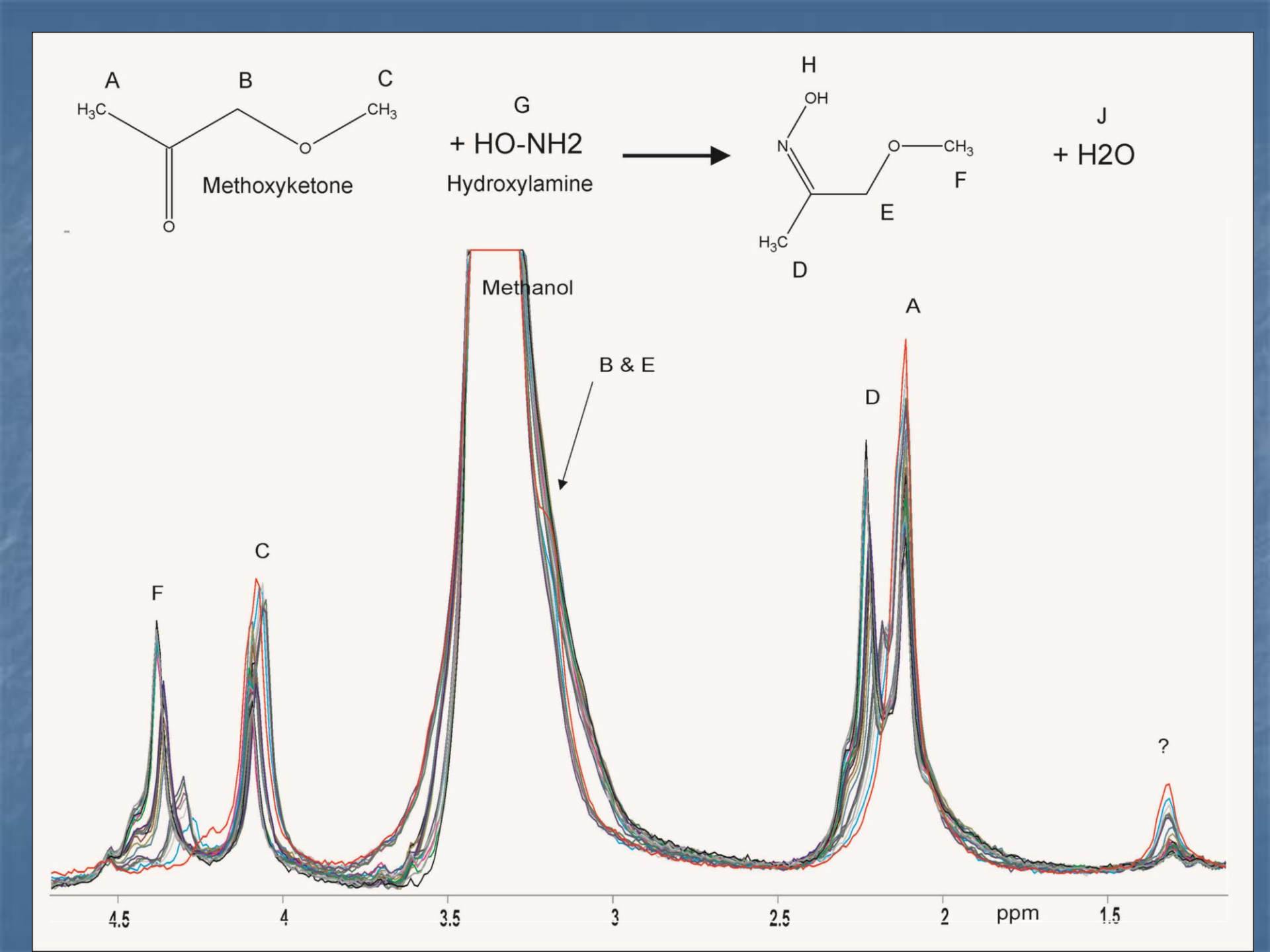

Ester
Ethanol
Ester
Ethanol
4.5
4
3.5
3
2.5
2
1.5
ppm
1
0.5

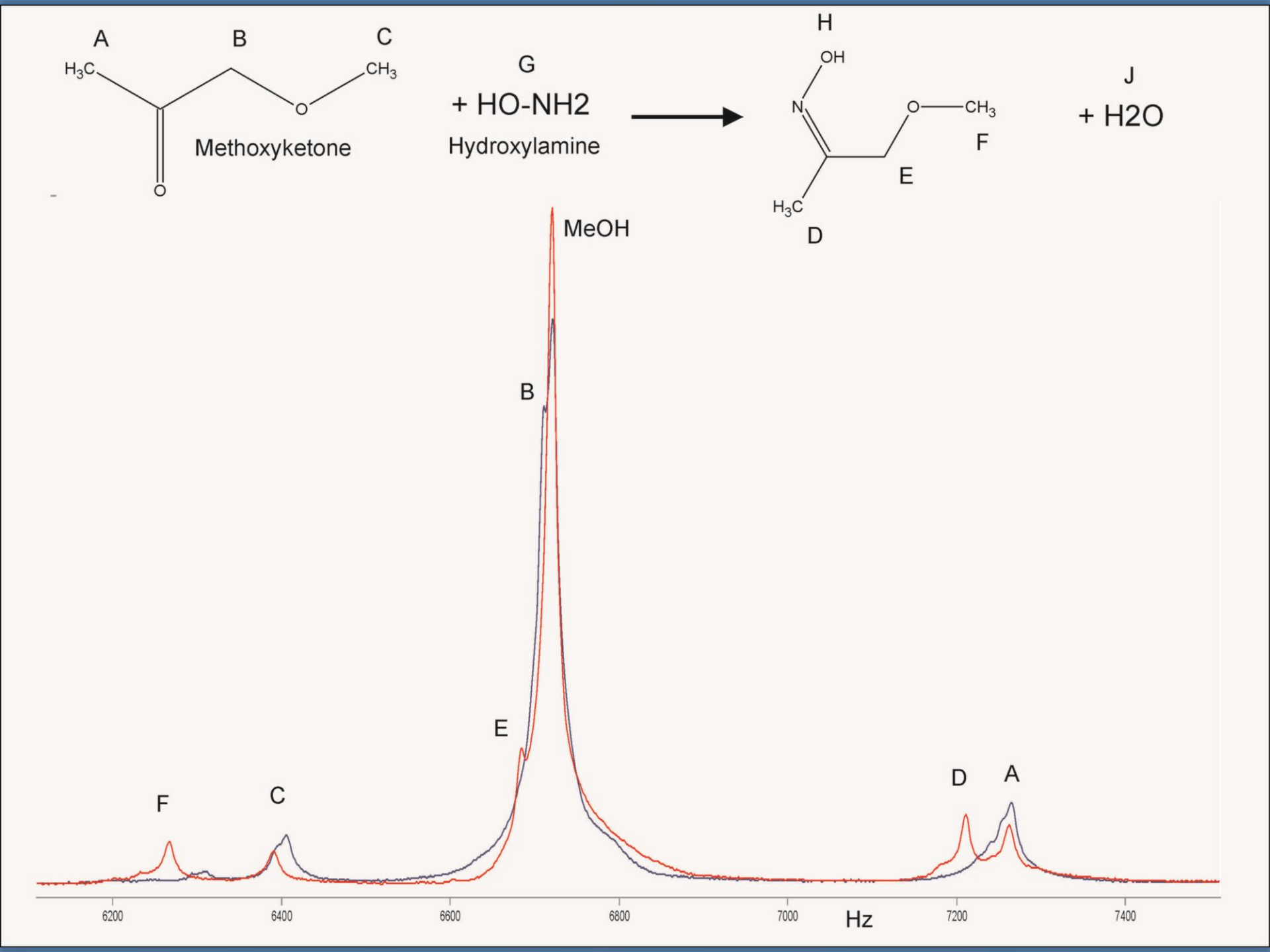

MeOH (m)
EtOH (e)
IPA (i)
t-BuOH (b)
+
AA
AA
acetic-ester
t
t-e
e,i
m-e
m
OH - pH shift
i-e
e-e
l
e
8
6
4
2
0

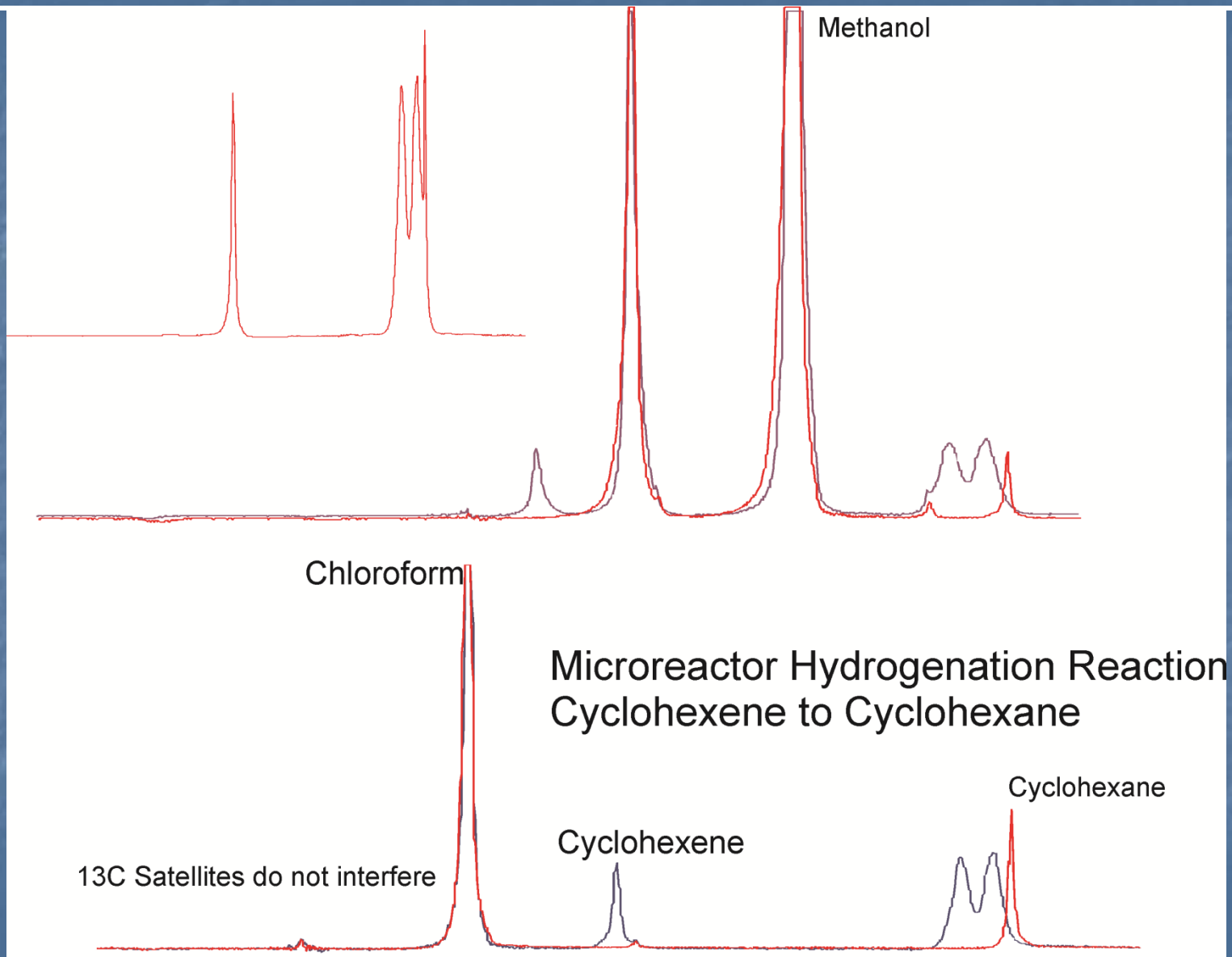

MeOH (m)
EtOH (e)
IPA (l)
t-BuOH (b)
+
AA
i-ester
e-ester
+ i
m
ester
m
e
b
ester
b
e,i
5
4
3
2
ppm
1

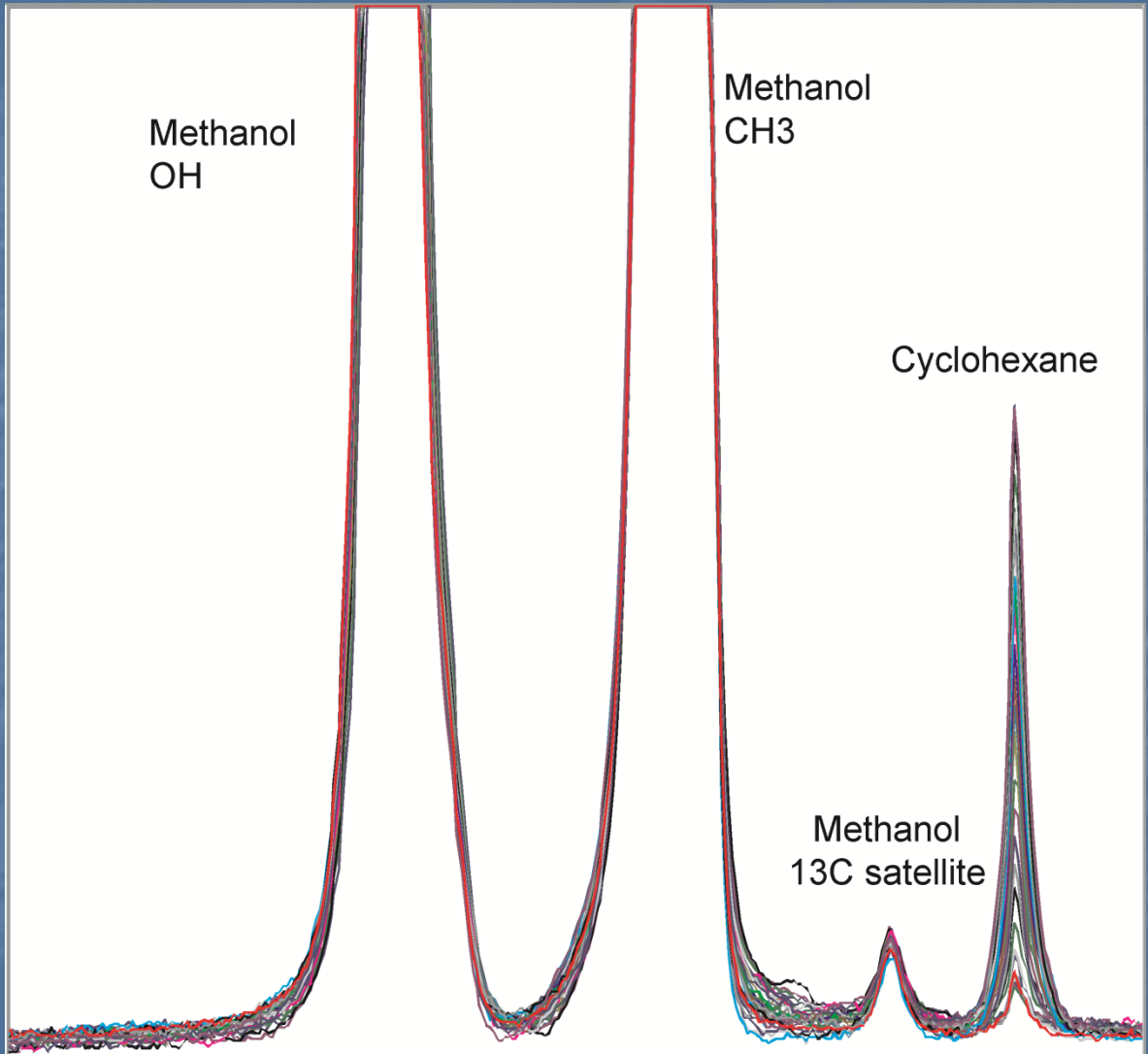

AA
b
m ester
Acetic
Acid
and Ester
Acetate CH3
MeOH (m)
EtOH (e)
IPA (I)
t-BuOH (b)
+
AA
m
b
ester
OH
OH
OH
e
i-ester
I
?
5
4.5
4
3.5
3
2.5
2
1.5
ppm
1


A
B
C
H_3C
CH_3
O
O
Methoxyketone
G
+ HO-NH2
Hydroxylamine
Methanol
H
OH
N
O
CH_3
F
E
H_3C
D
J
+ H2O
G,J,H
Shake 2
Shake 1
Initial
Dissolution
G
C
F
B & E
A
D
8
7
6
5
4
3
2
ppm
1
0

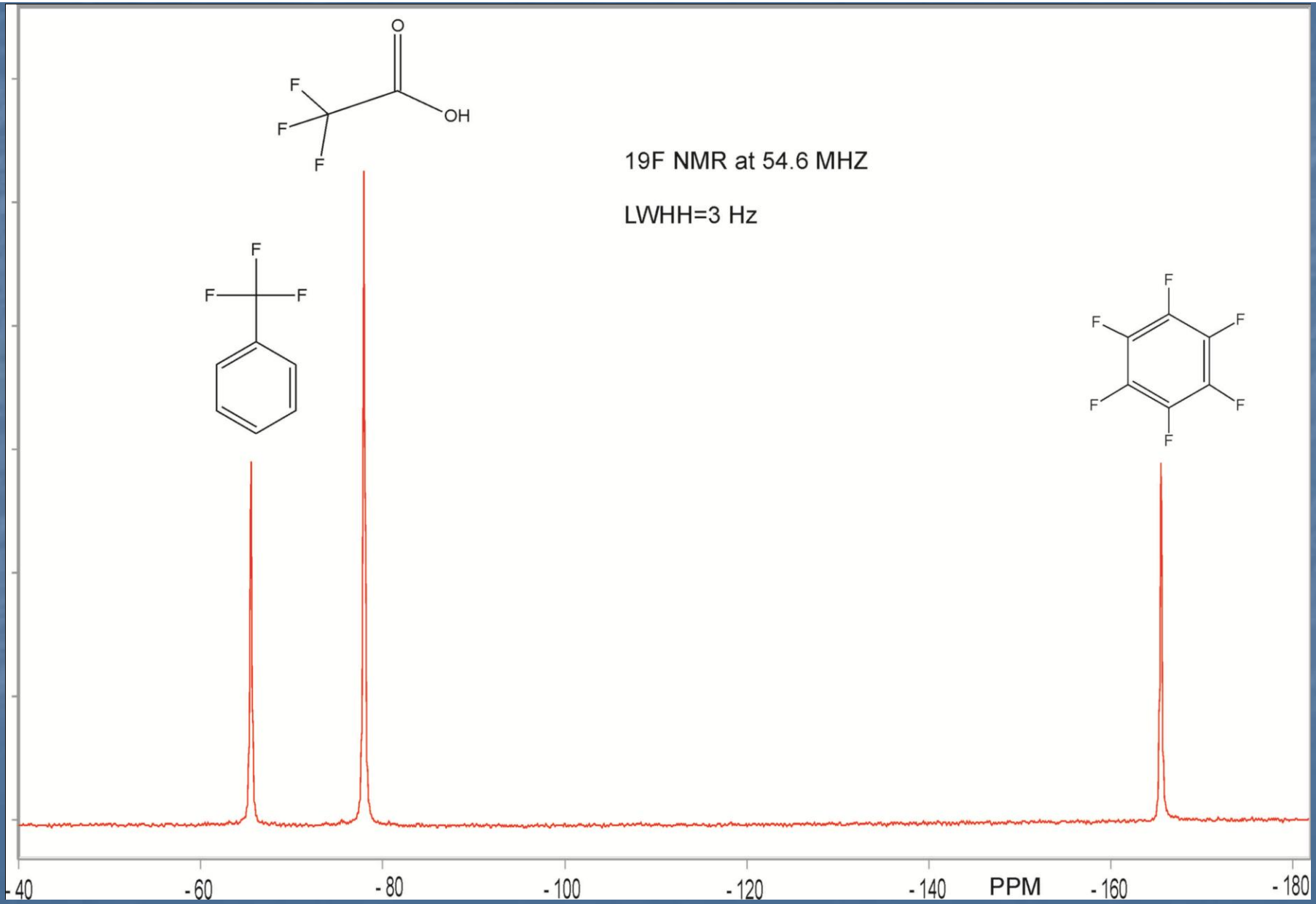

A
B
C
H3C
CH3
O
O
Methoxyketone
G
+ HO-NH2
Hydroxylamine
H
OH
N
O
CH3
F
E
H3C
D
J
+ H2O
Methanol
B & E
A
D
C
F
?
4.5
4
3.5
3
2.5
2
ppm
1.5


A
B
C
H_3C
CH_3
O
O
Methoxyketone
G
+ HO-NH2
Hydroxylamine
H
OH
N
O
CH_3
F
E
H_3C
D
J
+ H2O
MeOH
B
E
F
C
D
A
6200
6400
6600
6800
7000
Hz
7200
7400


Methanol
Chloroform
Microreactor Hydrogenation Reaction
Cyclohexene to Cyclohexane
Cyclohexane
Cyclohexene
13C Satellites do not interfere



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.


O
F
F
F
OH
19F NMR at 54.6 MHZ
LWHH=3 Hz
F
F
F
F
F
F
F
F
F
-40
-60
-80
-100
-120
-140
PPM
-160
-180

Acknowledgements

Paul Giammatteo – PNA

Qualion NMR – Israel

Tal Cohen – ASPECT Italia

Leonid Grunin – Resonance Systems, Russia

Mark Zell – Pfizer – Groton CT