Gas Chromatography - Vacuum Ultraviolet Spectroscopy: A Versatile Tool for Analysis of Gasoline and Jet Fuels

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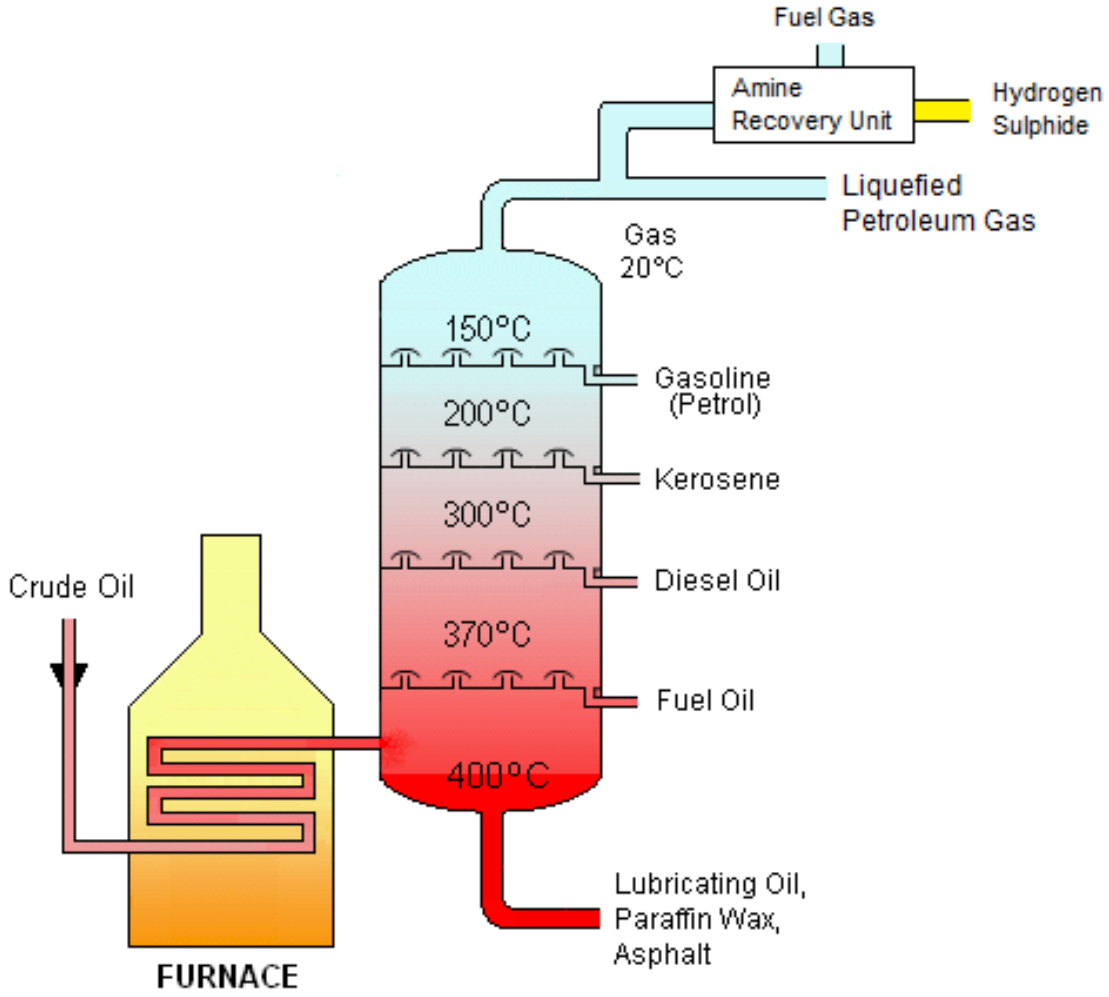
VUV Analytics, Inc.

PEFTEC 2019

Overview of Crude Oil Refining Products

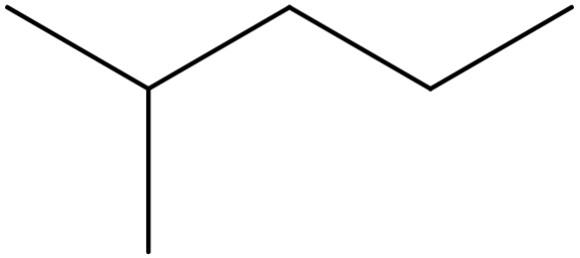


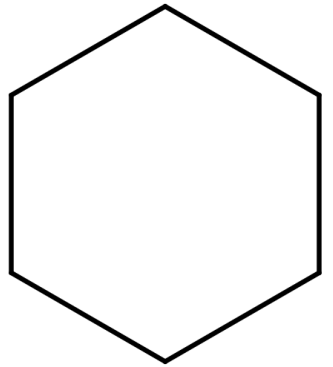
- Liquefied petroleum gases (LPG): C_1- C_4
- Gasoline: C_5 - C_{12}
- Middle distillates (e.g., jet, diesel): C_{10} - C_{20}
- Heavier oils and waxes: C_{20}+

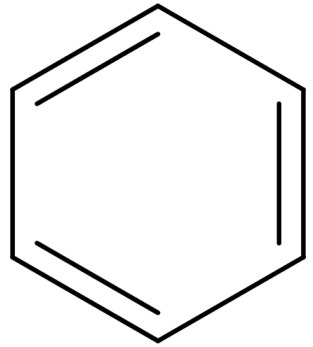
https://www.enggcyclopedia.com/2011/05/crude-oil-refining-products/

What is PIONA?

- **P**araffins (linear alkanes)
- **I**soparaffins (branched alkanes)
- **O**lefins (alkenes)
- **N**aphthenes (cycloalkanes)
- **A**romatics







Classical GC Detectors

Flame ionization detection (FID)

- Good LODs
- Wide dynamic range
- Cheap
- Robust
- Great for process applications

Mass spectrometry (MS)

- The “gold standard” (R&D)
- Compound identification
- Tunable physical selectivity (SIM, SRM, MRM)
- Very low LODs (MS/MS)

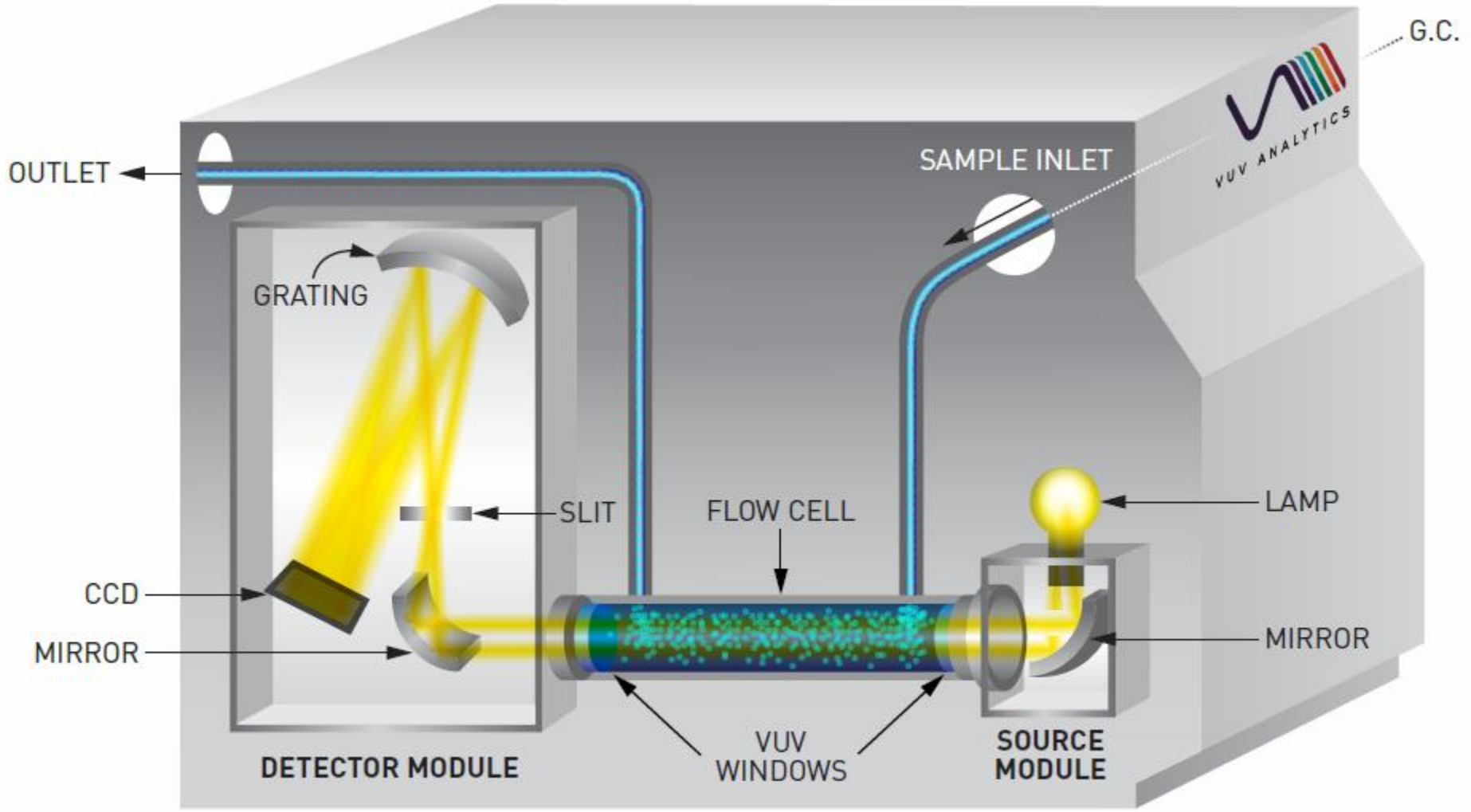
Shortcomings, and how VUV fits in

- FID requires baseline separation of peaks for accurate quantitation
- MS has limited flow rates due to vacuum pump considerations; can struggle with isomer differentiation

- ***VUV combines the speeds of FID with the qualitative spectral information of MS, and unique spectral fingerprints make deconvolution of coeluting isomers straightforward***

Vacuum Ultraviolet (VUV) Absorption Spectroscopy

- Absorption spectroscopy in a new spectral region (<200 nm)
  - Previously only measurable using synchrotrons
- A universal technique that provides unique spectral fingerprints
  - High energy, low wavelength exposure produces electronic transitions between $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, and $\pi \rightarrow \pi^*$ molecular orbitals
- ***Unambiguous compound identification, even for structural isomers***
- 1st order quantitation following Beer-Lambert Law ($A=\varepsilon bc$)
- ***Chromatography runs can be deliberately compressed, leading to higher sample throughput***



	VGA-100	VGA-101
Max Temp	300°C	430°C
λ Range	125 - 240 nm	125 - 430 nm
Acq Rate	75 Hz	75 Hz

VUV ANALYTICS

Traditional Gasoline Analysis

The current playing field of PIONA

DHA – Overview and Setup

- GC-FID (ASTM D6730), though sometimes simultaneously run on GC-MS for confirmation
- Speciation of up to 600 compounds in gasoline-range fuels (though not all compounds are identified by name)
- 100m non-polar column, 5% diphenyl “tuning” precolumn
- Cryogenic oven start (5°C)
- Run time: 174 minutes
  - Run time subsequently cut to 38 minutes

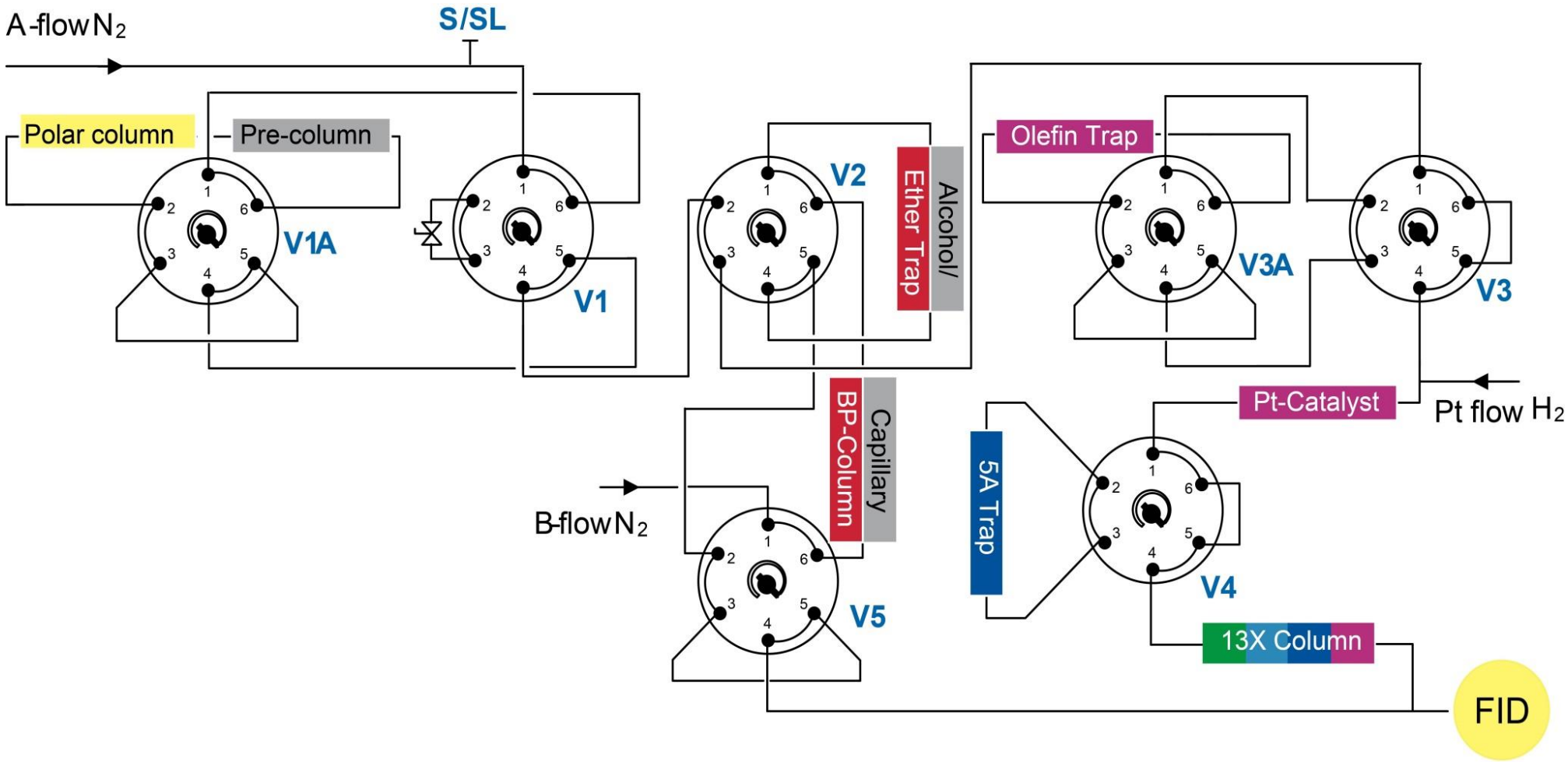
DHA – Drawbacks

- Relies solely on retention time
- Tuning precolumn necessary to baseline separate known coelutions
  - Benzene/1-Methylcyclopentene
  - m-/p-Xylene
- Any unexpected coelutions cannot be identified with the FID data, requires MS analysis
- Requires a trained user to go through data peak by peak

Reformulyzer – Overview and Setup

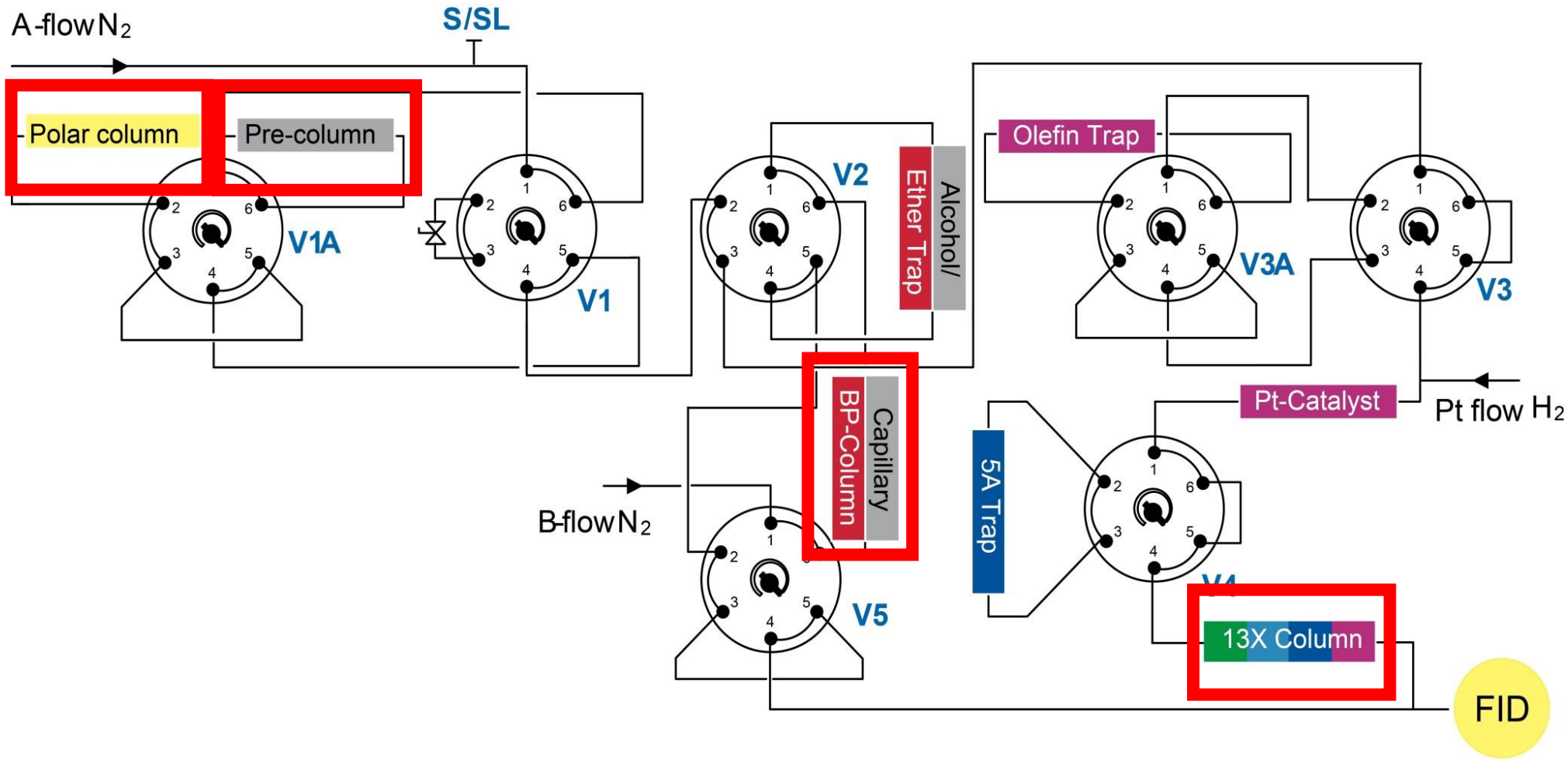
- Multi-dimensional GC-FID (ASTM D6839)
- Measures PONA compounds and oxygenates in gasoline and gasoline blend streams
  - Physically separates compounds using a series of columns and traps actuated by 6-port valves
  - Paraffins and isoparaffins not separated
- 39-minute run time

A “basic” schematic of the Reformulyzer…



VUV ANALYTICS

A “basic” schematic of the Reformulyzer…



VUV ANALYTICS

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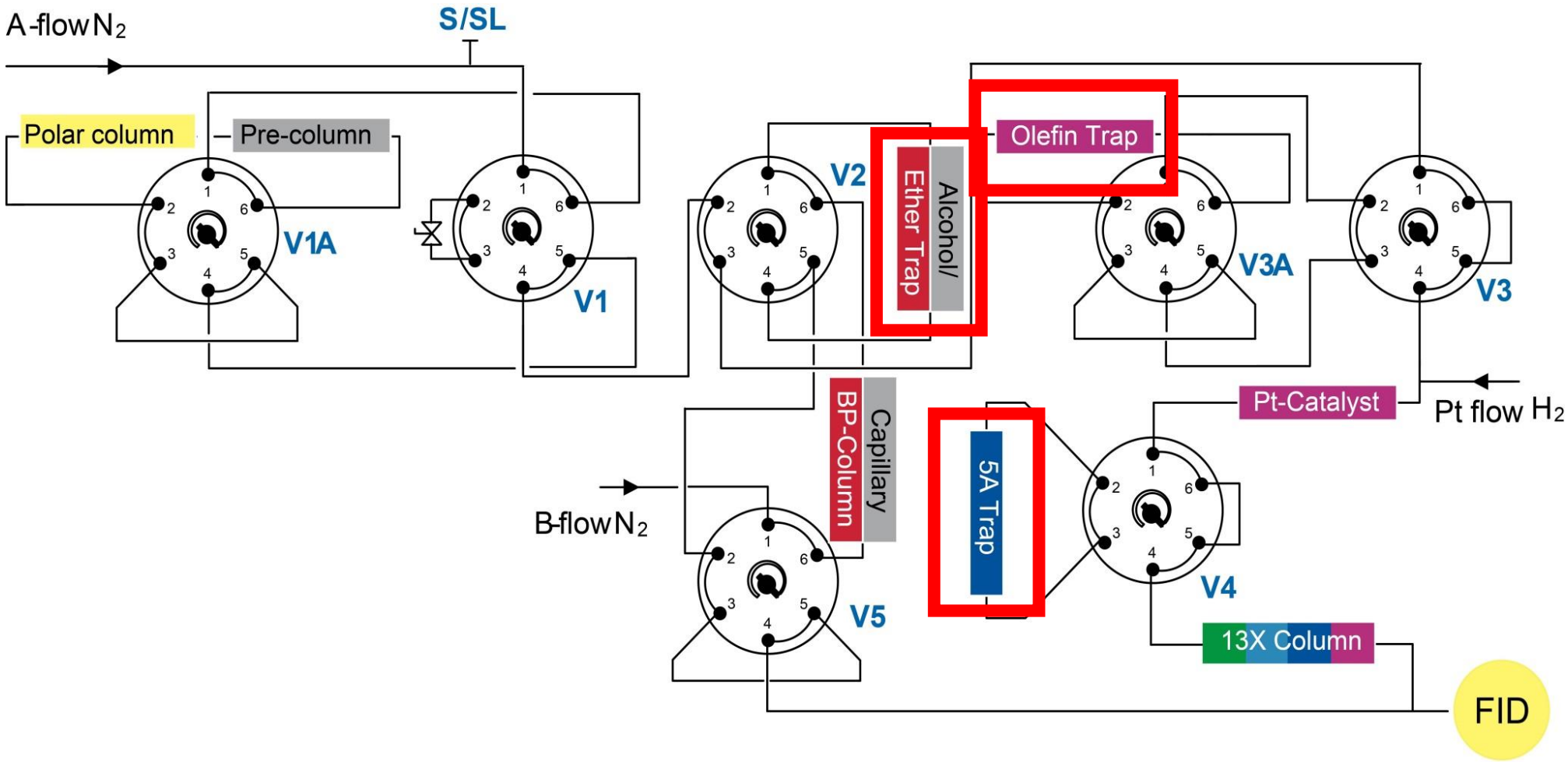

VUV ANALYTICS

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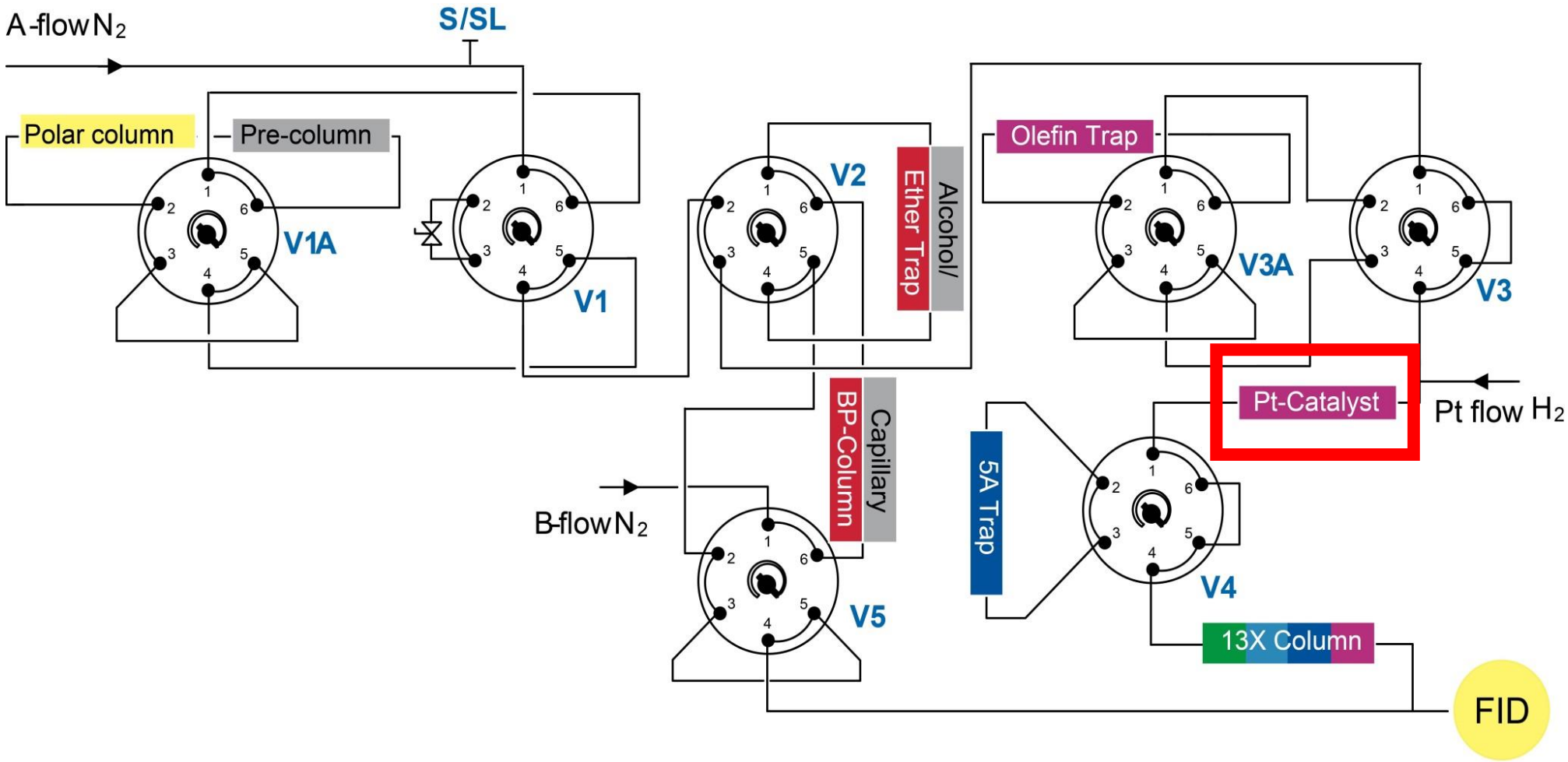

VUV ANALYTICS

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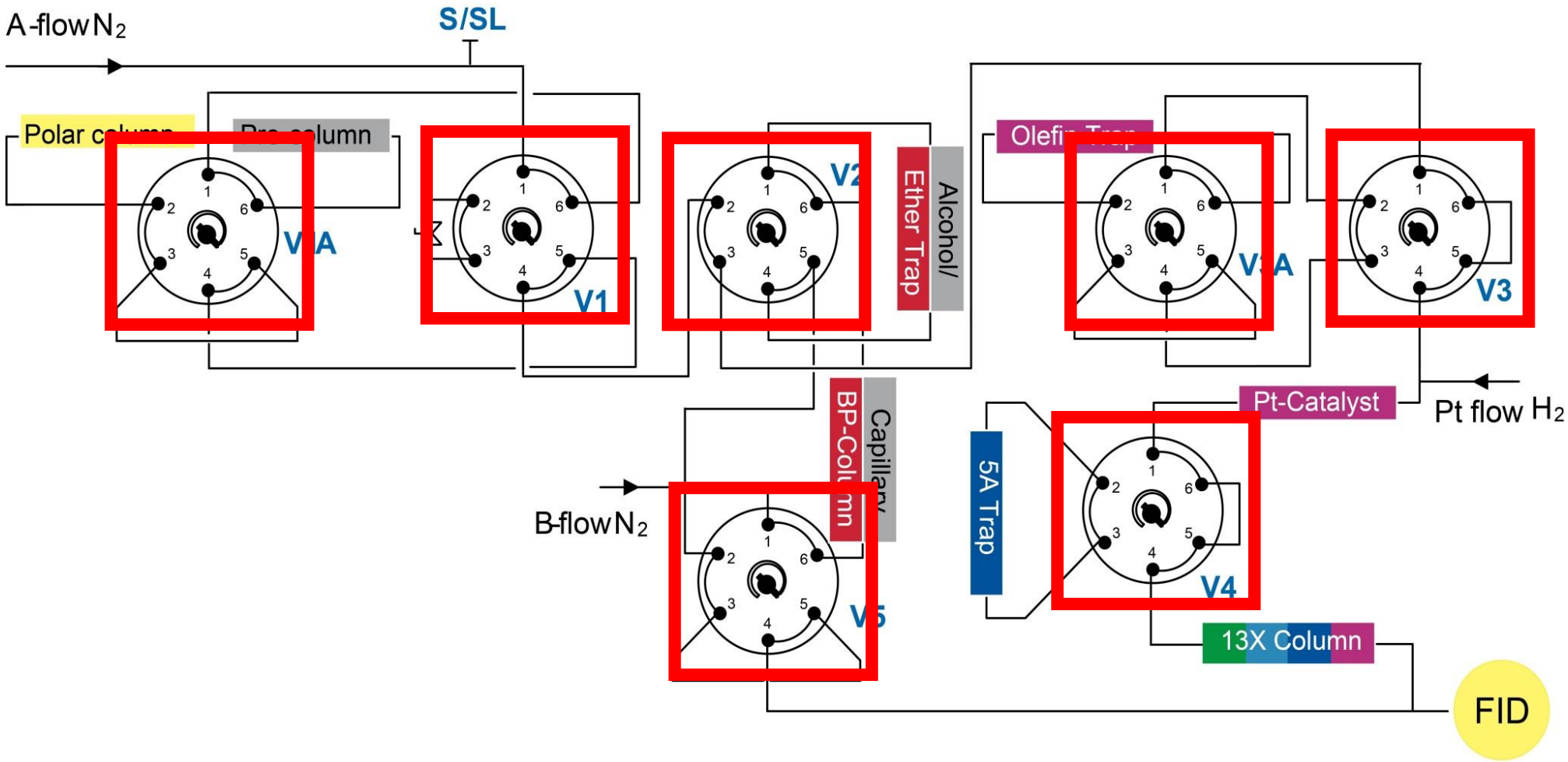

VUV ANALYTICS

Reformulyzer – Drawbacks

- Multiple columns and connections → greater chance for leaks or restrictions
- Access to certain areas only possible by removing all traps and fans, disconnecting columns
- Problems take longer to troubleshoot and repair
- Longer down time

VUV ANALYTICS

PIONA by VUV: ASTM D8071

GC-VUV Analysis of Gasoline-Range Fuels

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ASTM D8071-17

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Authors
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Reading Room
Product Update
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Enterprise Solutions

Standard Test Method for Determination of Hydrocarbon Group Types and Select Hydrocarbon and Oxygenate Compounds in Automotive Spark-Ignition Engine Fuel Using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV)

Active Standard ASTM D8071 | Developed by Subcommittee: D02.04.0L

Recommended
Standards Tracker
Standards Subscriptions

Paraffins, Isoparaffins, Olefins, Naphthenes, Aromatics by Carbon Number from C1 to C15

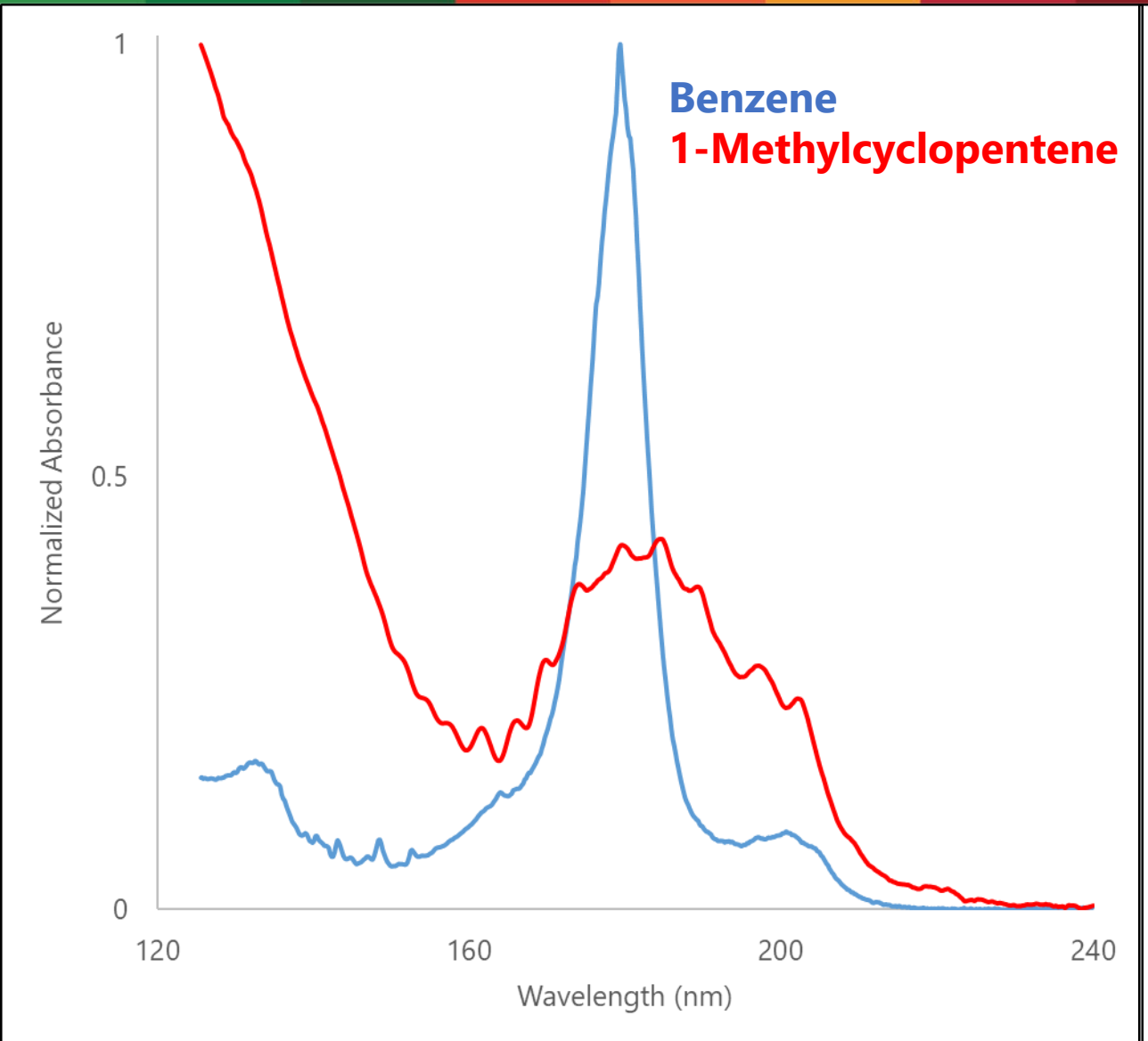
Methanol, Ethanol, Benzene, Toluene, Ethylbenzene, Xylenes, Naphthalene, Methylnaphthalenes, Isooctane

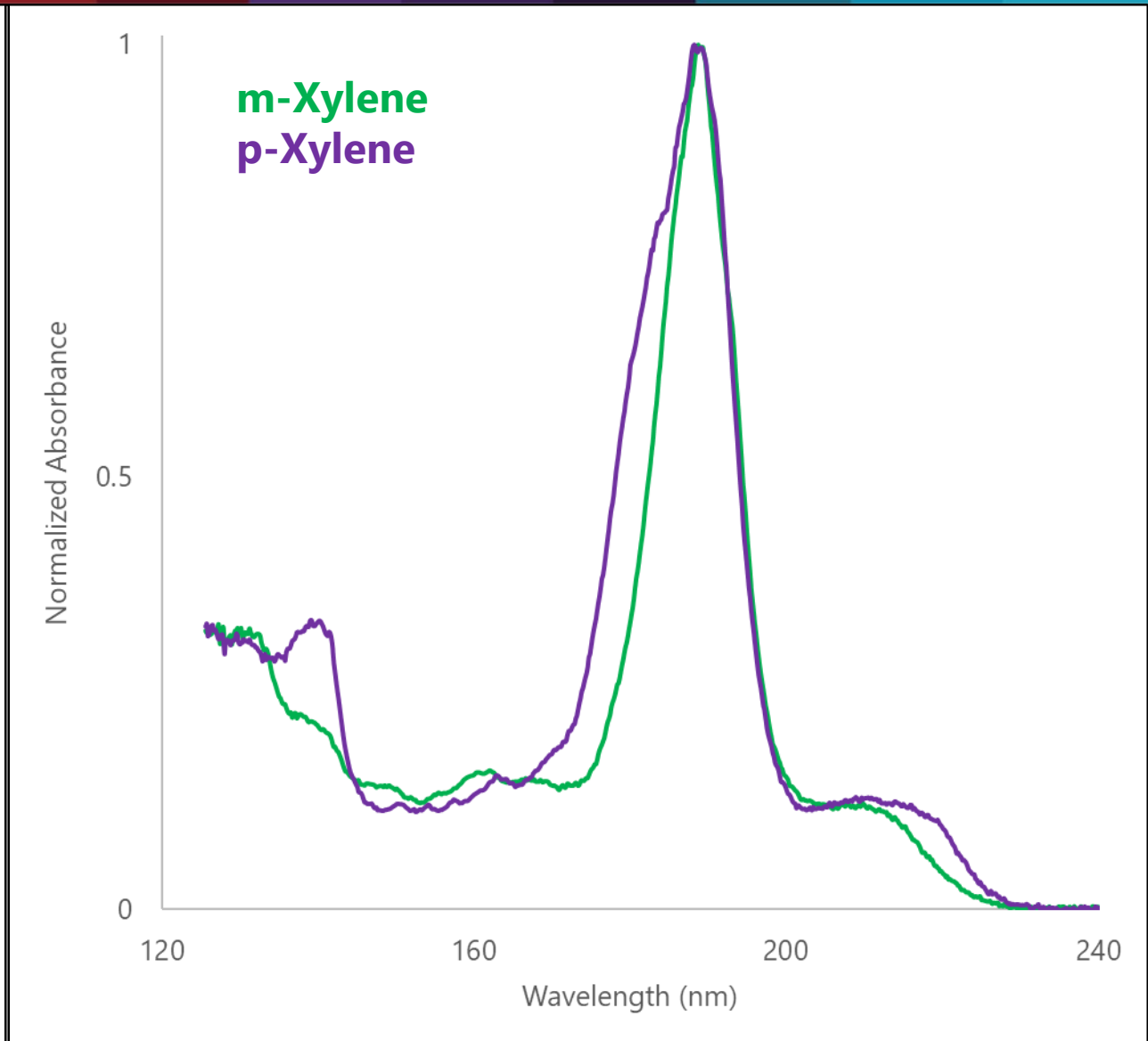
Copyright Clearance Center

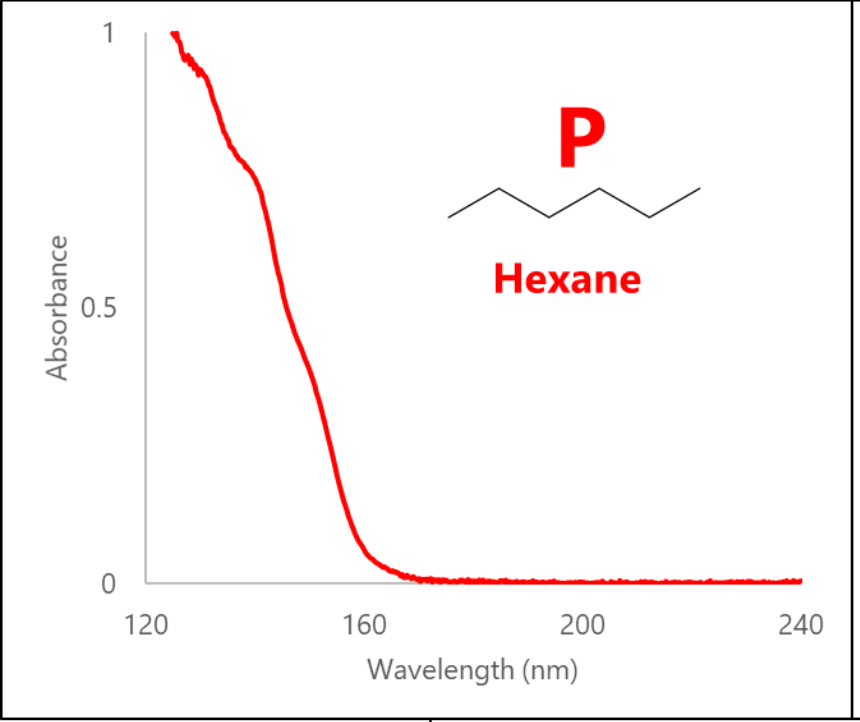
PIONA Analysis of Gasoline with GC-VUV

- 30m x 0.25mm x 0.25µm 100% dimethylpolysiloxane column
  - About 33.5 min run versus two hours for DHA
  - No precolumn for benzene/1-methylcyclopentene separation, e.g.
- Collect VUV absorbance data (125-240 nm)
  - Spectra can be unique and class-indicating
- Fully automated data processing with VUV Analyze PIONA +
  - Spectral library, retention index, relative response factors
  - “Separation” of coelutions with Time Interval Deconvolution
  - Mass % and Volume % reports, carbon number breakdown

Precolumn? We don't need no stinkin' precolumn…



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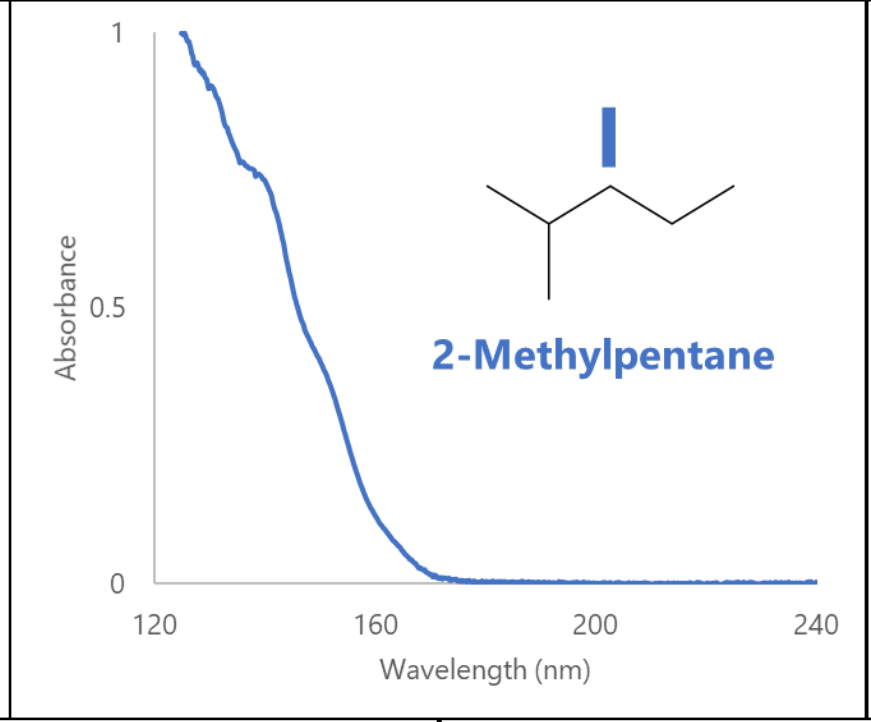
Hexane
Absorbance
1
0.5
0
120
160
200
240
Wavelength (nm)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Absorbance
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0.5
0
120
160
200
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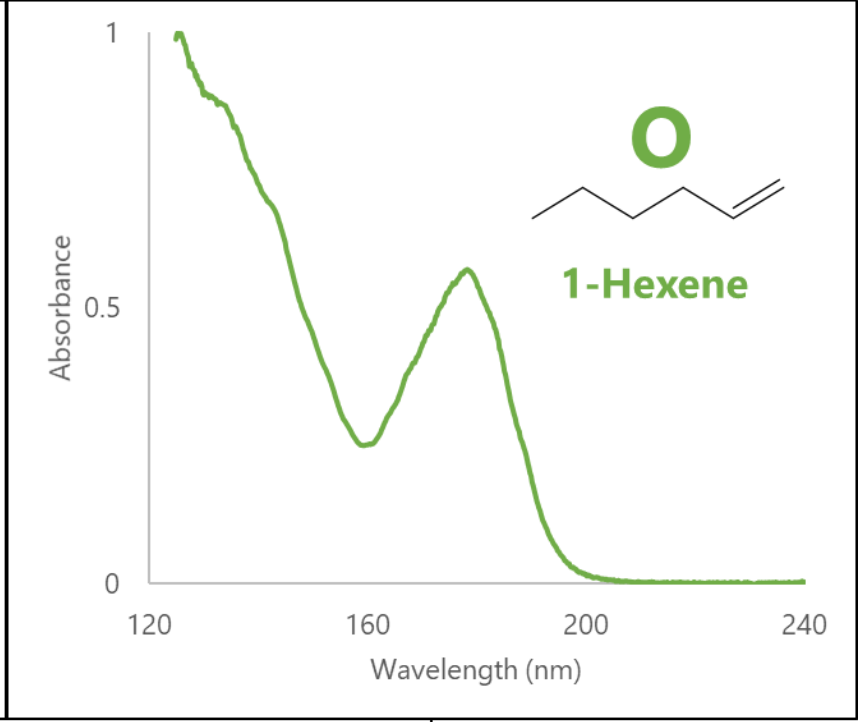
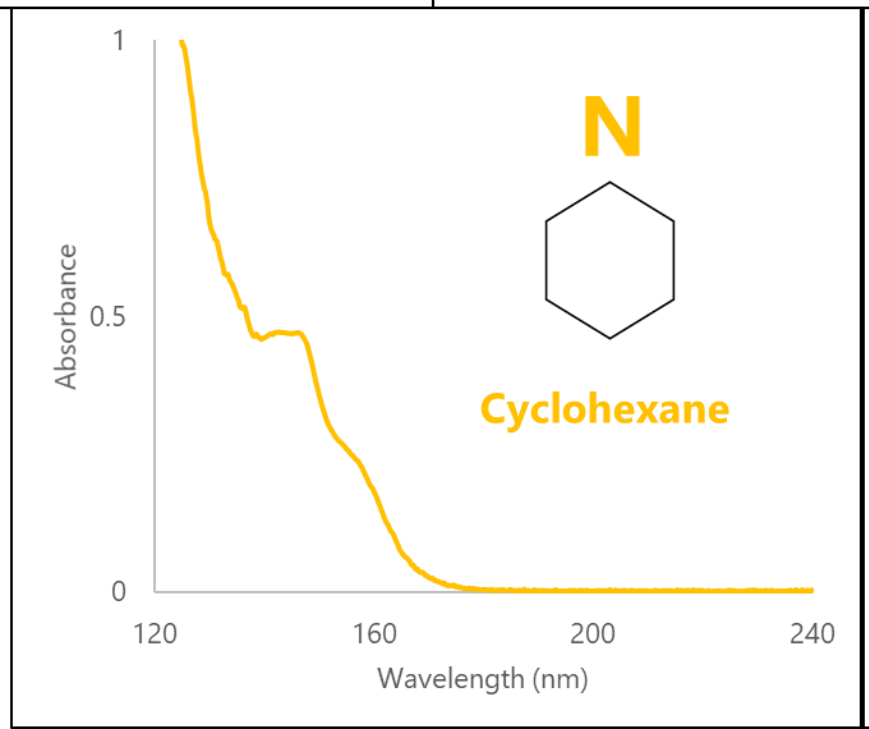
Wavelength (nm)


O
1-Hexene
Absorbance
1
0.5
0
120
160
200
240
Wavelength (nm)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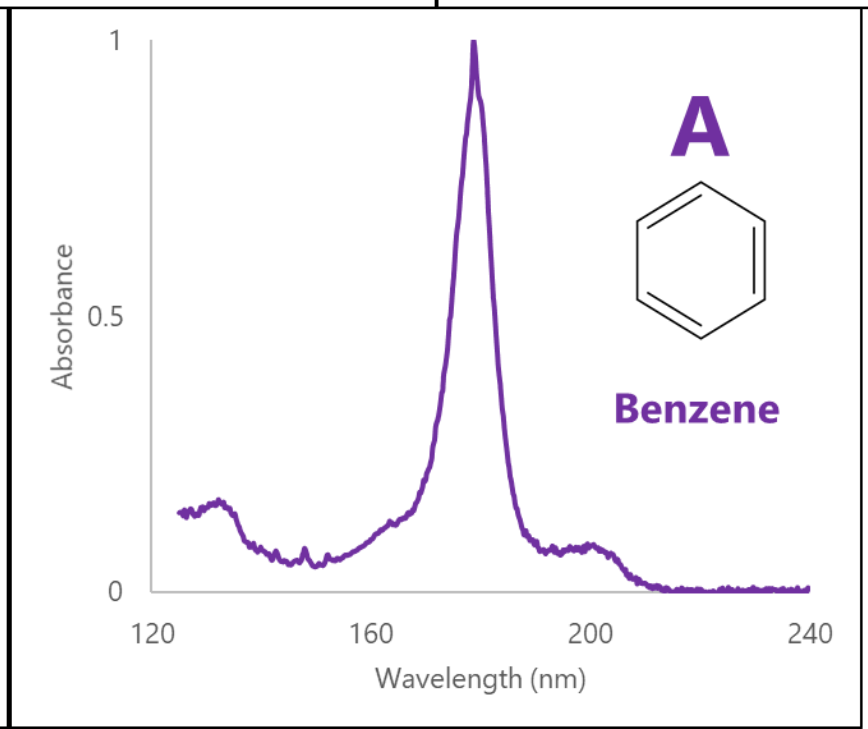
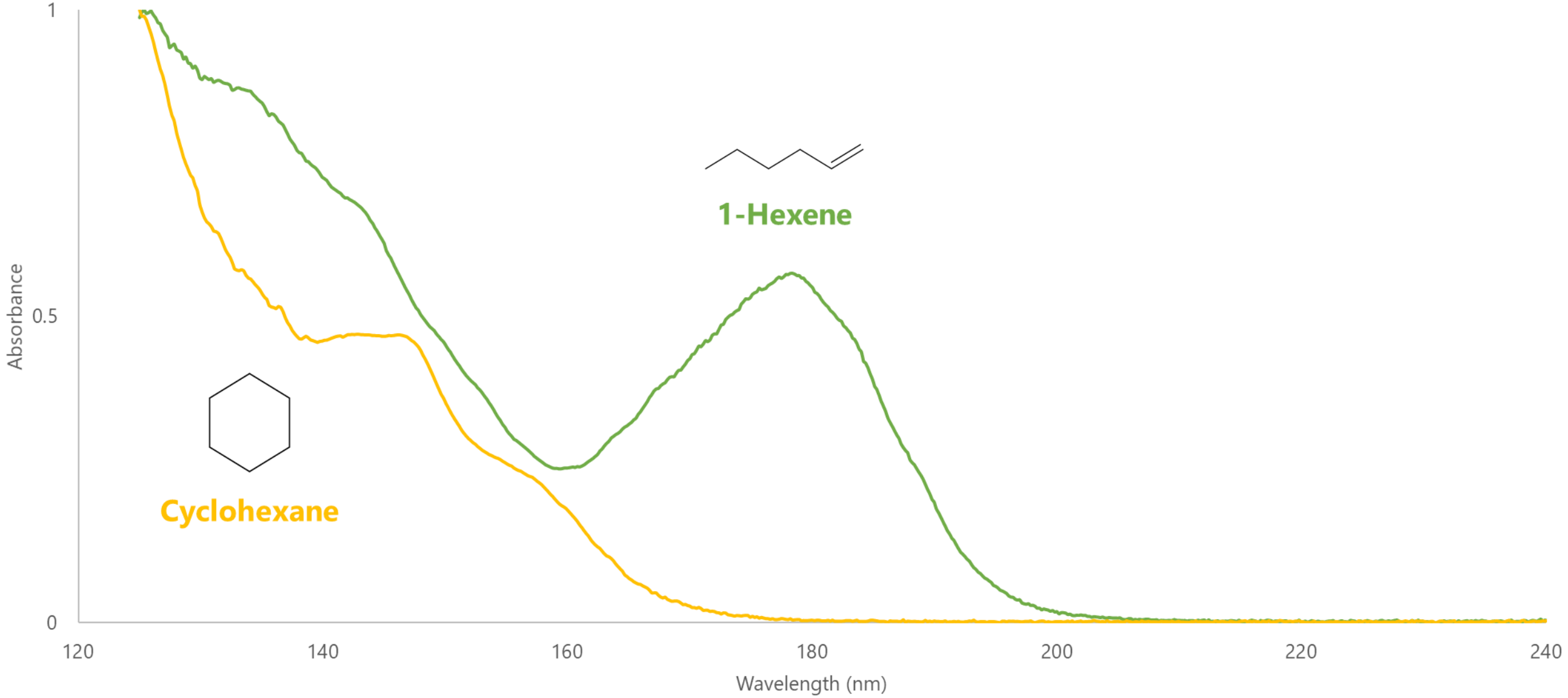
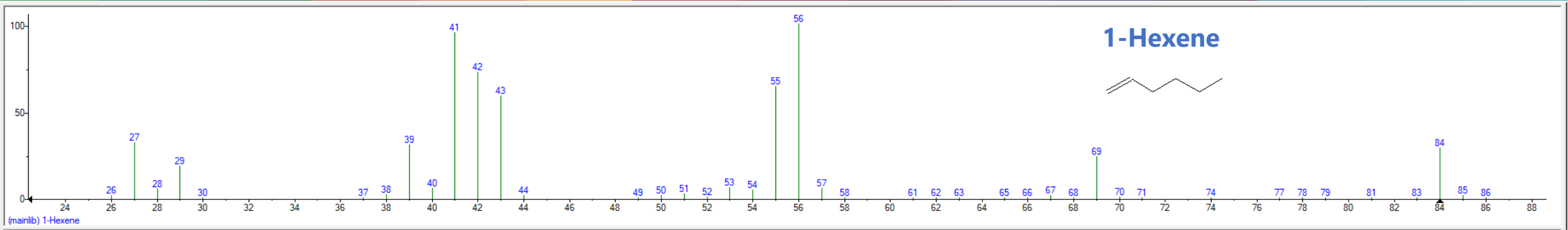
Cyclohexane
Absorbance
1
0.5
0
120
160
200
240
Wavelength (nm)

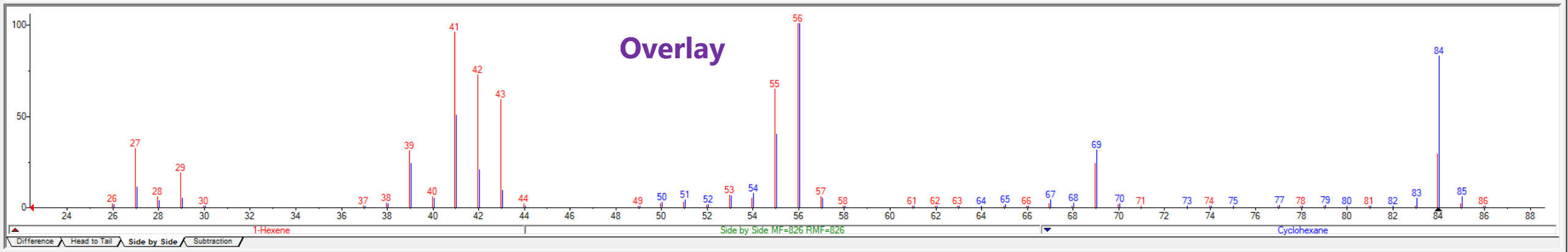

A
Benzene
Absorbance
1
0.5
0
120
160
200
240
Wavelength (nm)

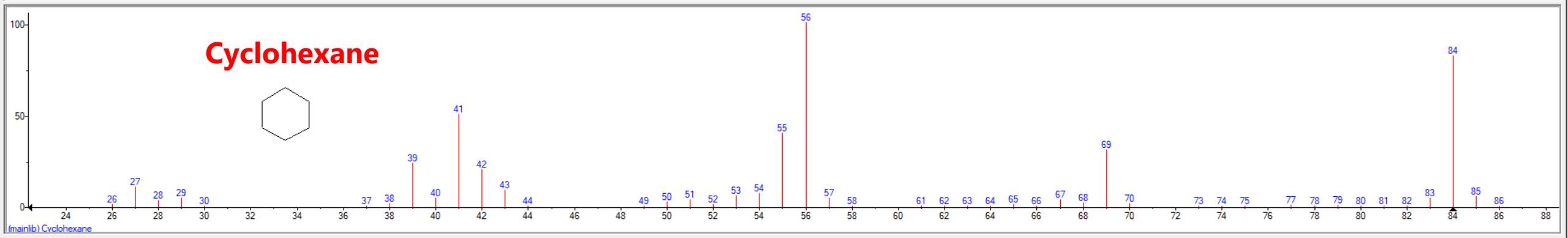
Olefin/Naphthene Differentiation using VUV Spectroscopy



Issues with Olefin/Naphthene Differentiation using MS

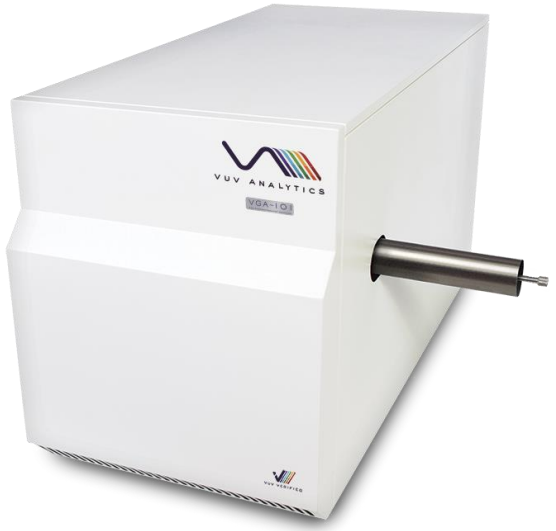


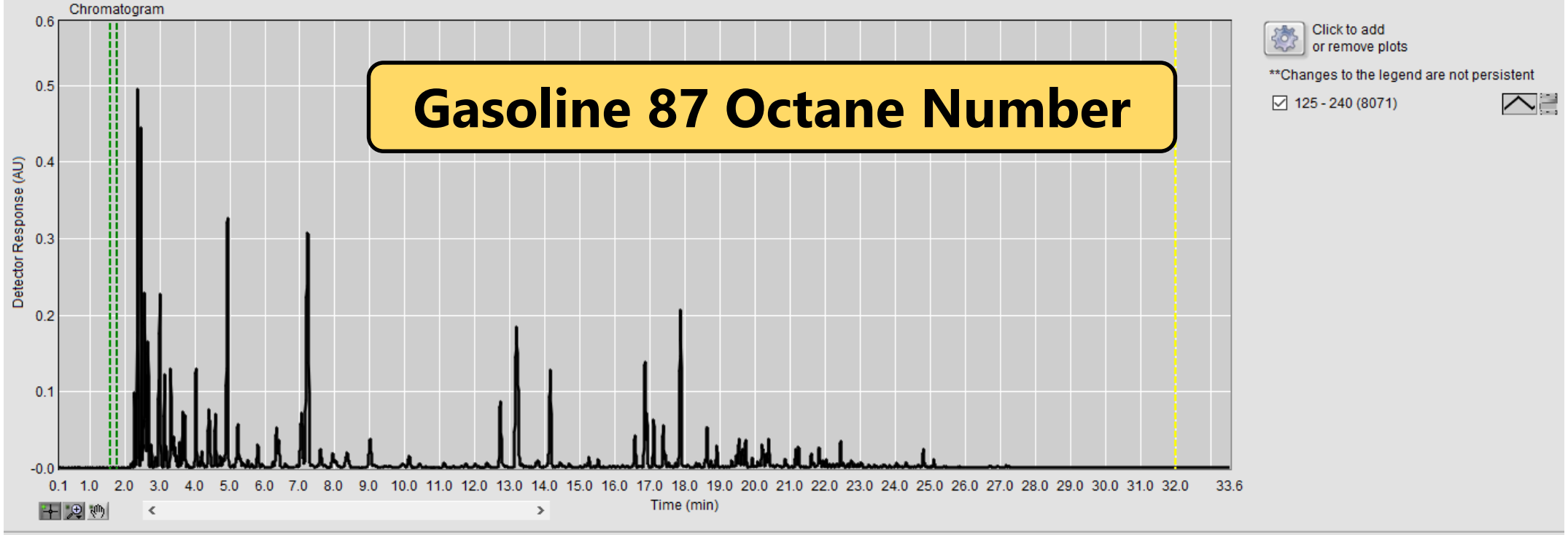




ASTM D8071 Run Conditions

- Agilent 6890 GC
  - 1 µL injection
  - Inlet: 250°C, split 300:1
  - Column: Restek Rxi-1ms (30 m x 0.25 mm, 0.25-µm)
  - Flow: 1 mL/min helium, constant flow
  - Oven: 35°C, hold 10 min; 7°C/min to 200°C (run time – 33.6 min)
- VUV Analytics VGA-100
  - Makeup gas: 0.40 psi N_2
  - Flow cell and transfer line: 275°C
  - Acquisition rate: 4.5 spectra/sec
  - Acquisition range: 125-240 nm





R & D | Results

Report File | View Report | Export to Excel

Input Files | Reverse Search | Create RI File | D8071 | Analytes to Include | Advanced | Spectra | Fit Info

Run File (*.db) or Directory: C:\Program Files\VUV Analytics\VUV Analyze 130 1953\Demos\D8071\Demo VUV-CS.db — Refresh

Retention Index Markers File: C:\Program Files\VUV Analytics\VUV Analyze 130 1953\Demos\D8071\Demo VUV RI.txt — Refresh

Reference Library File: C:\Program Files\VUV Analytics\VUV Analyze 130 1953\Demos\VUV PIONA ASTM D8071 rev 1.1.0.db — Refresh

Report Method: C:\Program Files\VUV Analytics\VUV Analyze 130 1953\Demos\D8071\D8071-18 Report Method.VUV_RM — Refresh | Edit / Create ...

Analysis Parameters

Initial Background Time (min): Begin 1.600, End 1.800

Analysis Time (min): Begin 1.800, End 32.000, Time Step 0.020

Methods: PIONA

Tiered Search Limit: 3 Analytes

Chromatogram Filter: 8071 Filters

Chi^2 Min: 1.0000E-9

Chi^2 Max: 1.0000E-1

Chi^2 delta (%): 60.00

R^2 Limit: 0.4000

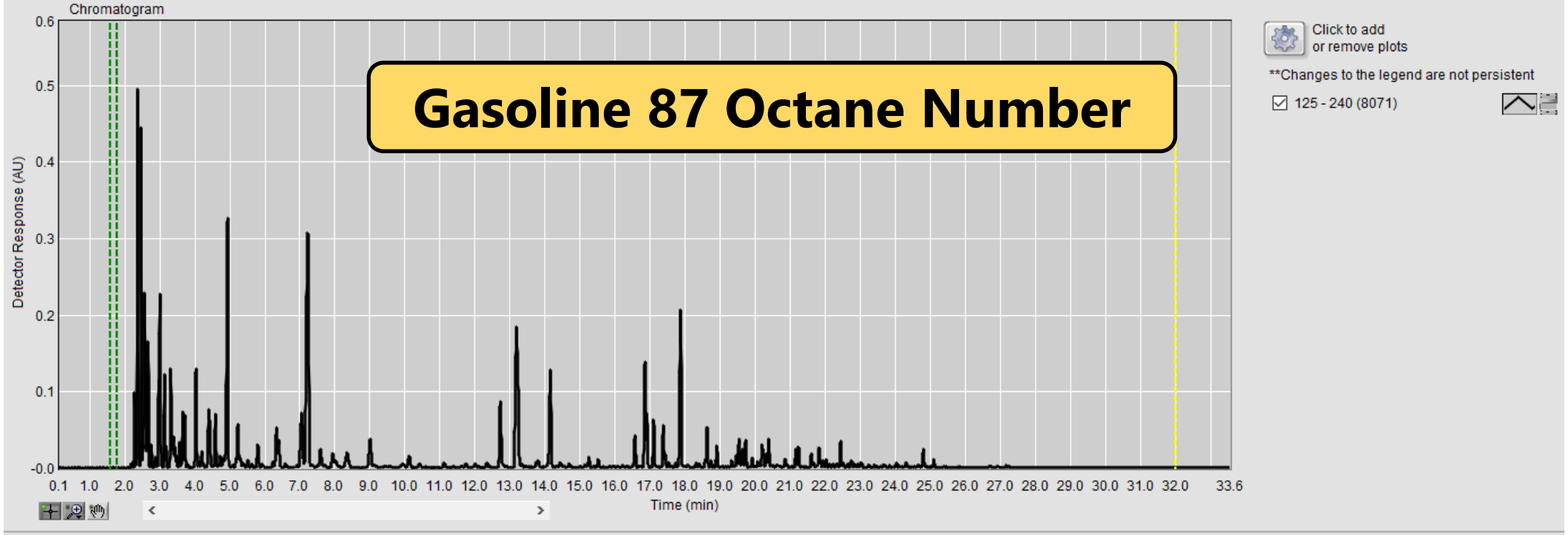
Abs Threshold: 0.00050

BG Threshold: 0.00025

BG Scalar: 1.5

RI window +/-: 25

Analyze | Load Parameters | Time Step Status | Save Parameters | Stop Analyzing



R & D | Results

Report File | View Report | Export to Excel

Input Files | Fit Info

File from gasoline analysis with GC-VUV

Run File (*.db) or Directory

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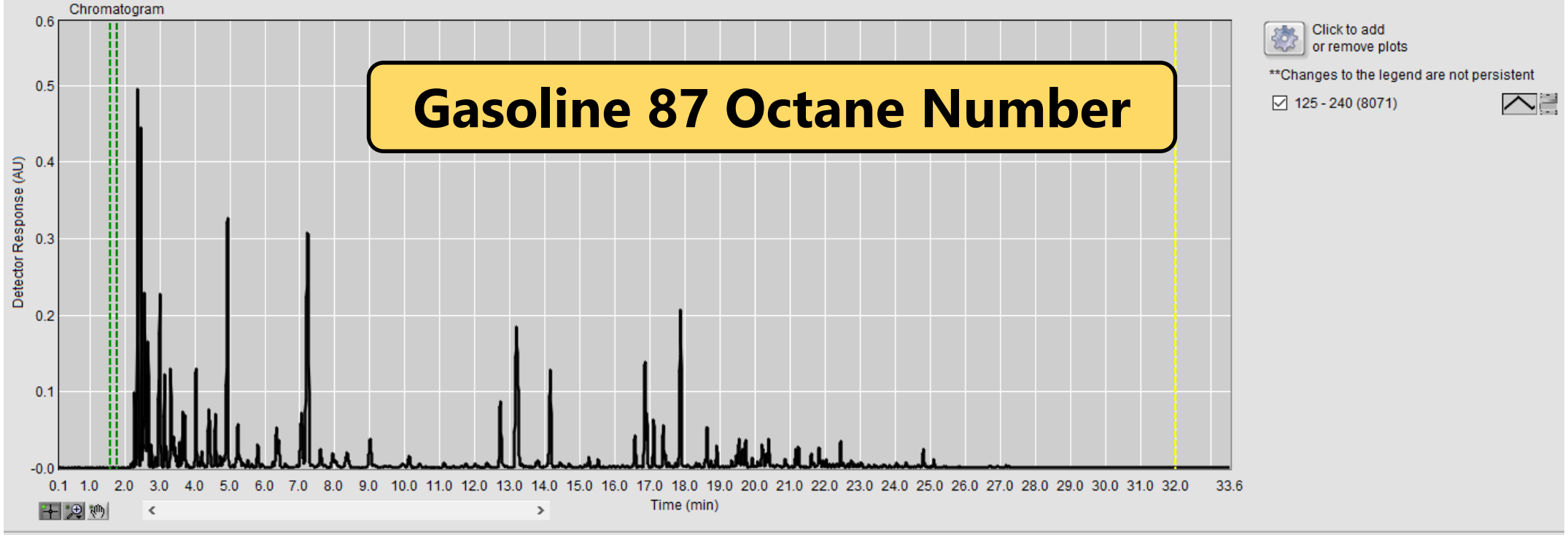
Report Method: C:\Program Files\VUV Analytics\VUV Analyze 130 1953\Demos\D8071\D8071-18 Report Method.VUV_RM — Refresh | Edit / Create ...

Analysis Parameters

Initial Background Time (min)		Analysis Time (min)		Methods		Tiered Search Limit	Chi^2 Min	Chi^2 delta (%)	Abs Threshold	BG Scalar
Begin	1.600	Begin	1.800	PIONA		3 Analytes	1.0000E-9	60.00	0.00050	1.5
End	1.800	End	32.000			Chromatogram Filter	Chi^2 Max	R^2 Limit	BG Threshold	RI window +/-
		Time Step	0.020			8071 Filters	1.0000E-1	0.4000	0.00025	25

Analyze | Load Parameters | Time Step Status | Save Parameters | Stop Analyzing



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Run File (*.db) or Directory

Retention Index Markers File

Reference Library File: C:\Program Files\VUV Analytics\VUV Analyze 130 1953\Demos\VUV PIONA ASTM D8071 rev 1.1.0.db

Report Method: C:\Program Files\VUV Analytics\VUV Analyze 130 1953\Demos\D8071\D8071-18 Report Method.VUV_RM

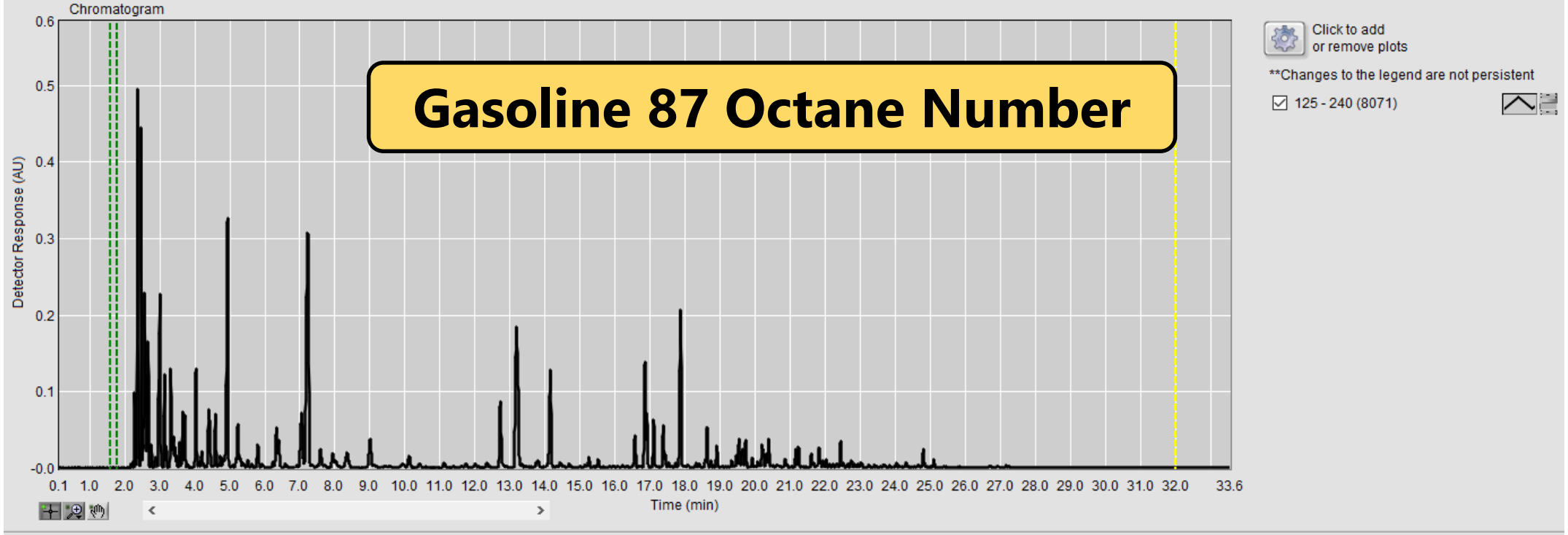
Refresh | Edit / Create ...

Retention Index markers file

Analysis Parameters

Initial Background Time (min)		Analysis Time (min)		Methods		Tiered Search Limit	Chi^2 Min	Chi^2 delta (%)	Abs Threshold	BG Scalar
Begin	1.600	Begin	1.800	PIONA		3 Analytes	1.0000E-9	60.00	0.00050	1.5
End	1.800	End	32.000			Chromatogram Filter	Chi^2 Max	R^2 Limit	BG Threshold	RI window +/-
		Time Step	0.020			8071 Filters	1.0000E-1	0.4000	0.00025	25

Analyze | Load Parameters | Time Step Status | Save Parameters | Stop Analyzing



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Run File (*.db) or Directory: C:\Program Files\VUV Analytics\VUV Analyze 130 1953\Demos\D8071\Demo VUV-CS.db — Refresh

Retention Index Markers File

Reference Library File

PIONA compound absorbance spectra library

Report Method: C:\Program Files\VUV Analytics\VUV Analyze 130 1953\Demos\D8071\D8071-18 Report Method.VUV_RM — Refresh | Edit / Create ...

Analysis Parameters

Initial Background Time (min): Begin 1.600, End 1.800

Analysis Time (min): Begin 1.800, End 32.000, Time Step 0.020

Methods: PIONA

Tiered Search Limit: 3 Analytes

Chromatogram Filter: 8071 Filters

Chi^2 Min: 1.0000E-9

Chi^2 Max: 1.0000E-1

Chi^2 delta (%): 60.00

R^2 Limit: 0.4000

Abs Threshold: 0.00050

BG Threshold: 0.00025

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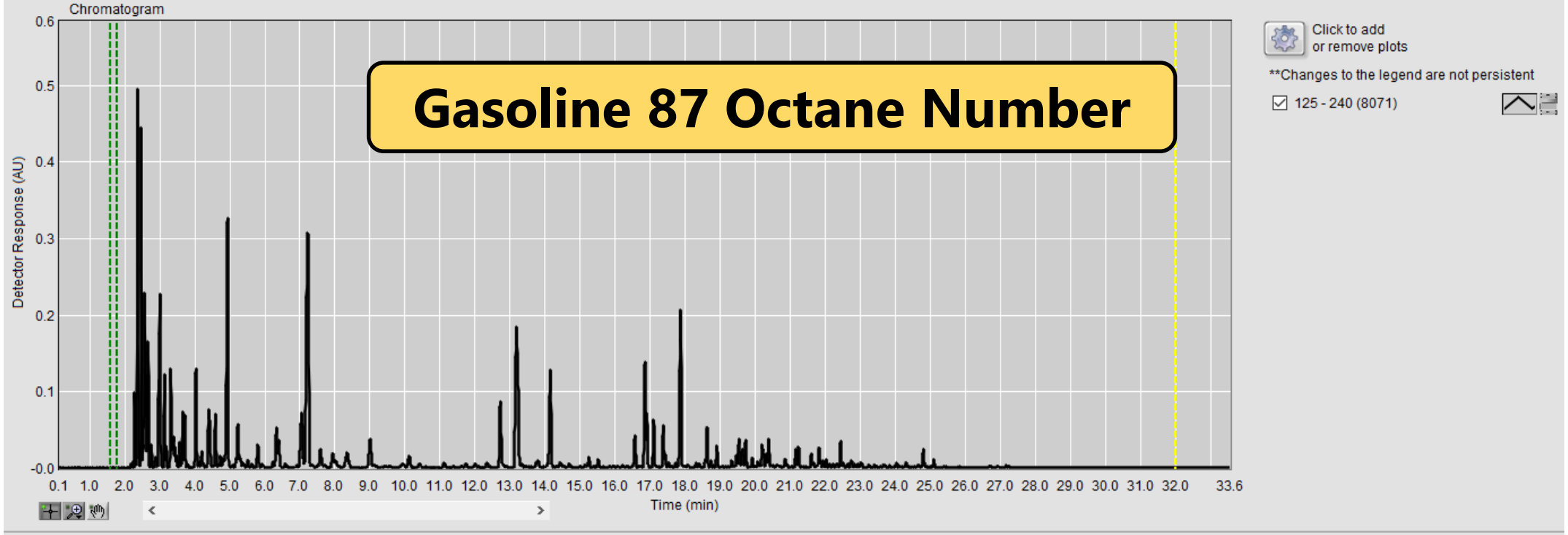
RI window +/-: 25

Analyze | Load Parameters | Time Step Status | Save Parameters | Stop Analyzing



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Run File (*.db) or Directory: C:\Program Files\VUV Analytics\VUV Analyze 130 1953\Demos\D8071\Demo VUV-CS.db — Refresh

Retention Index Markers File: C:\Program Files\VUV Analytics\VUV Analyze 130 1953\Demos\D8071\Demo VUV RI.txt — Refresh

Reference Library File: C:\Program Files\VUV Analytics\VUV Analyze 130 1953\Demos\VUV PIONA ASTM D8071 rev 1.1.0.db — Refresh

Report Method: PIONA report method — Refresh | Edit / Create ...

Analysis Parameters

Initial Background Time (min): Begin 1.600, End 1.800

Analysis Time (min): Begin 1.800, End 32.000, Time Step 0.020

Methods: PIONA

Tiered Search Limit: 3 Analytes

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Chi^2 Min: 1.0000E-9

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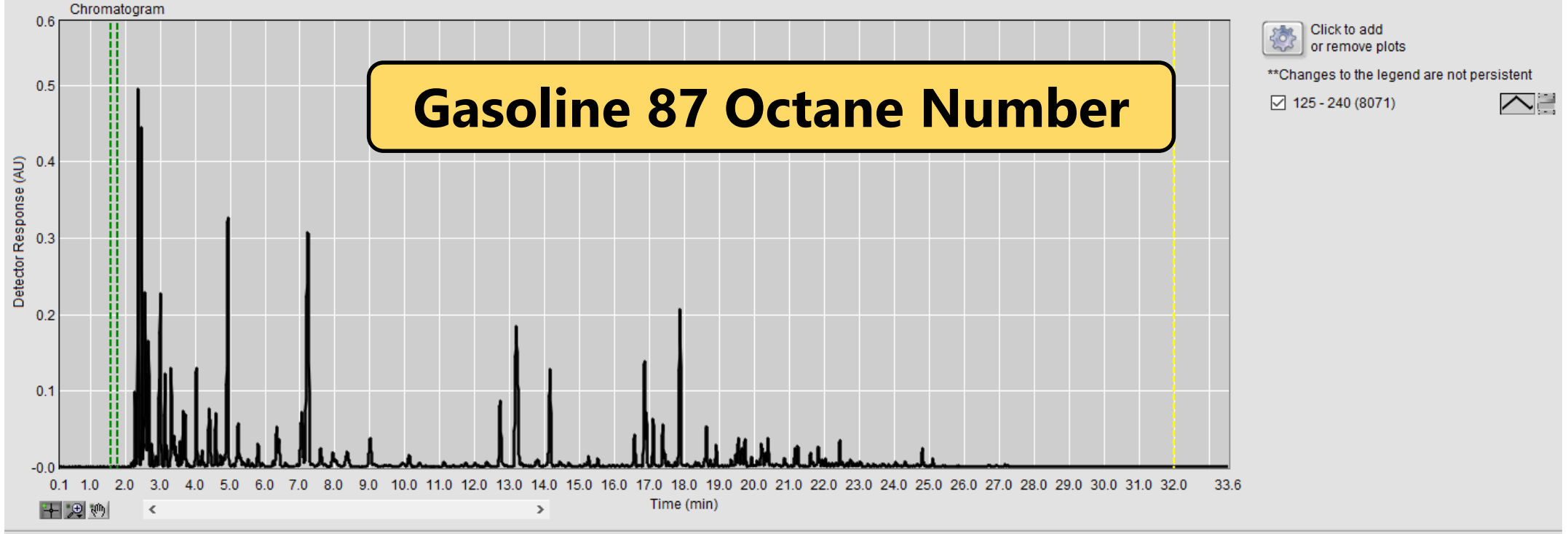
Analyze | Load Parameters | Time Step Status | Save Parameters | Stop Analyzing



Single File or Batch Processing

R & D | Results

Report File | View Report | Export to Excel

Input Files | Reverse Search | Create RI File | D8071 | Analytes to Include | Advanced | Spectra | Fit Info

Analytics\VUV Analyze 130 1953\Demos\D8071\Demo VUV-CS.db — Refresh

Analytics\VUV Analyze 130 1953\Demos\D8071\Demo VUV RI.txt — Refresh

Analytics\VUV Analyze 130 1953\Demos\VUV PIONA ASTM D8071 rev 1.1.0.db — Refresh

Report Method: C:\Program Files\VUV Analytics\VUV Analyze 130 1953\Demos\D8071\D8071-18 Report Method.VUV_RM — Refresh | Edit / Create ...

Analysis Parameters

Initial Background (min)
Begin 0.600
End 1.800

Analysis Time (min)
Begin 1.800
End 32.000
Time Step 0.020

Methods: PIONA

Tiered Search Limit: 3 Analytes
Chromatogram Filter: 8071 Filters

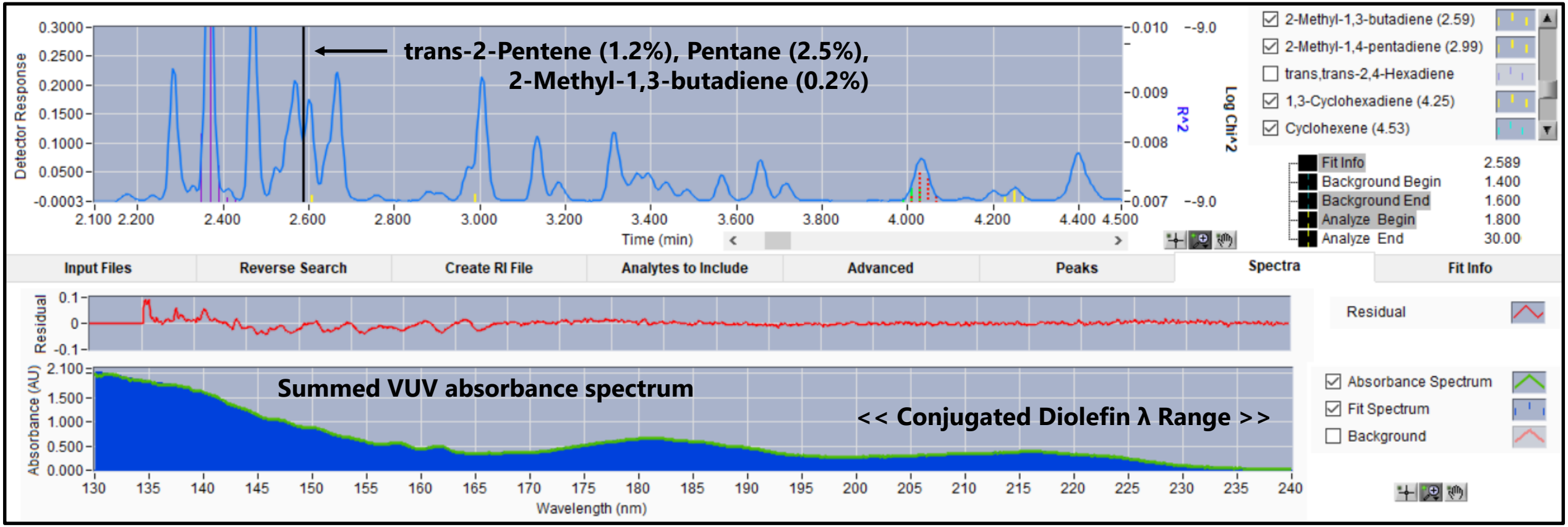
Chi^2 Min	Chi^2 delta (%)	Abs Threshold	BG Scalar
1.0000E-9	60.00	0.00050	1.5
Chi^2 Max	**R^2 Limit**	**BG Threshold**	**RI window +/-**
1.0000E-1	0.4000	0.00025	25

Analyze | Load Parameters | Time Step Status | Save Parameters | Stop Analyzing

Time Interval Deconvolution (TID)

- Alternative quantitation method using VUV Analyze™ software
- Chromatogram is divided into equal, small time intervals (typically <0.05 min)
- For each time interval, compare measured spectrum against reference spectra in designated library, best analyte(s) fit determined
- Can quickly be performed to measure total response per analyte for a chromatogram; this can be converted into a relative mass percentage and relative volume percentage

VUV Spectral Deconvolution of Hydrocarbons in Gasoline



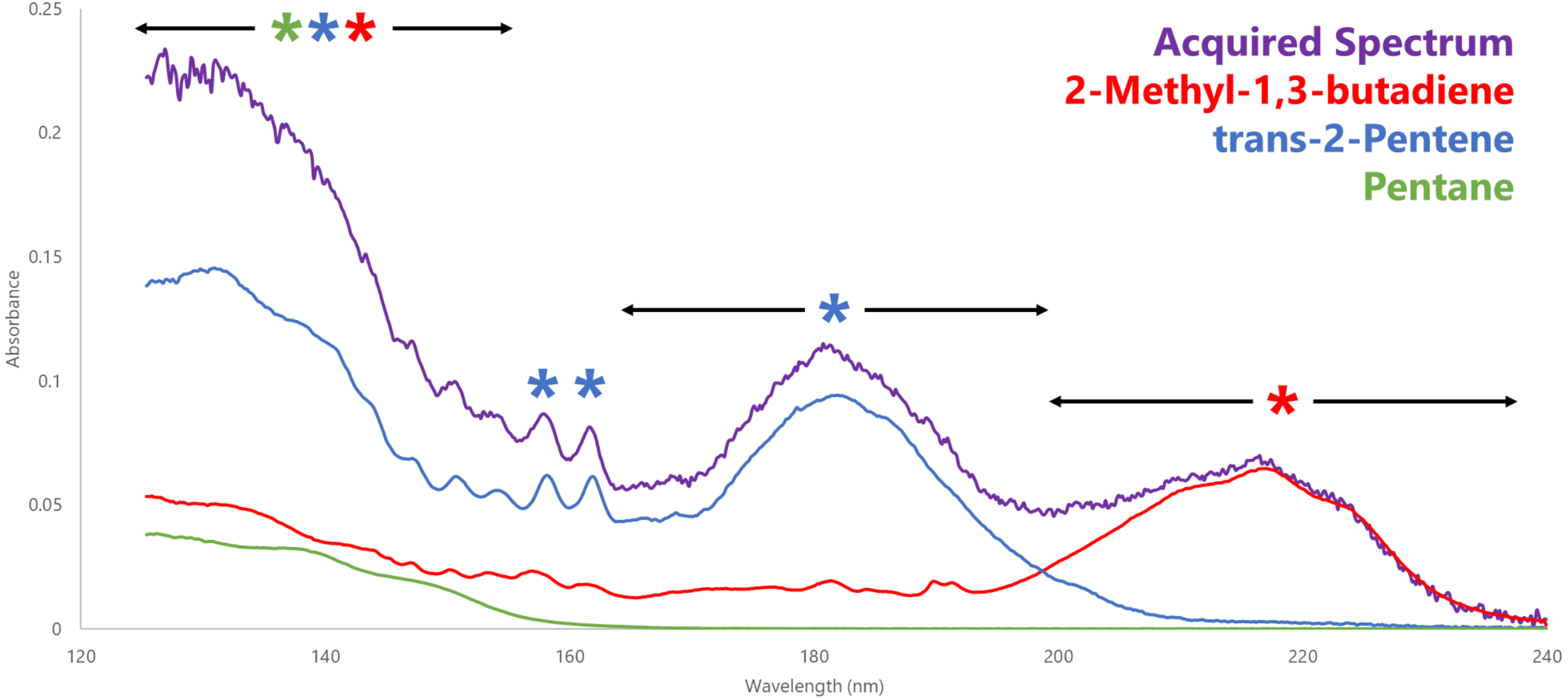
Chi^2 2
1.735E-4

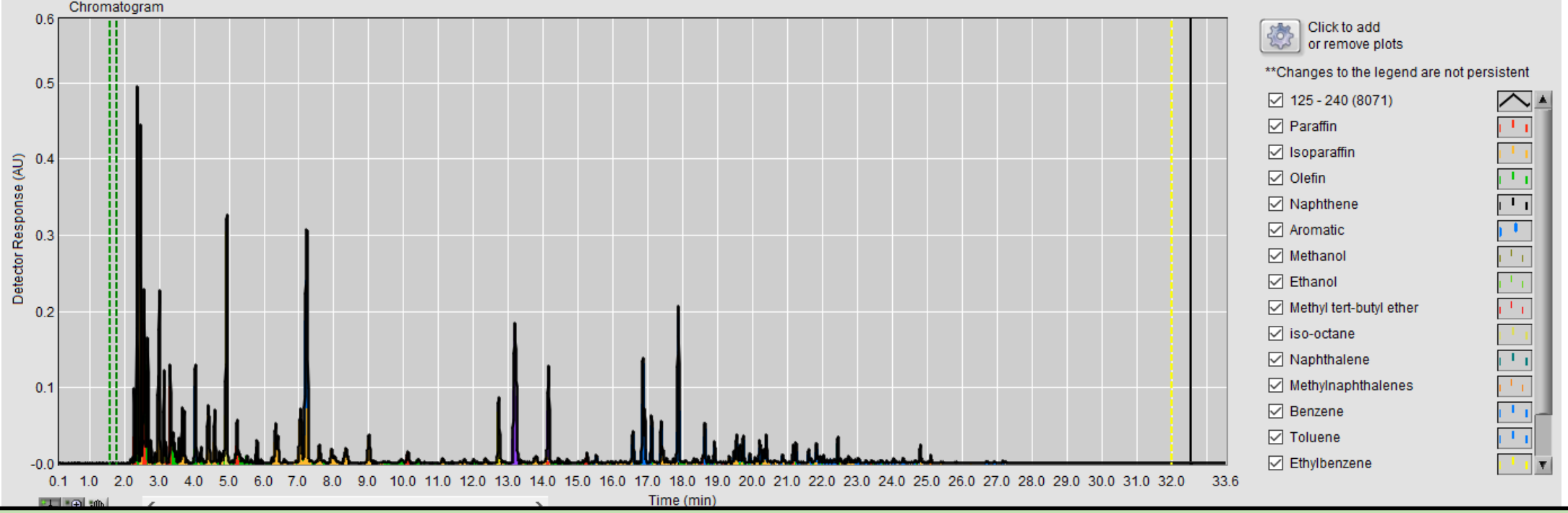
R^2
0.9992

Analyte Table

RRF Display	Analyte Name	Analyte Category	Fit Values	Spectra Ave.	Response	Area	Ret. Index
Olefin	trans-2-Pentene	Olefin	0.85770	0.35124	0.30126	0.001115	506.73599
Paraffin	Pentane	Linear alkane	0.96550	0.18176	0.17549	0.0006493	500.00000
2-Methyl-1,3-butadiene	2-Methyl-1,3-butadiene	Olefin	0.36569	0.45053	0.16476	0.0006096	503.70239

Spectral Deconvolution of Coeluting Hydrocarbons





Mass % Report for PIONA + Select Individual Hydrocarbons and Ethanol

Response | **Mass %** | **Volume %** | **Amount** | **Config**

	P	I	O	N	A
C1					
C2					
C3					
C4	1.2604	0.1114	0.0581		
C5	3.1375	6.7534	3.7404	0.1456	
C6	1.9858	7.3473	2.8238	1.6022	0.8250
C7	1.1744	5.6581	1.0126	2.2271	3.9218
C8	0.5486	18.1335	1.0130	1.6267	5.7333
C9	0.3854	2.8188	0.1990	1.3372	5.8269
C10	0.1992	0.8996	0.2441	0.7377	2.6590
C11	0.0894	0.6189	0.0679	0.4207	1.2177
C12	0.0385	0.1390	0.0232	0.0588	0.2667
C13		0.0514			0.0350
C14		0.0047			
C15					
C16					
C17					
C18					
C19					
Total	8.8192	42.5362	9.1821	8.1559	20.4855

Category	Mass %	RT (min.)	RRF	Density
Paraffin	8.8192			
Isoparaffin	42.5362			
Olefin	9.1821			
Naphthene	8.1559			
Aromatic	20.4855			
Methanol	0.0000			
Ethanol	10.8211	2.370	1.029	0.789
Methyl tert-butyl ether	0.0000			
iso-octane	7.5817	4.930	0.674	0.692
Naphthalene	0.1886	22.429	0.207	1.025
Methylnaphthalenes	0.2171	24.810	0.250	1, 1.010
Benzene	0.8250	4.029	0.258	0.879
Toluene	3.9218	7.209	0.267	0.867
Ethylbenzene	0.9860	12.730	0.284	0.867
Xylenes	4.7461	13.190	0.284	0.870

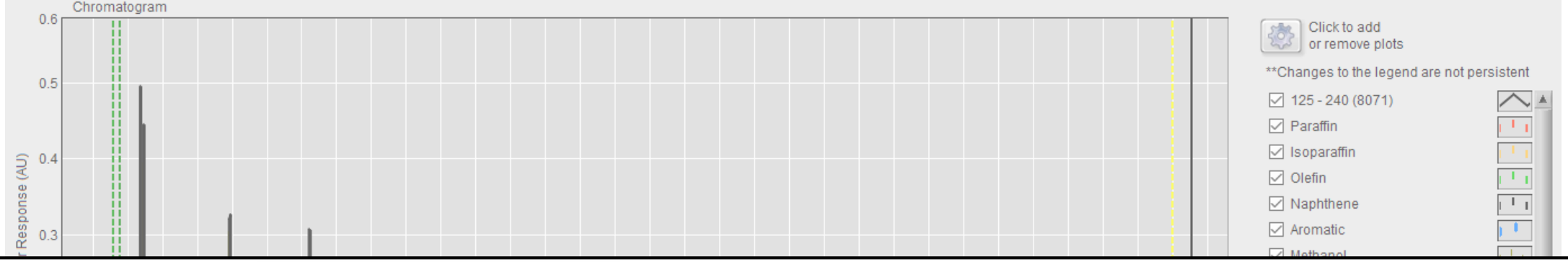
Area Rejected %
(Chi^2 Limit)
0.46

Negative Fit %
0.04

No. of Background
Time steps
215

Total No. of Time steps
1510

List Poor Fits



Response | **Mass %** | **Volume %** | **Amount** | **Config**

	P	I	O	N	A
C1					
C2					
C3					
C4	1.2604	0.1114	0.0581		
C5	3.1375	6.7534	3.7404	0.1456	
C6	1.9858	7.3473	2.8238	1.6022	0.8250
C7	1.1744	5.6581	1.0126	2.2271	3.9218
C8	0.5486	18.1335	1.0130	1.6267	5.7333
C9	0.3854	2.8188	0.1990	1.3372	5.8269
C10	0.1992	0.8996	0.2441	0.7377	2.6590
C11	0.0894	0.6189	0.0679	0.4207	1.2177
C12	0.0385	0.1390	0.0232	0.0588	0.2667
C13		0.0514			0.0350
C14		0.0047			
C15					
C16					
C17					
C18					
C19					
Total	8.8192	42.5362	9.1821	8.1559	20.4855

Category	Mass %	RT (min.)	RRF	Density
Paraffin	8.8192			
Isoparaffin	42.5362			
Olefin	9.1821			
Naphthene	8.1559			
Aromatic	20.4855			
Methanol	0.0000			
Ethanol	10.8211	2.370	1.029	0.789
Methyl tert-butyl ether	0.0000			
iso-octane	7.5817	4.930	0.674	0.692
Naphthalene	0.1886	22.429	0.207	1.025
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Xylenes	4.7461	13.190	0.284	0.870

C17
C18
C19
Total 8.8192 42.5362 9.1821 8.1559 20.4855

List Poor Fits

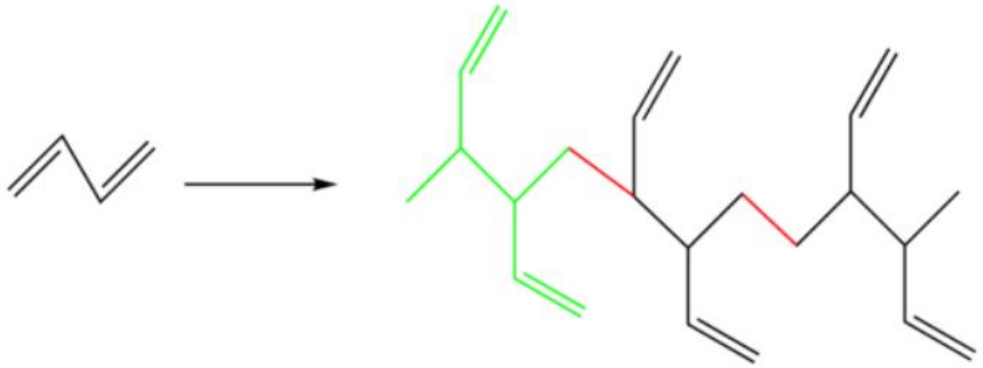
Conjugated Diolefin Analysis by GC-VUV

Putting the “+” in PIONA+™

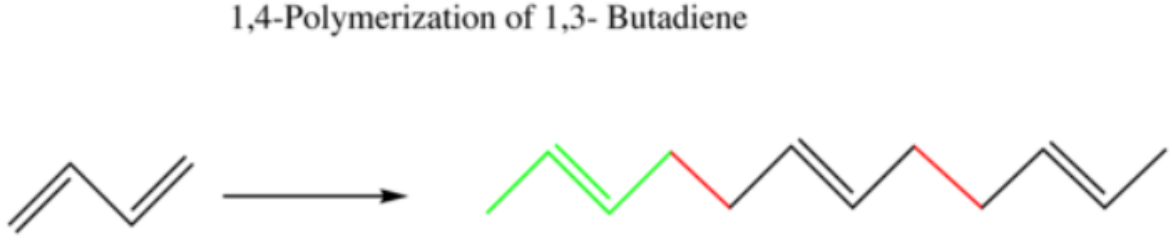
The Trouble with Conjugated Diolefins (CDOs)

- Easily polymerize in high enough concentrations
  - Used in synthesis of rubber and other polymers
- Polymers can foul hydrocarbon streams of petrochemical refineries
- CDO levels must be kept below a threshold to prevent polymerization

1,2-Polymerization of 1,3- Butadiene



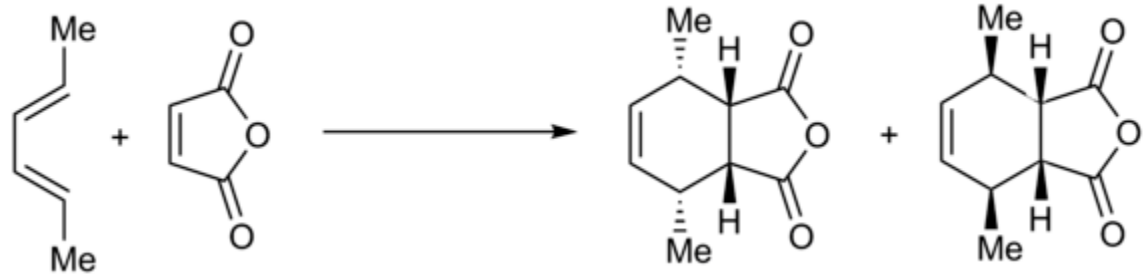
1,4-Polymerization of 1,3- Butadiene



https://chem.libretexts.org/Textbook_Maps/Organic_Chemistry/Supplemental_Modules_(Organic_Chemistry)/Conjugation/Polymerization_of_Conjugated_Dienes

UOP-326: Maleic Anhydride Method

- Common method for determining diene content in lighter hydrocarbon mixtures
- Maleic anhydride consumed via Diels-Alder reaction with dienes; remaining maleic anhydride converted to maleic acid, which is measured by colorimetric titration



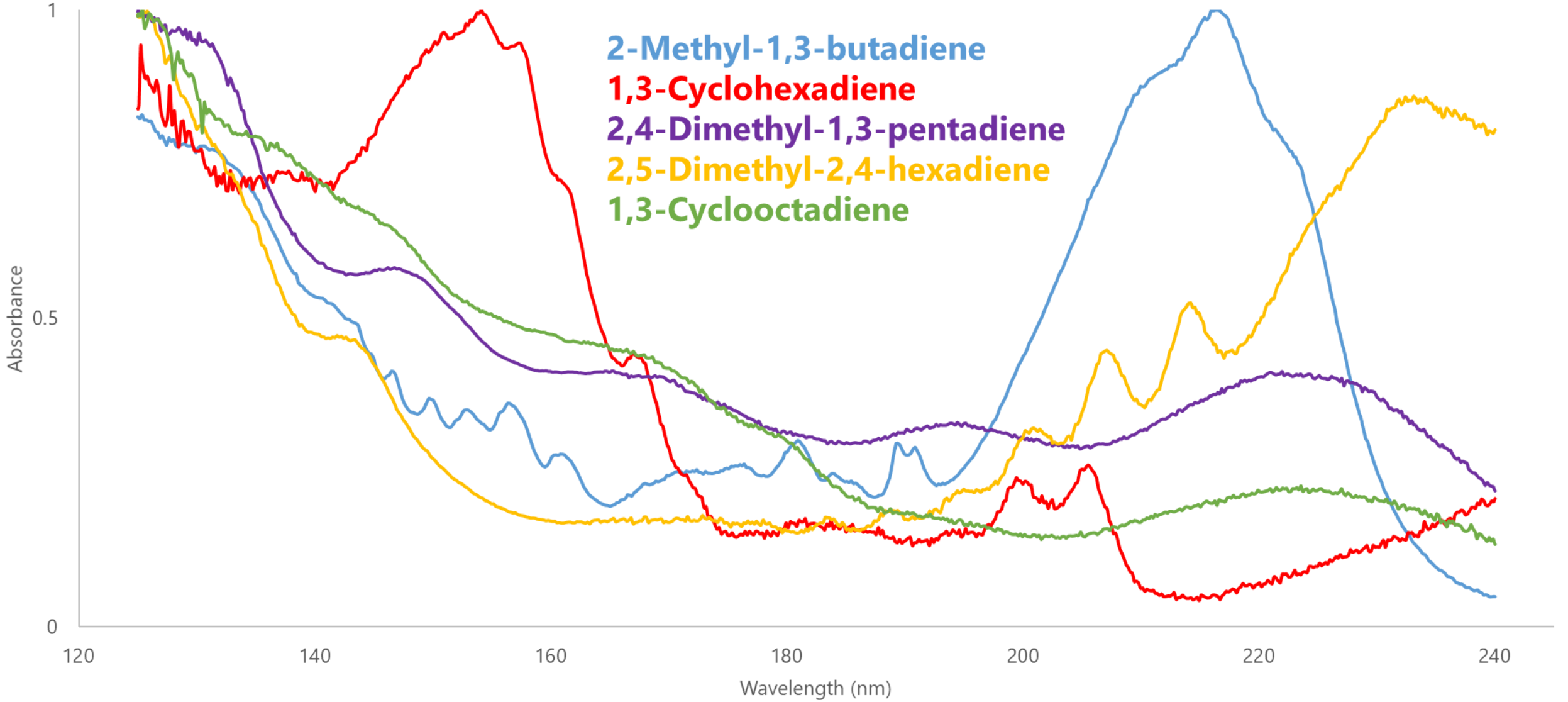
Andrade, et al. *Fuel* 89 (2010)

Drawbacks of Using Maleic Anhydride

- >3-hour analysis time (both manual and automated)
- Nucleophiles (e.g. alcohols, thiols) will also react with maleic anhydride; high diene values reported for samples containing MeOH and EtOH
- Some sterically-hindered dienes (e.g. 2,5-dimethyl-2,4-hexadiene) will not react
- Only semiquantitative, as reaction is not selective
- No qualitative information (i.e. identification of diolefin species)

Andrade, et al. *Fuel* 89 (2010)

VUV Absorbance Spectra for Conjugated Diolefins



Conjugated Diolefin Run Conditions

- Agilent 6890 GC
  - 1 µL injection
  - Inlet: 250°C, split 300:1
  - Column: Restek Rxi-1ms (30 m x 0.25 mm, 0.25-µm)
  - Flow: 1 mL/min helium, constant flow
  - Oven: 35°C, hold 10 min; 7°C/min to 200°C (run time – 33.6 min)

- VUV Analytics VGA-100
  - Makeup gas: 0.40 psi N_2
  - Flow cell and transfer line: 275°C
  - Acquisition rate: 4.5 spectra/sec
  - Acquisition range: 125-240 nm

Conjugated Diolefin Run Conditions

- Agilent 6890 GC
  - 1 µL injection
  - Inlet: 250°C, split 300:1
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  - Flow: 1 mL/min helium, constant flow
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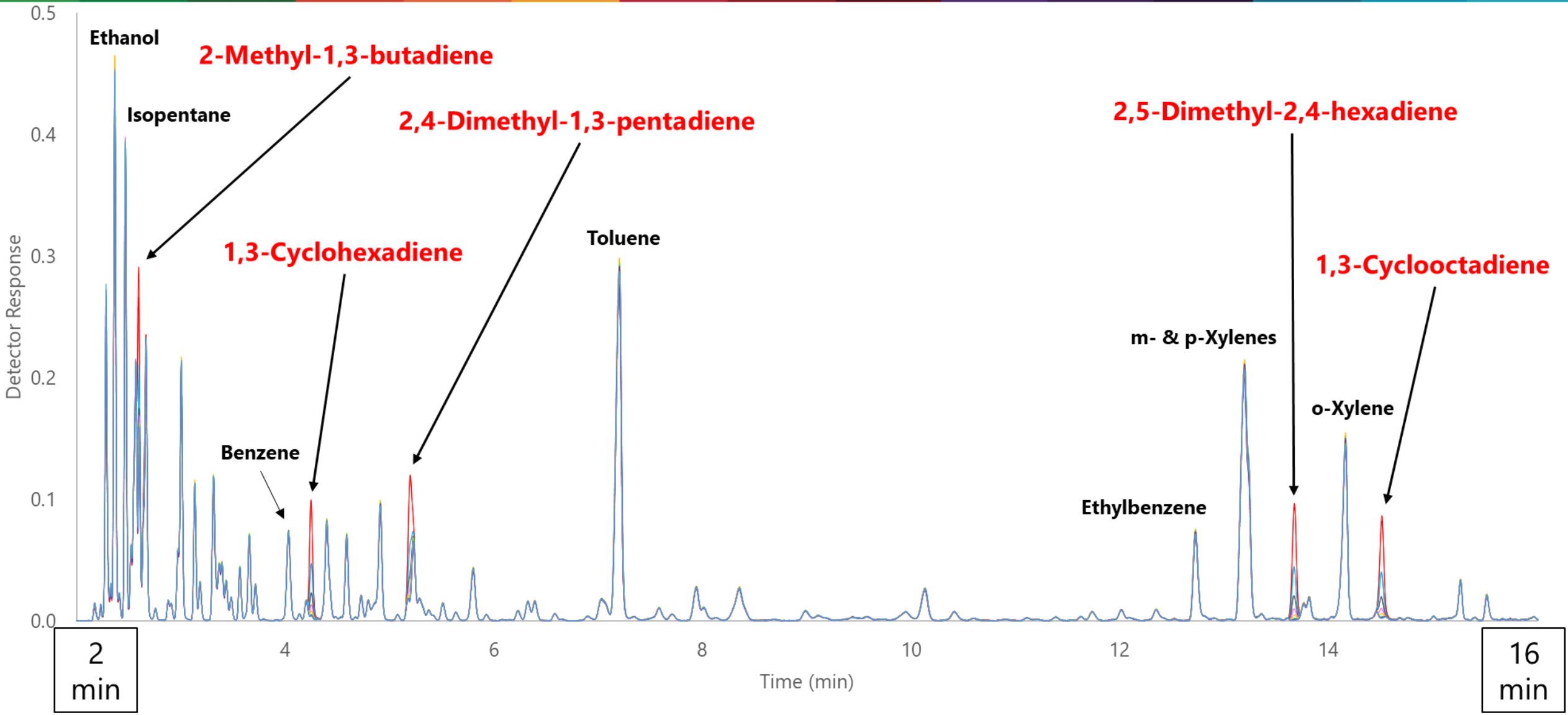
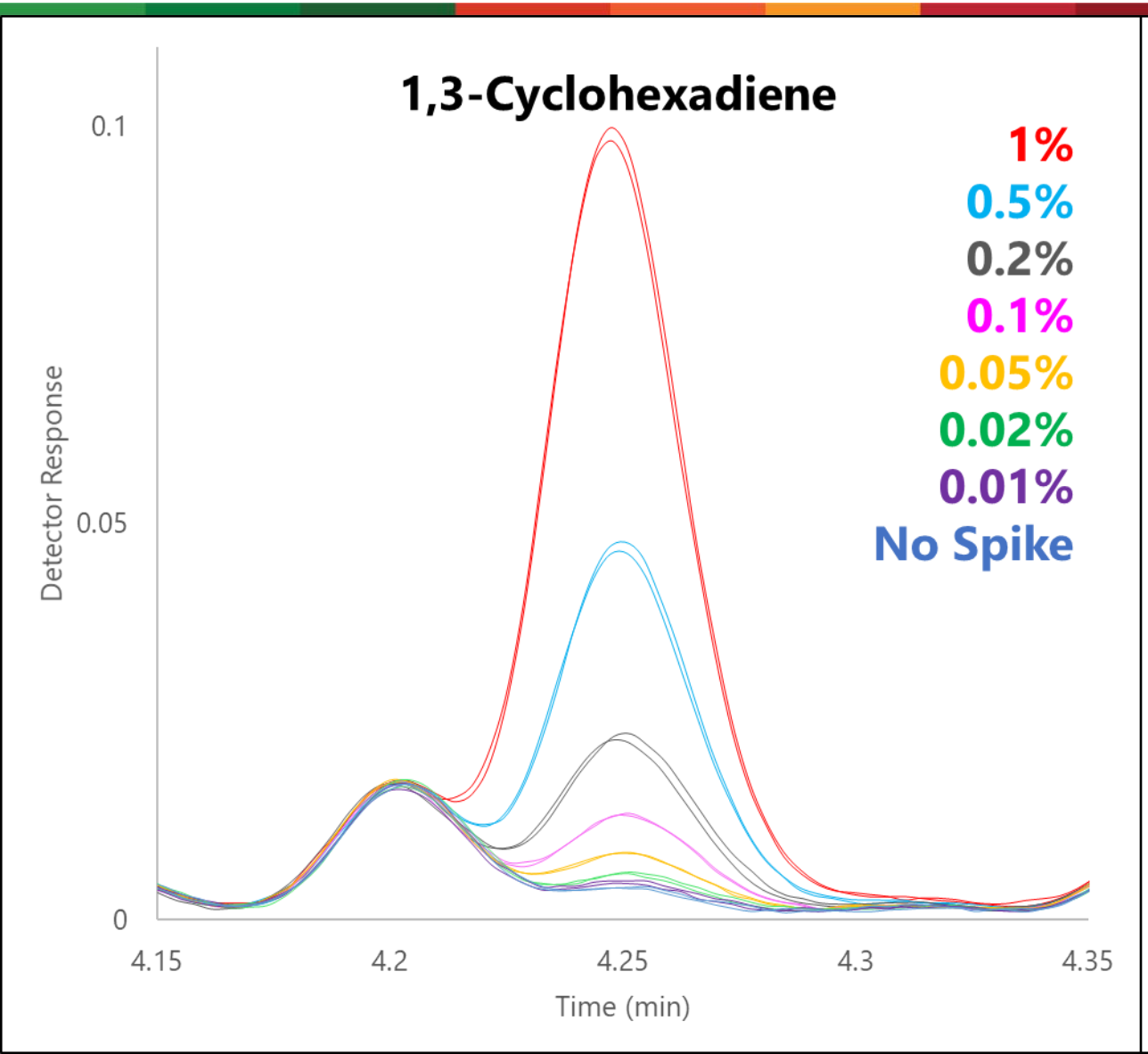
- VUV Analytics VGA-100
  - Make up gas: 0.40 psi N_2
  - Flow cell and transfer line: 275°C
  - Acquisition rate: 4.5 spectra/sec
  - Acquisition range: 125-240 nm

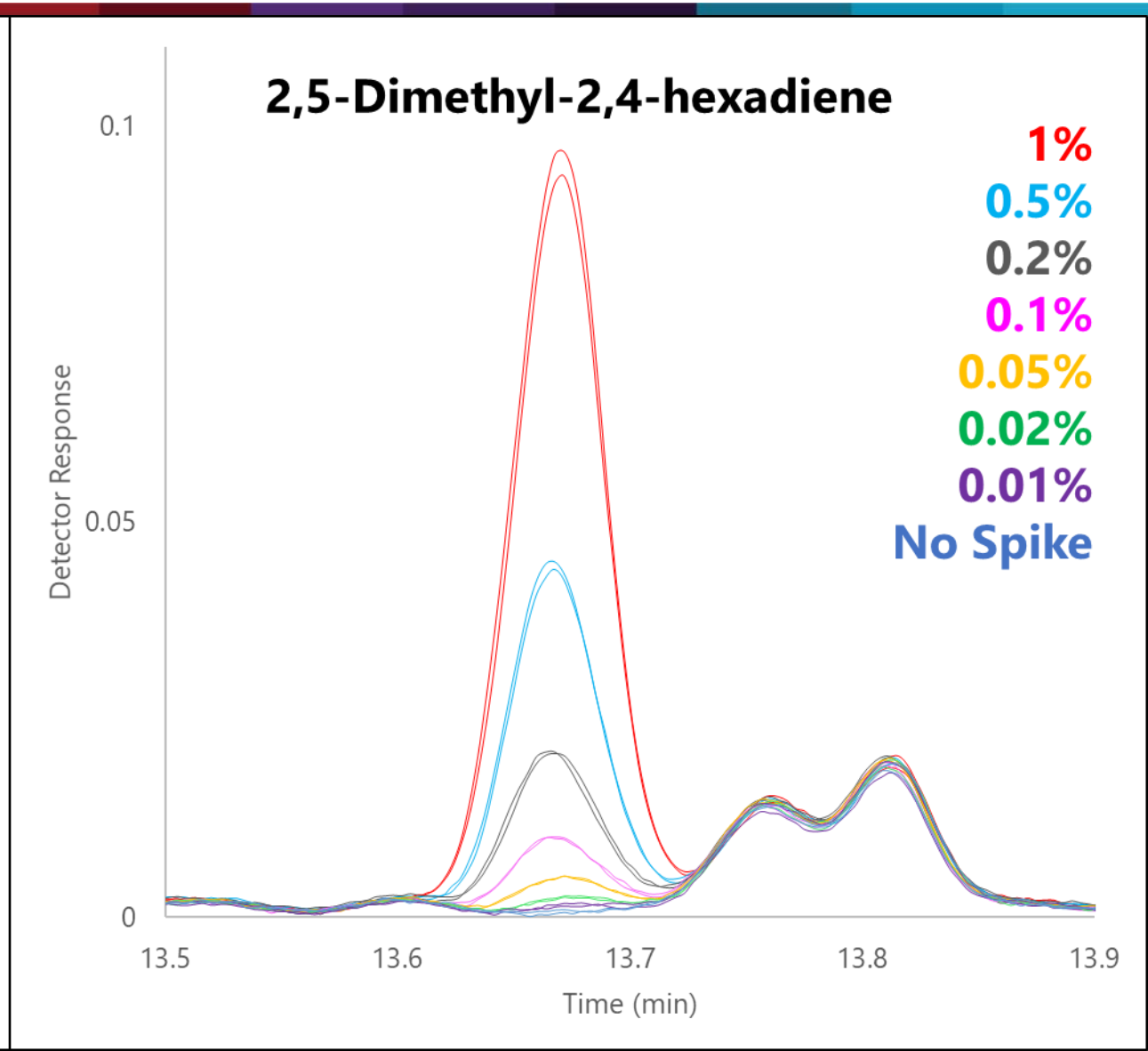
SAME METHOD AS ASTM D8071!

Gasoline Spiked with 0-1% Conjugated Diolefins



Spiked Gasoline Overlays: 0-1% CDOs



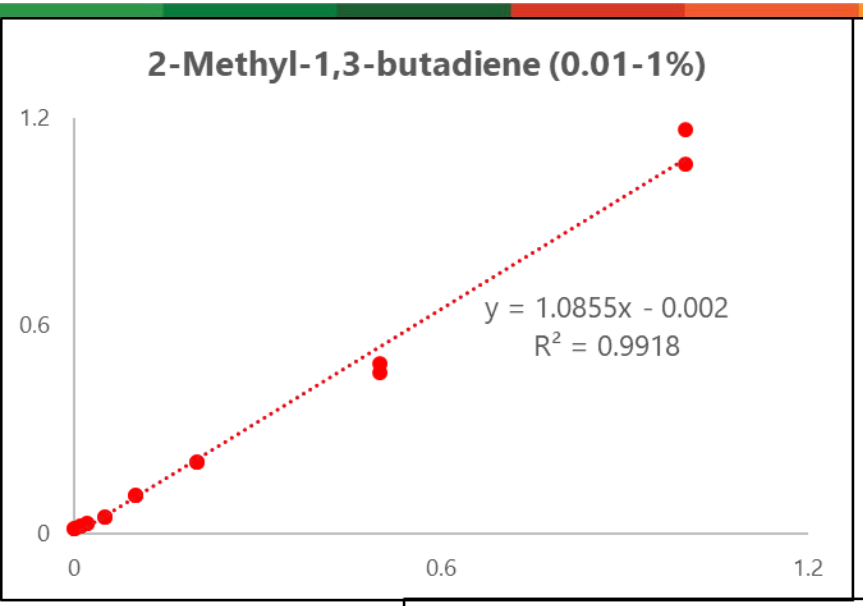


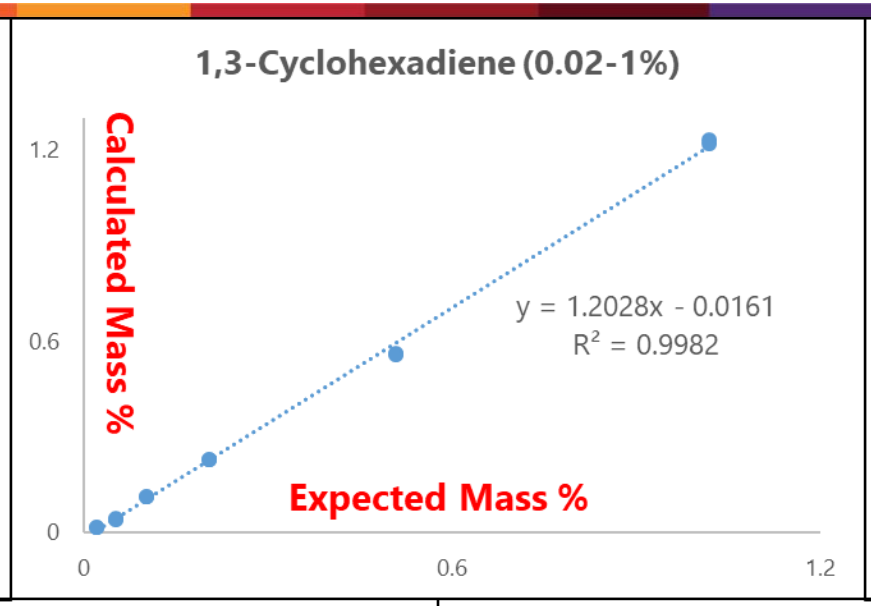
Quantitative Analysis of CDO-Spiked Gasoline

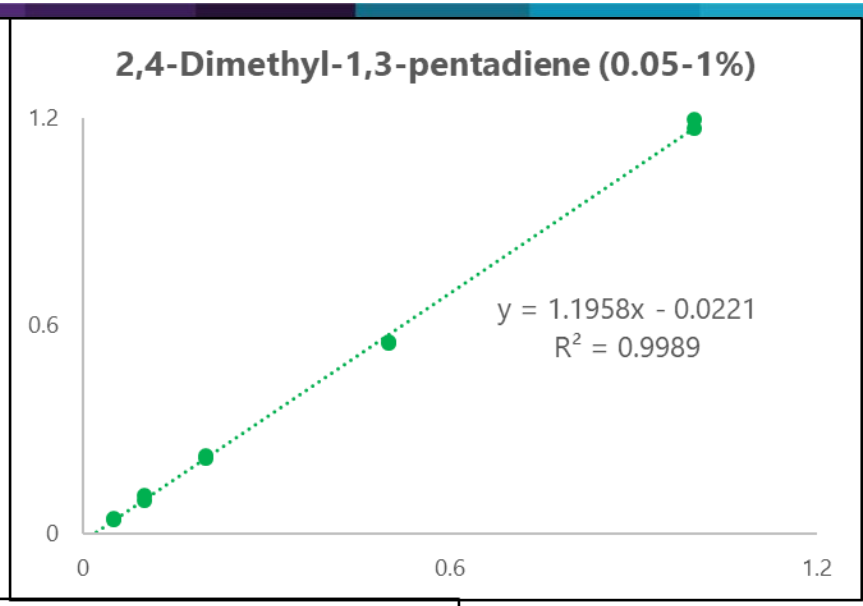
2-Methyl-1,3-butadiene		1,3-Cyclohexadiene		2,4-Dimethyl-1,3-pentadiene		2,5-Dimethyl-2,4-hexadiene		1,3-Cyclooctadiene	
Expected Conc	Measured Conc	Expected Conc	Measured Conc	Expected Conc	Measured Conc	Expected Conc	Measured Conc	Expected Conc	Measured Conc
0	0.015	0	-	0	-	0	-	0	-
0.010	0.022	0.010	-	0.010	-	0.010	-	0.010	-
0.020	0.029	0.020	0.019	0.020	-	0.020	-	0.020	-
0.050	0.047	0.051	0.044	0.050	0.042	0.051	0.048	0.050	0.028
0.10	0.11	0.10	0.12	0.10	0.10	0.10	0.11	0.10	0.099
0.20	0.21	0.20	0.23	0.20	0.22	0.20	0.22	0.20	0.24
0.50	0.48	0.51	0.56	0.50	0.55	0.51	0.52	0.50	0.58
1.0	1.1	1.0	1.2	1.0	1.2	1.0	1.1	1.0	1.3

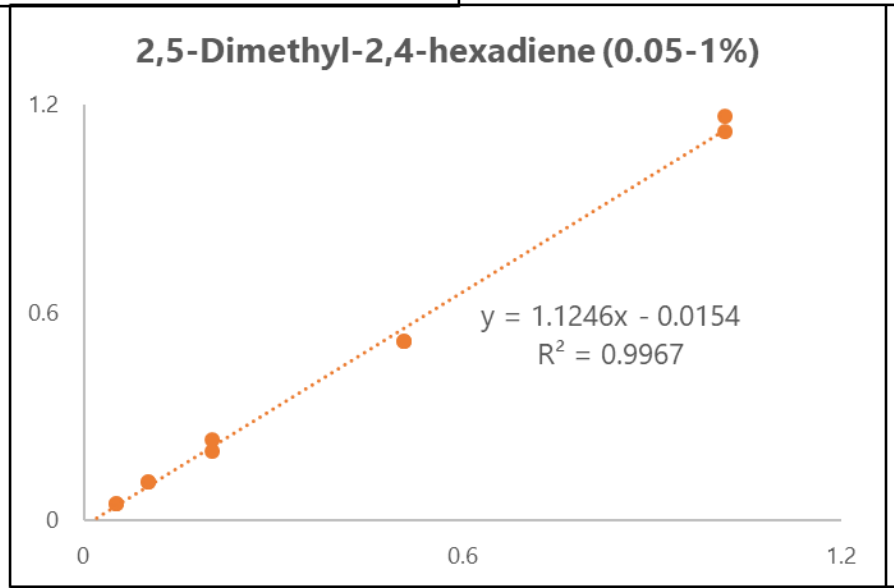
*All concentrations in mass %

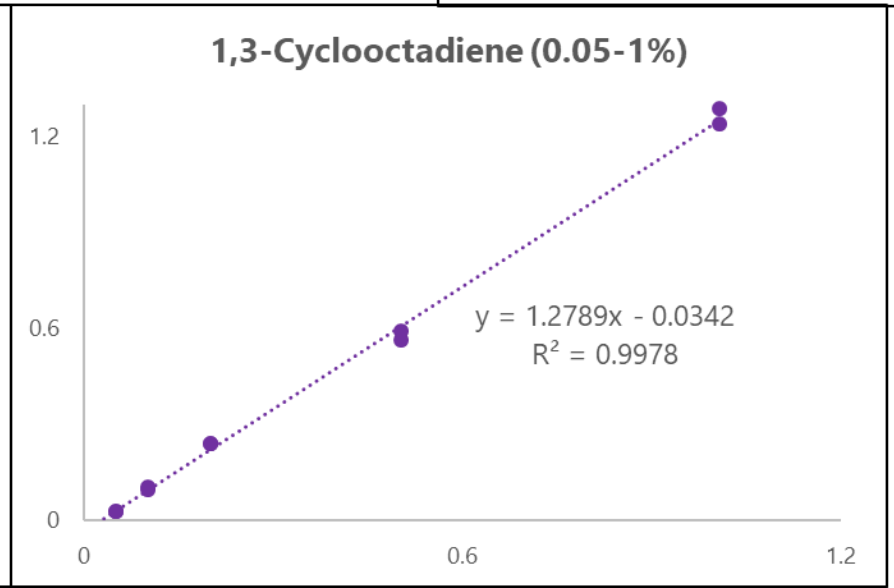
Linearity for Conjugated Diolefins in Gasoline









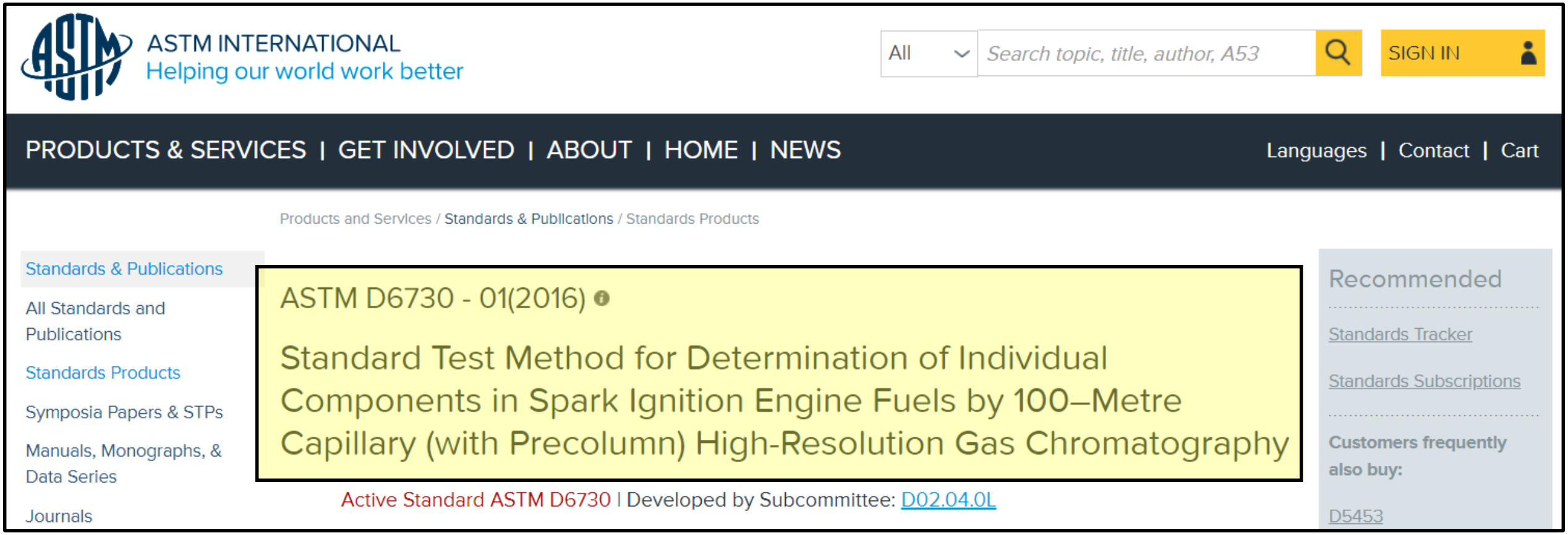


VUV ANALYTICS

VUV Verified™ Hydrocarbon Analysis (VHA™)

Detailed Hydrocarbon Analysis with GC-VUV

The Starting Point for VUV VHA – ASTM D6730



Strategy for Prototype DHA (VHA) with GC-VUV

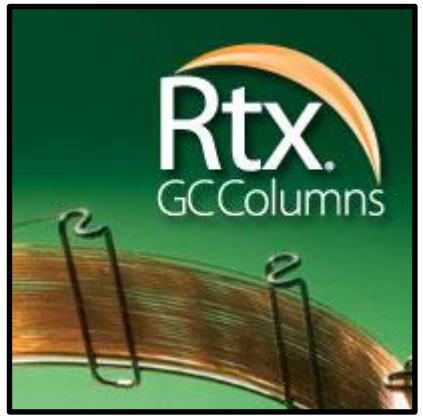
- Use ASTM D6730 GC conditions
  - 100m x 0.25mm x 0.50µm "methyl silicone" GC column
  - Exception; ***no precolumn*** for critical separations
  - Cryogenic oven start (5°C)
- Build VUV VHA gasoline compound retention time table using D6730 DHA Component Table
  - Starting with higher mass % compounds in gasoline
- Use VUV Analyze software for automated data processing
  - "Analytes to Include"
  - Time Interval Deconvolution

VUV ANALYTICS

GC Conditions – VUV VHA

- Agilent 6890 GC

- Precision 4mm Split liner with Wool (Restek)
- 250°C, 1 µL
- Split ratio 300:1



- 100m x 0.25mm x 0.50µm Rtx-DHA GC Column (Restek)
- Helium 40 psi (constant pressure)
- 5°C (10 min), 5°C/min to 50°C (50 min), 1.5°C/min to 200°C (5 min)
- **Run time: 174 min**

VUV Spectrometer Conditions – VUV VHA

- VUV Analytics VGA-100
- Transfer line temperature: 275°C
- Flow cell temperature: 275°C
- Makeup gas pressure: 0.25 psi
- Acquisition range: 125 to 240 nm
- Acquisition rate: 4 spectra/sec

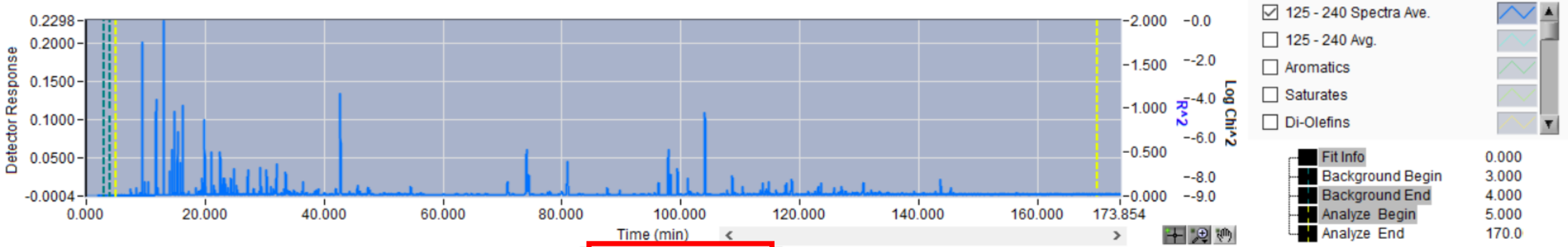
VUV PIONA+™ v1.1.1 (1905)

Status: Reference Library: C:\Users\Jack Cochran\Documents\VUV Data\D6730 20180224\VUV Analyze Files D6730\VUV IIb D6730 20180224.db
Last Mod Date: 2018/02/23 14:16:24

Current Run File: C:\Users\Jack Cochran\Documents\VUV Data\D6730 20180224\PONA VI and VII\Data Files\VUV1 D6730 0223 054 08 25 22.db

ENGR Mode

Production | **Analyze** | **Results**



Input Files | **Reverse Search** | **Create RI File** | **Analytes to Include** | **Advanced** | **Peaks** | **Spectra** | **Fit Info**

Name	Include in the...	Start time (min)	End time (min)	Use during
Butane	List of possible analytes	9.22	9.62	Only during time range
iso-pentane	List of possible analytes	12.83	13.23	Only during time range
1-Pentene	List of possible analytes	13.81	14.21	Only during time range
2-Methyl-1-butene	List of possible analytes	14.28	14.68	Only during time range
Pentane	List of possible analytes	14.57	14.97	Only during time range
trans-2-Pentene	List of possible analytes	15.14	15.54	Only during time range

Analysis Parameters

Initial Background Time (min): Begin 3.000, End 4.000

Analysis Time (min): Begin 5.000, End 170.000, Time Step 0.020

Methods: PIONA, Oxygenates, DHA

Tiered Search Limit: 3 Analytes

Chromatogram Filter: 140 - 160

Chi^2 Min: 1.0000E-9

Chi^2 Max: 1.0000E-1

Chi^2 delta (%): 40

R^2 Limit: 0.8000

Abs Threshold: 0.0010

BG Threshold: 0.0003

Use Peak Detection
- Analyze Spectra Within Peaks
- Use Initial Background Time

RI window +/-: 25

Analyze | **Load Parameters** | **Save Parameters** | **Stop Analyzing**

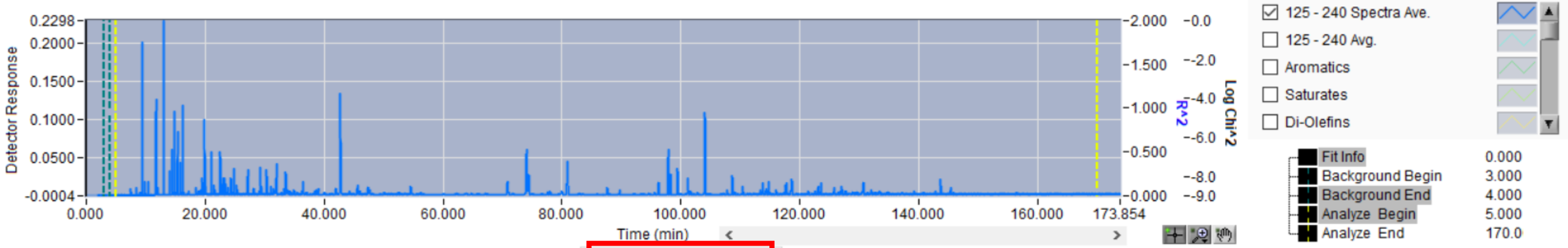
VUV PIONA+™ v1.1.1 (1905)

Status: Reference Library: C:\Users\Jack Cochran\Documents\VUV Data\D6730 20180224\VUV Analyze Files D6730\VUV IIb D6730 20180224.db
Last Mod Date: 2018/02/23 14:16:24

Current Run File: C:\Users\Jack Cochran\Documents\VUV Data\D6730 20180224\PONA VI and VII\Data Files\VUV1 D6730 0223 054 08 25 22.db

ENGR Mode

Production | **Analyze** | **Results**



Input Files | **Reverse Search** | **Create RI File** | **Analytes to Include** | **Advanced** | **Peaks** | **Spectra** | **Fit Info**

Name	Include in the...	Start time (min)	End time (min)	Use during
1,2-Dimethyl-3-ethylbenzene	List of possible analytes	121.22	121.62	Only during time range
1,2,4,5-Tetramethylbenzene	List of possible analytes	122.91	123.31	Only during time range
1,2,3,5-Tetramethylbenzene	List of possible analytes	123.36	123.76	Only during time range
Naphthalene	List of possible analytes	130.49	130.89	Only during time range
2-Methylnaphthalene	List of possible analytes	143.47	143.87	Only during time range
1-Methylnaphthalene	List of possible analytes	145.15	145.55	Only during time range

Analysis Parameters

Initial Background Time (min): Begin 3.000, End 4.000

Analysis Time (min): Begin 5.000, End 170.000, Time Step 0.020

Methods: PIONA, Oxygenates, DHA

Tiered Search Limit: 3 Analytes

Chromatogram Filter: 140 - 160

Chi^2 Min: 1.0000E-9

Chi^2 Max: 1.0000E-1

Chi^2 delta (%): 40

R^2 Limit: 0.8000

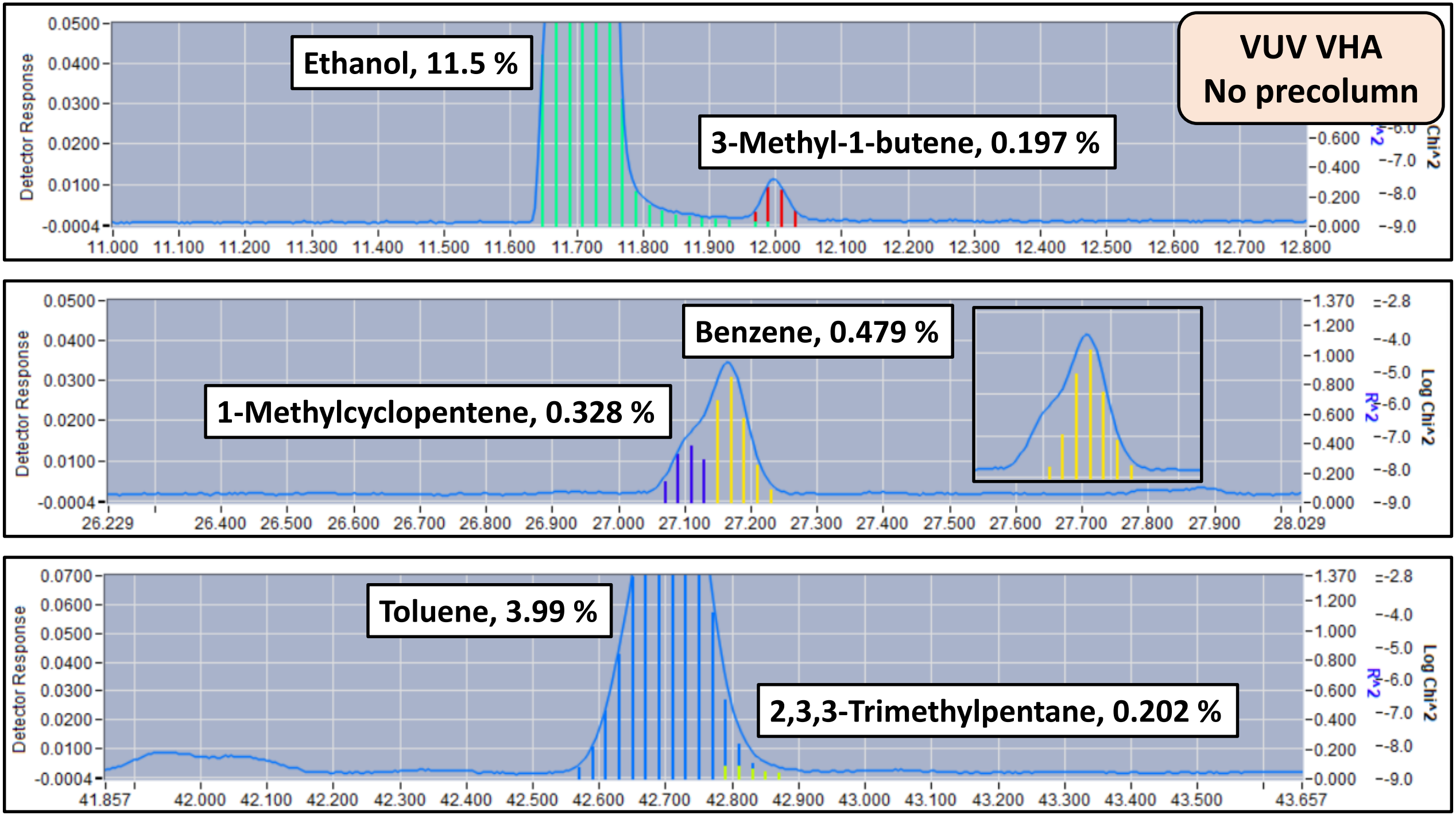
Abs Threshold: 0.0010

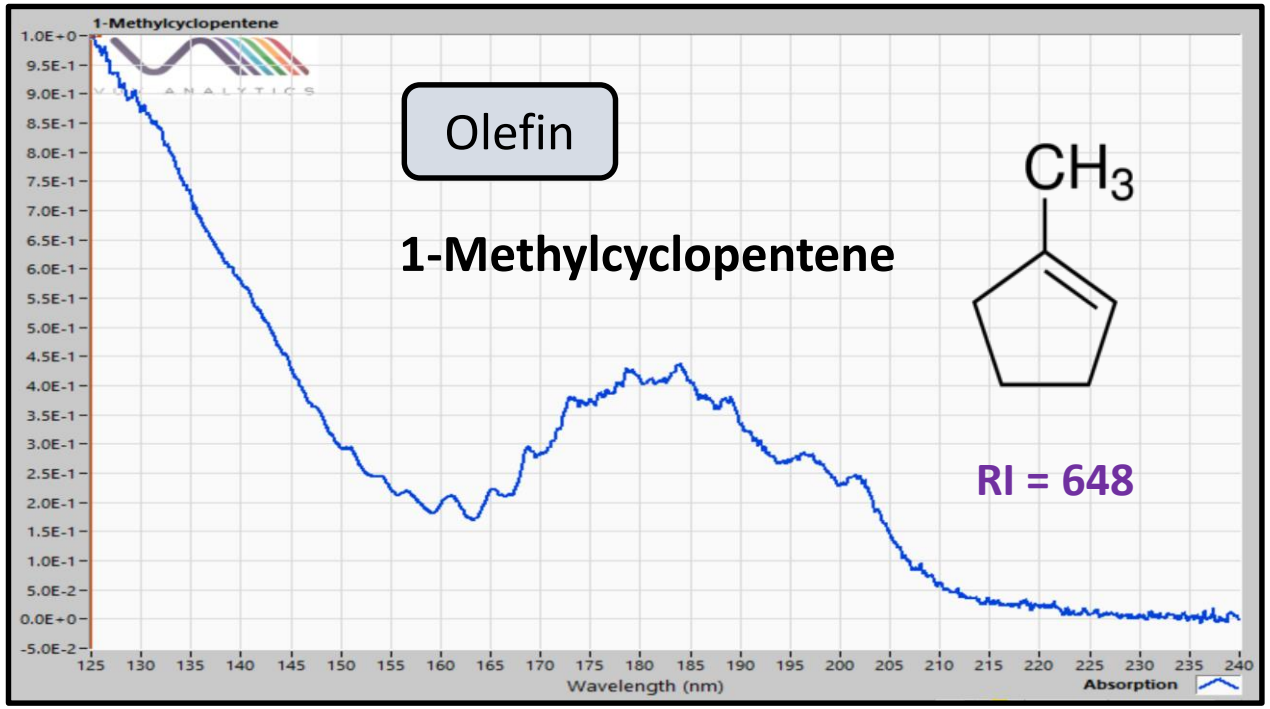
BG Threshold: 0.0003

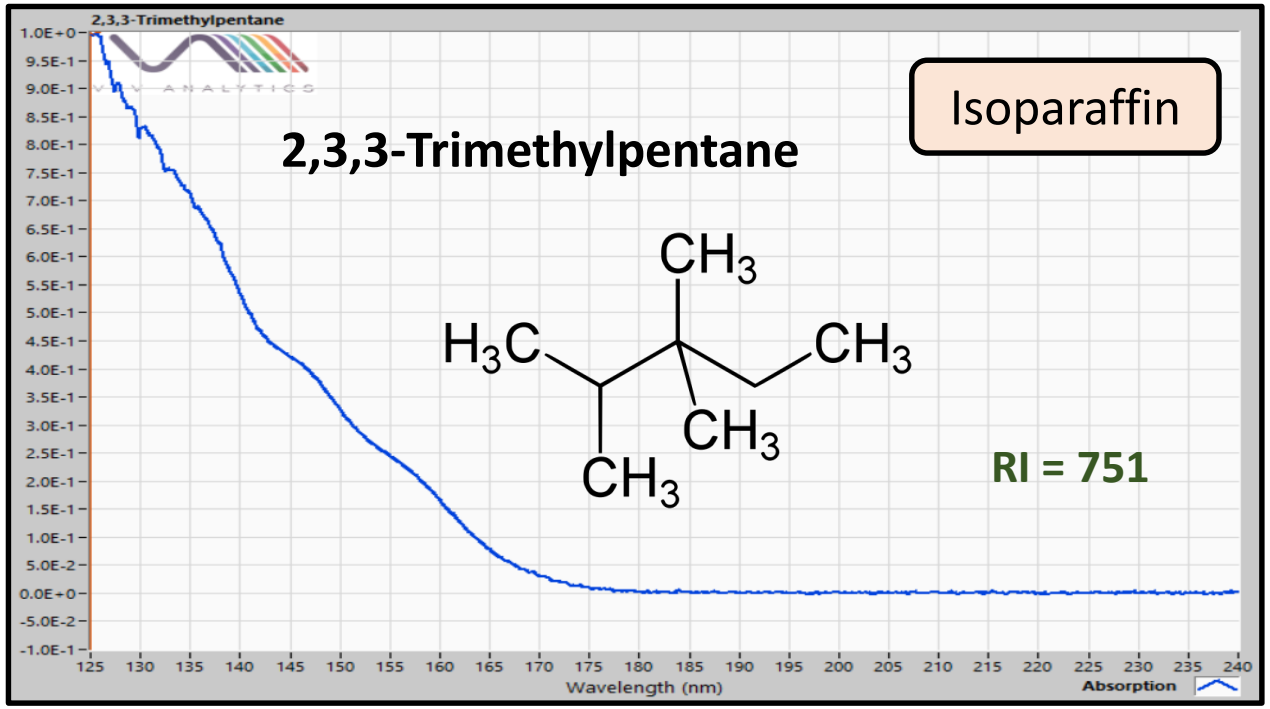
Use Peak Detection
- Analyze Spectra Within Peaks
- Use Initial Background Time

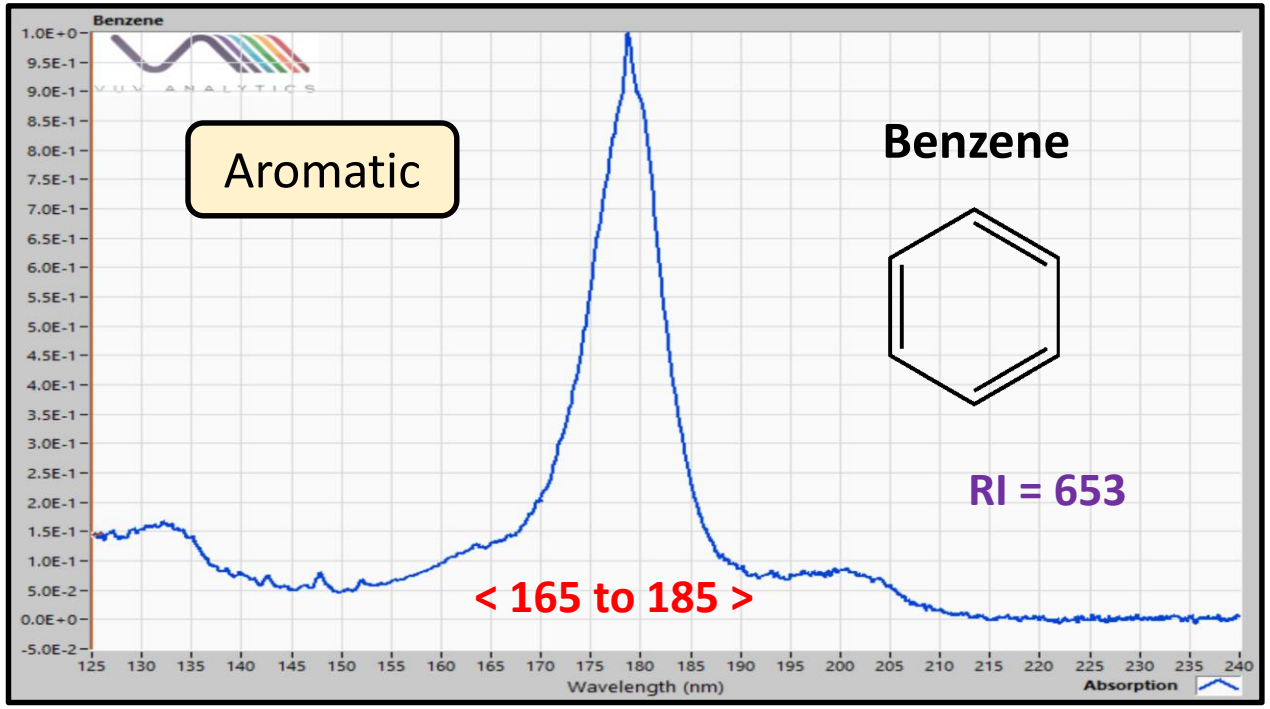
RI window +/-: 25

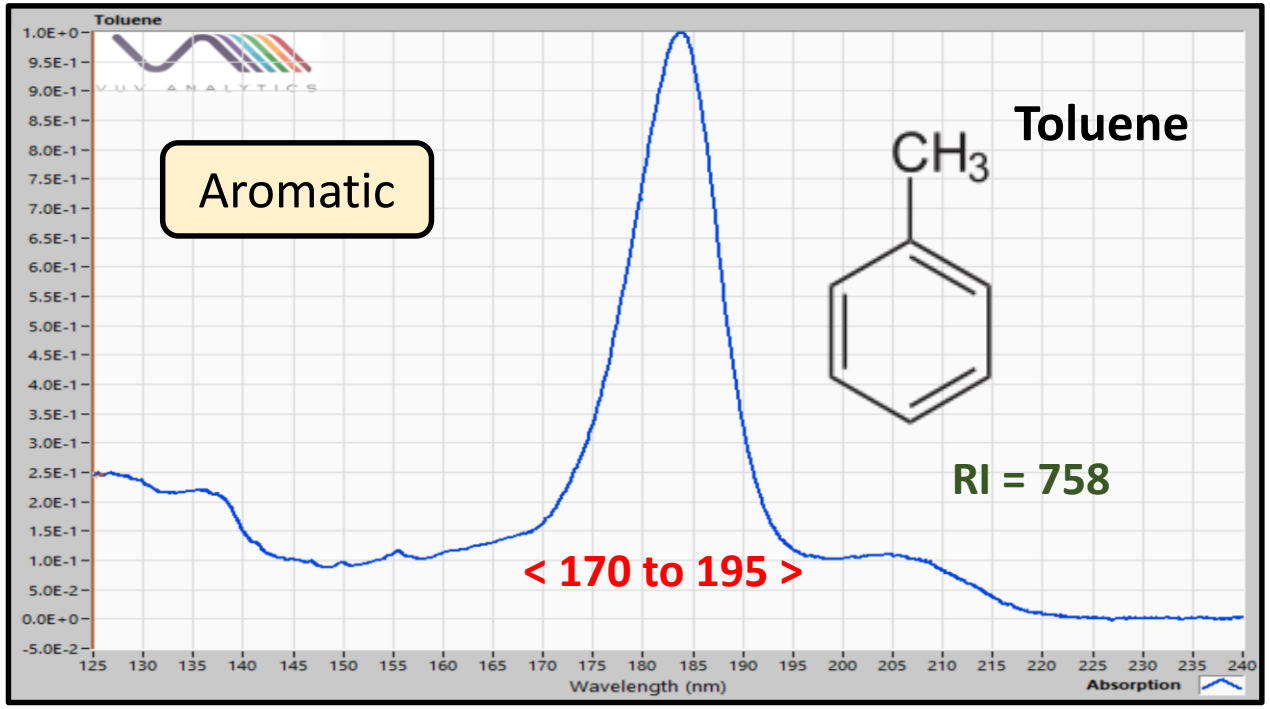
Analyze | **Load Parameters** | **Save Parameters** | **Stop Analyzing**


VUV VHA
No precolumn
Ethanol, 11.5 %
3-Methyl-1-butene, 0.197 %
Benzene, 0.479 %
1-Methylcyclopentene, 0.328 %
Toluene, 3.99 %
2,3,3-Trimethylpentane, 0.202 %
Detector Response
Log Chi^2
R^2


1-Methylcyclopentene
Olefin
1-Methylcyclopentene
CH3
RI = 648
Wavelength (nm)
Absorption


2,3,3-Trimethylpentane
Isoparaffin
2,3,3-Trimethylpentane
CH3
H3C
CH3
CH3
CH3
RI = 751
Wavelength (nm)
Absorption

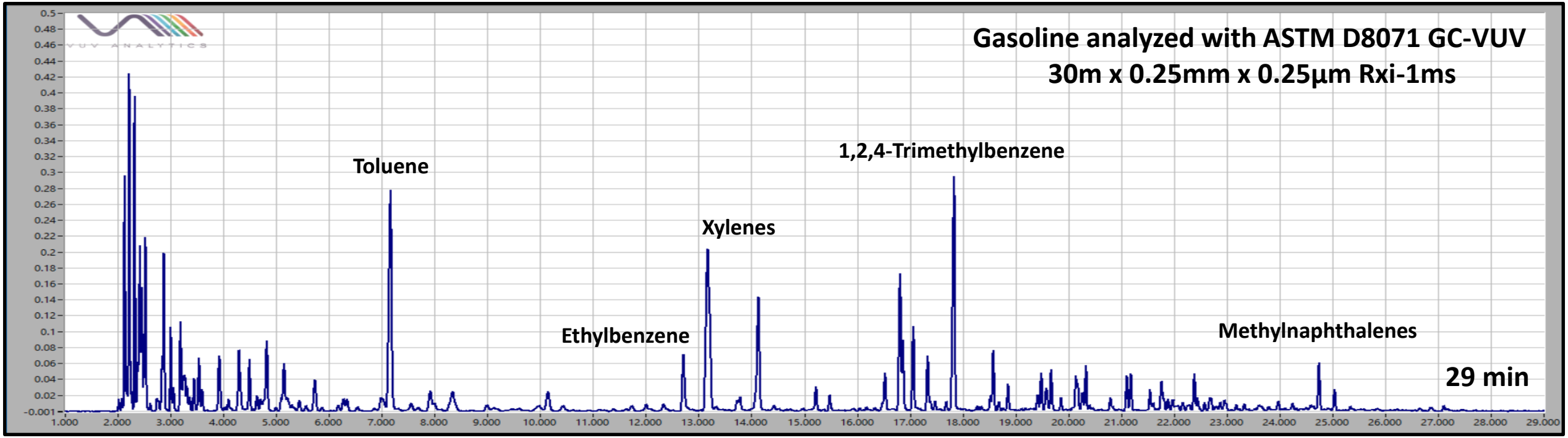

Benzene
Aromatic
Benzene
RI = 653
< 165 to 185 >
Wavelength (nm)
Absorption

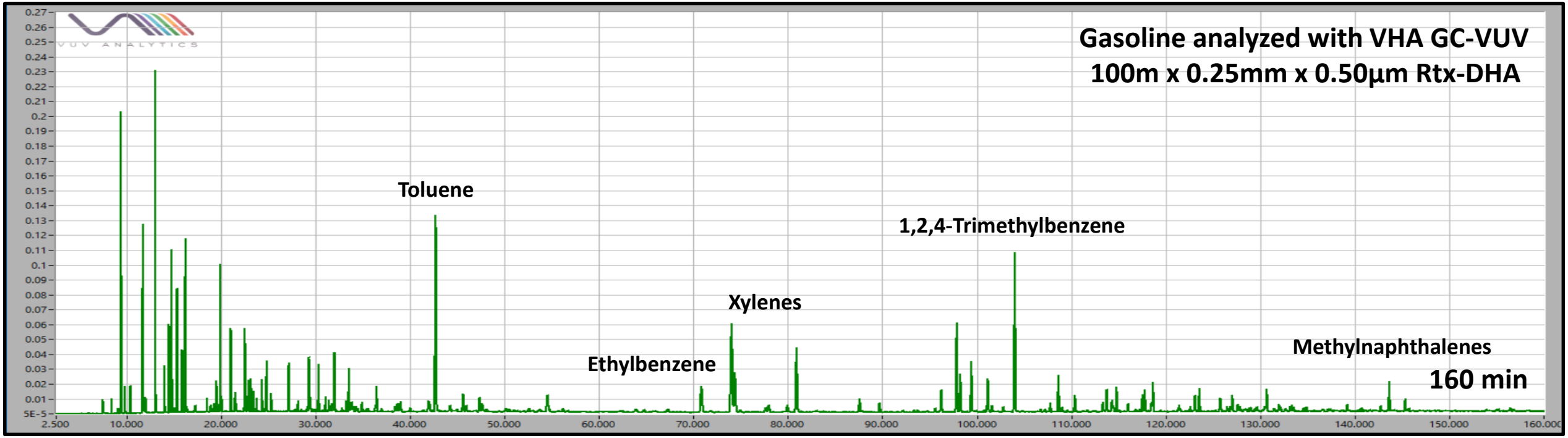

Toluene
Aromatic
Toluene
CH3
RI = 758
< 170 to 195 >
Wavelength (nm)
Absorption

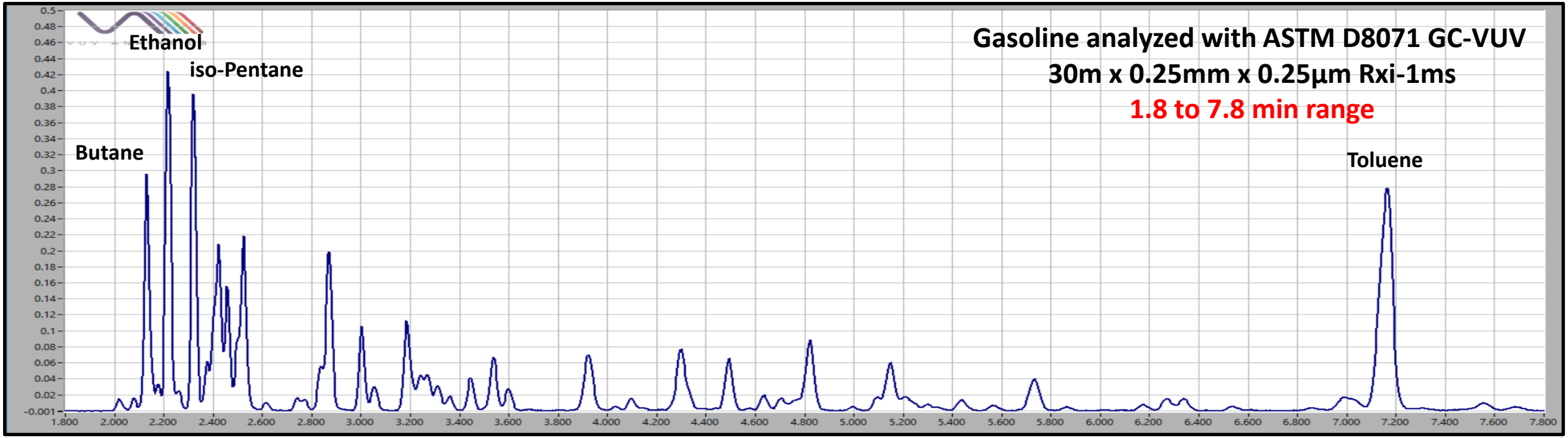
VUV VHA - By the Numbers

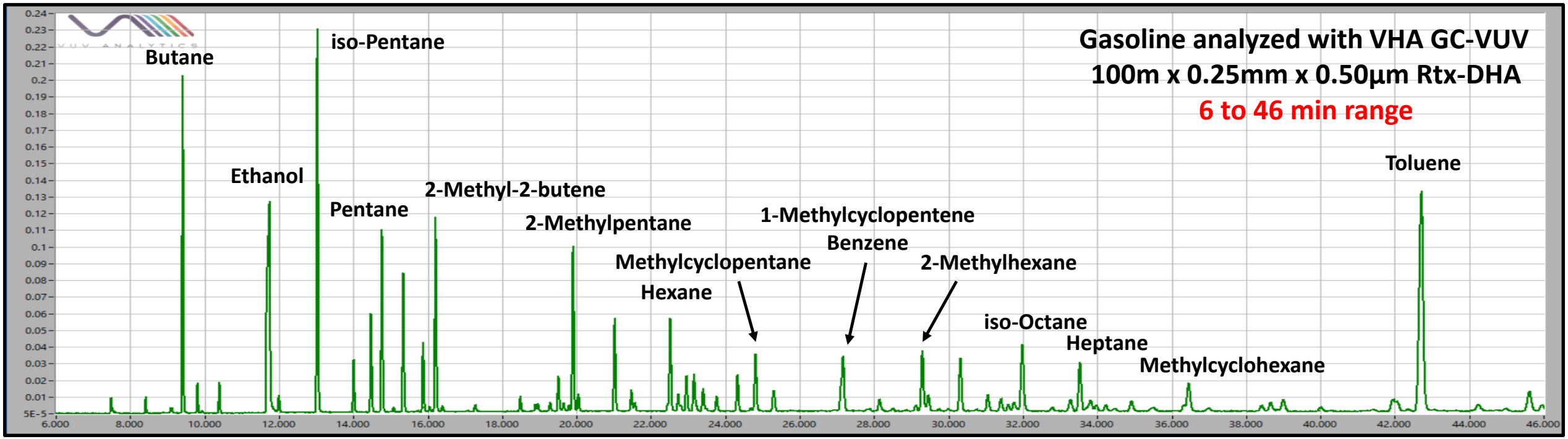
- Currently report mass and volume % data for 151 compounds
- Individual compounds add up to about 90% of gasoline composition
  - Other compounds are classed through absorbance spectra shape and RI
  - Class carbon number report from C_3 to C_{15}
- VHA (PIONA) absorbance spectra library contains ~ 750 spectra
  - Additional spectra always being added

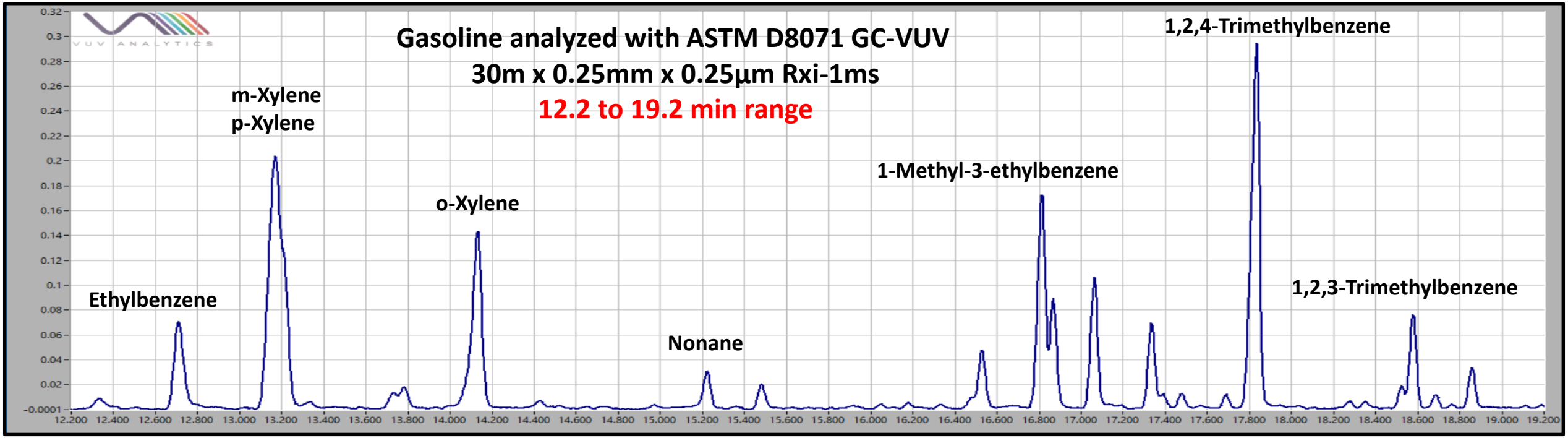
Class	#
Paraffins	13
Isoparaffins	27
Olefins	45
Naphthenes	24
Aromatics	28
Di-Aromatics	9
Alcohols	2
Ethers	3

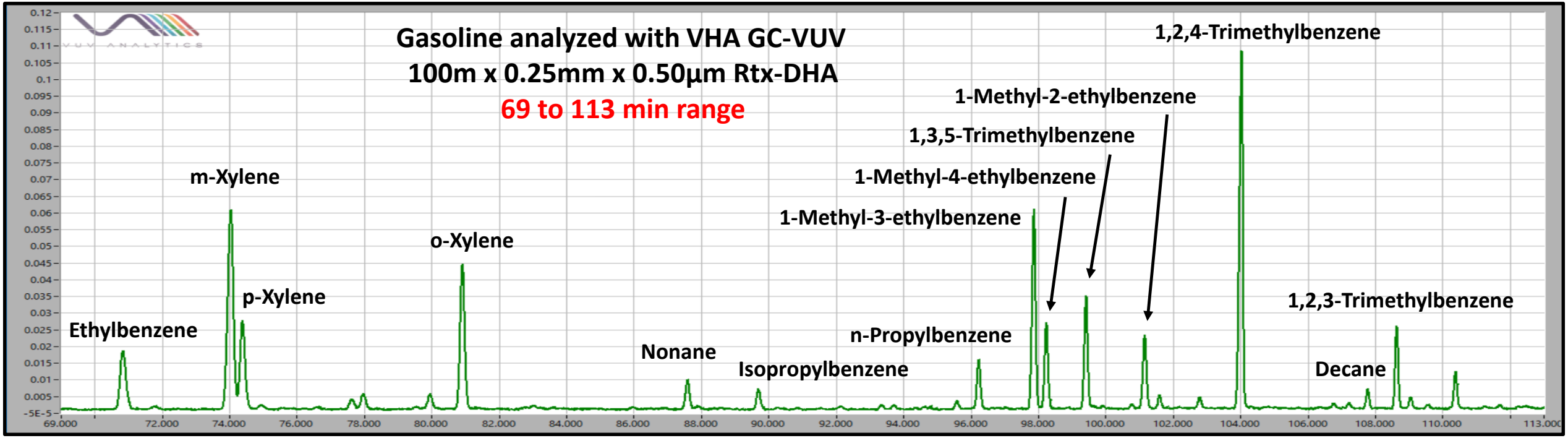

Gasoline analyzed with ASTM D8071 GC-VUV
30m x 0.25mm x 0.25µm Rxi-1ms
Toluene
Ethylbenzene
Xylenes
1,2,4-Trimethylbenzene
Methylnaphthalenes
29 min

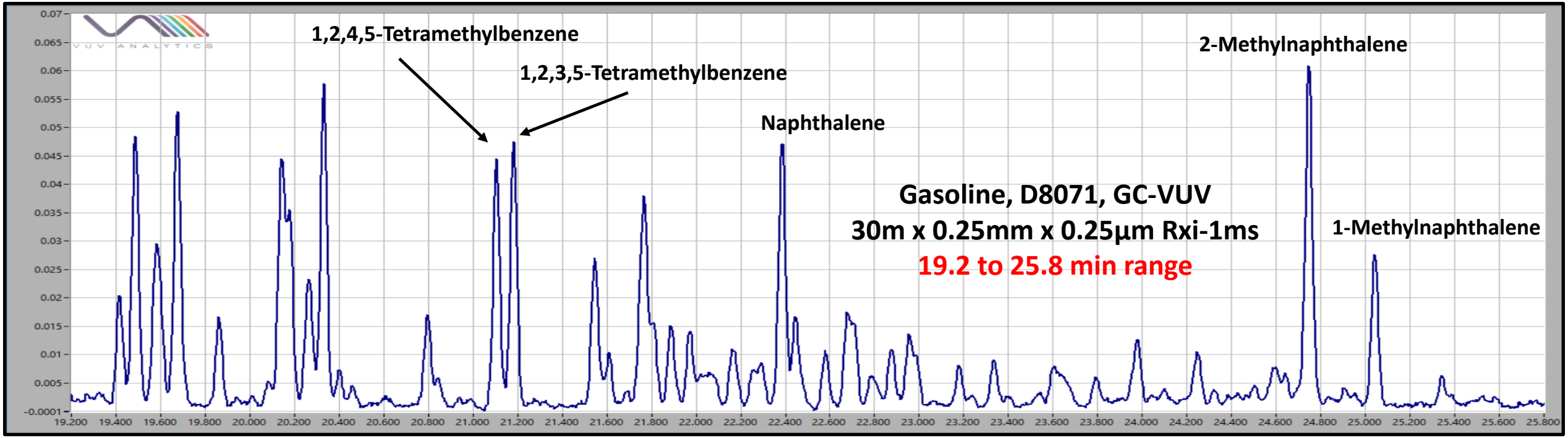

Gasoline analyzed with VHA GC-VUV
100m x 0.25mm x 0.50µm Rtx-DHA
Toluene
Ethylbenzene
Xylenes
1,2,4-Trimethylbenzene
Methylnaphthalenes
160 min

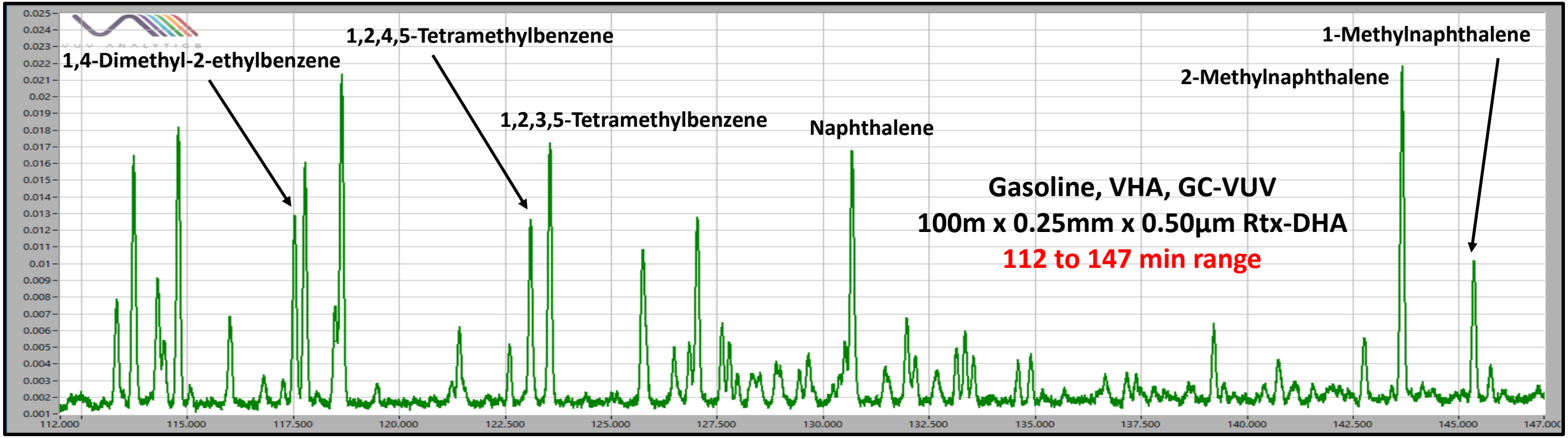

Gasoline analyzed with ASTM D8071 GC-VUV
30m x 0.25mm x 0.25µm Rxi-1ms
1.8 to 7.8 min range
Ethanol
iso-Pentane
Butane
Toluene


Gasoline analyzed with VHA GC-VUV
100m x 0.25mm x 0.50µm Rtx-DHA
6 to 46 min range
Butane
iso-Pentane
Ethanol
Pentane
2-Methyl-2-butene
2-Methylpentane
1-Methylcyclopentene
Benzene
Methylcyclopentane
Hexane
2-Methylhexane
iso-Octane
Heptane
Methylcyclohexane
Toluene


Gasoline analyzed with ASTM D8071 GC-VUV
30m x 0.25mm x 0.25µm Rxi-1ms
12.2 to 19.2 min range
Ethylbenzene
m-Xylene
p-Xylene
o-Xylene
Nonane
1-Methyl-3-ethylbenzene
1,2,4-Trimethylbenzene
1,2,3-Trimethylbenzene


Gasoline analyzed with VHA GC-VUV
100m x 0.25mm x 0.50µm Rtx-DHA
69 to 113 min range
Ethylbenzene
m-Xylene
p-Xylene
o-Xylene
Nonane
Isopropylbenzene
n-Propylbenzene
1-Methyl-3-ethylbenzene
1-Methyl-4-ethylbenzene
1,3,5-Trimethylbenzene
1-Methyl-2-ethylbenzene
1,2,4-Trimethylbenzene
Decane
1,2,3-Trimethylbenzene


1,2,4,5-Tetramethylbenzene
1,2,3,5-Tetramethylbenzene
Naphthalene
2-Methylnaphthalene
1-Methylnaphthalene
Gasoline, D8071, GC-VUV
30m x 0.25mm x 0.25µm Rxi-1ms
19.2 to 25.8 min range


1,4-Dimethyl-2-ethylbenzene
1,2,4,5-Tetramethylbenzene
1,2,3,5-Tetramethylbenzene
Naphthalene
2-Methylnaphthalene
1-Methylnaphthalene
Gasoline, VHA, GC-VUV
100m x 0.25mm x 0.50µm Rtx-DHA
112 to 147 min range

Mass %

Category	MEG D8071	MEG VHA		B02 D8071	B02 VHA		M872 D8071	M872 VHA		M873 D8071	M873 VHA
Paraffin	13.7	15.2		17.6	17.5		7.93	8.18		12.8	12.9
Isoparaffin	27.6	28.5		18.9	18.7		68.6	70.0		25.1	24.5
Olefin	13.2	12.7		13.4	14.5		1.98	0.929		0.276	0.003
Naphthene	8.84	6.37		2.26	1.84		2.12	1.06		5.65	5.54
Aromatic	25.6	24.8		36.6	36.1		19.3	19.9		55.4	56.3
Di-Aromatic	0.970	0.859		0.063			0.152			0.788	0.760
Ethanol	10.1	11.5		11.1	11.4						
Iso-octane	1.91	2.08		4.87	5.07		16.6	17.7			
Benzene	0.426	0.479					0.222	0.234		0.446	0.451
Toluene	3.51	3.99		15.4	16.0		6.91	7.70		15.1	15.5
Ethylbenzene	0.875	0.847		1.37	1.15		1.37	1.31		3.25	3.03
Xylenes	5.55	5.83		6.50	6.81		6.88	7.40		16.1	17.2
Naphthalene	0.266	0.279		0.063			0.053			0.401	0.437
Methylnaphthalenes	0.590	0.580					0.099				

Mass %

Category	MEG D8071	MEG VHA	B02 D8071	B02 VHA	M872 D8071	M872 VHA	M873 D8071	M873 VHA
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Ethanol	10.1	11.5	11.1	11.4				
Iso-octane	1.91	2.08	4.87	5.07	16.6	17.7		
Benzene	0.426	0.479			0.222	0.234	0.446	0.451
Toluene	3.51	3.99	15.4	16.0	6.91	7.70	15.1	15.5
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Xylenes	5.55	5.83	6.50	6.81	6.88	7.40	16.1	17.2
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Mass %

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Iso-octane	1.91	2.08	4.87	5.07	16.6	17.7		
Benzene	0.426	0.479			0.222	0.234	0.446	0.451
Toluene	3.51	3.99	15.4	16.0	6.91	7.70	15.1	15.5
Ethylbenzene	0.875	0.847	1.37	1.15	1.37	1.31	3.25	3.03
Xylenes	5.55	5.83	6.50	6.81	6.88	7.40	16.1	17.2
Naphthalene	0.266	0.279	0.063		0.053		0.401	0.437
Methylnaphthalenes	0.590	0.580			0.099			

	P	I	O	N	A
C0					
C1					
C2					
C3					
C4	5.1914	0.2350	0.6322		
C5	3.5075	7.5802	6.8148	0.1822	
C6	2.1806	6.6897	3.7730	1.8755	0.4786
C7	1.5994	4.7750	0.9201	2.8040	3.9930
C8	1.0650	6.4443	0.5264	1.3166	6.6773
C9	0.7974	1.5549	0.0032	0.0670	9.1510
C10	0.4157	0.9806	0.0298	0.0140	3.5778
C11	0.2058	0.2394	0.0094	0.1076	0.8498
C12	0.1420	0.0058			0.0759
C13	0.0784	0.0115			0.0460
C14					
C15					
Total	**15.1833**	**28.5164**	**12.7089**	**6.3669**	**24.8493**

Gasoline analyzed on 100m x 0.25mm x 0.50µm Rtx-DHA using D6730 GC conditions and VUV VHA data processing…

Category	Mass %
Paraffin	15.1833
Isoparaffin	28.5163
Olefin	12.7089
Naphthene	6.3669
Aromatic	24.8493
Di-Aromatic	0.8587
iso-butane	0.2350
Methanol	0.0000
Isobutylene	0.0268
1-Butene	0.0424
1,3-Butadiene	0.0000
Butane	5.1914
Vinyl acetylene	0.0000
trans-2-Butene	0.2722
cis-2-Butene	0.2909
Ethyl Alcohol	11.5165
3-Methyl-1-butene	0.1967
iso-pentane	7.5605
1,4-Pentadiene	0.0000
1-Pentene	0.5959
2-Methyl-1-butene	1.1212

Category	Mass %
2,4-Dimethylpentane	0.4238
1-Methylcyclopentene	0.3283
Benzene	0.4786
Cyclohexane	0.3414
4-Methyl-1-hexene	0.0000
cis/trans-4-Methyl-2-hexene	0.1032
2-Methylhexane	1.9064
2,3-Dimethylpentane	0.4675
1,1-Dimethylcyclopentane	0.0329
tert-Amyl methyl ether	0.0000
Cyclohexene	0.0000
3-Methylhexane	1.7435
cis-1,3-Dimethylcyclopentane	0.5218
trans-1,3-Dimethylcyclopentane	0.4231
3-Ethylpentane	0.1286
trans-1,2-Dimethylcyclopentane	0.2884
iso-octane	2.0745
1-Heptene	0.0000
trans-3-Heptene	0.0247
Heptane	1.5994
trans-2-Heptene	0.1160

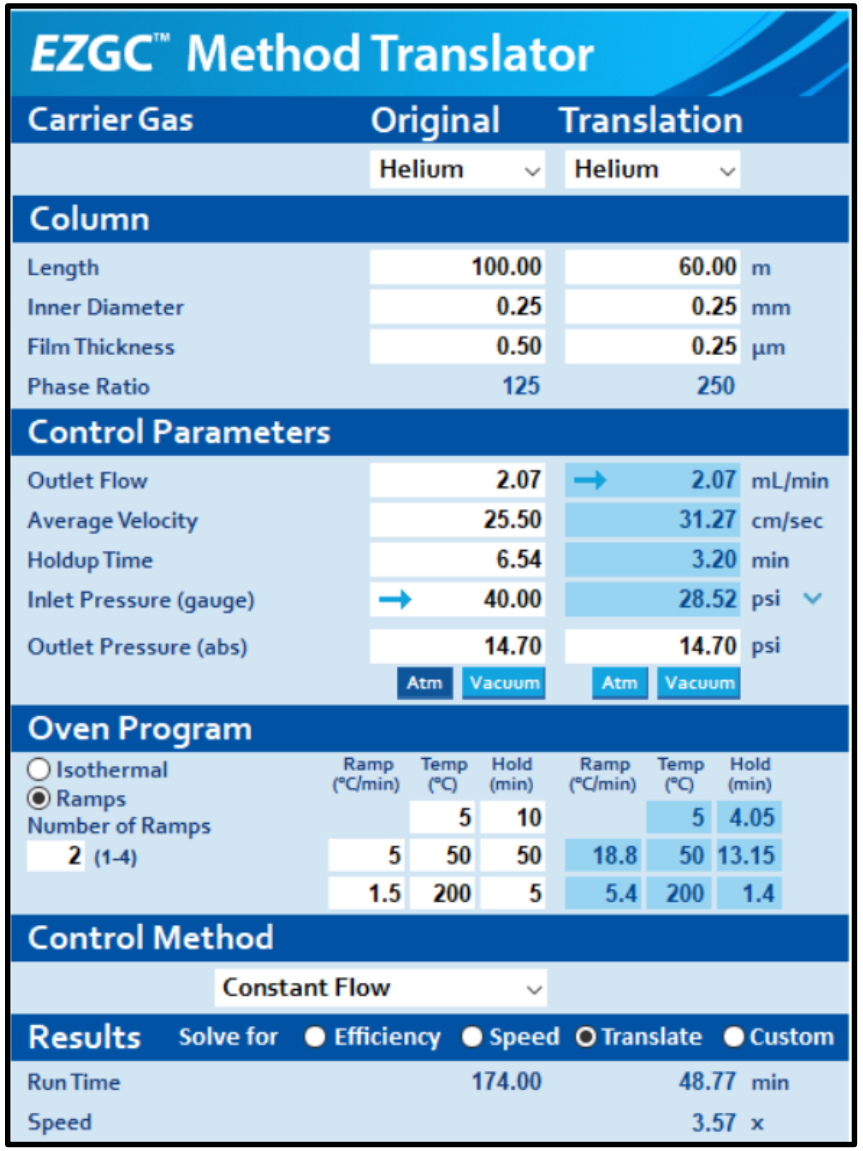
Category	Mass %
2,5-Dimethylhexane	0.3725
2,4-Dimethylhexane	0.4312
ctc-1,2,4-Trimethylcyclopentane	0.1041
ctc-1,2,3-Trimethylcyclopentane	0.0000
2,3,3-Trimethylpentane	0.2016
Toluene	3.9930
2,3-Dimethylhexane	0.2884
1,1,2-Trimethylcyclopentane	0.0000
2-Methylheptane	0.0000
4-Methylheptane	0.2470
3-Methylheptane	0.9112
trans-1,4-Dimethylcyclohexane	0.0991
2,2,5-Trimethylhexane	0.1434
3c-Ethylmethylcyclopentane	0.0744
3t-Ethylmethylcyclopentane	0.0900
2t-Ethylmethylcyclopentane	0.0000
trans-1,2-Dimethylcyclohexane	0.0171
Octane	1.0650
cis-1,2-Dimethylcyclohexane	0.0000
1,1,4-Trimethylcyclohexane	0.0000
Ethylcyclohexane	0.1275

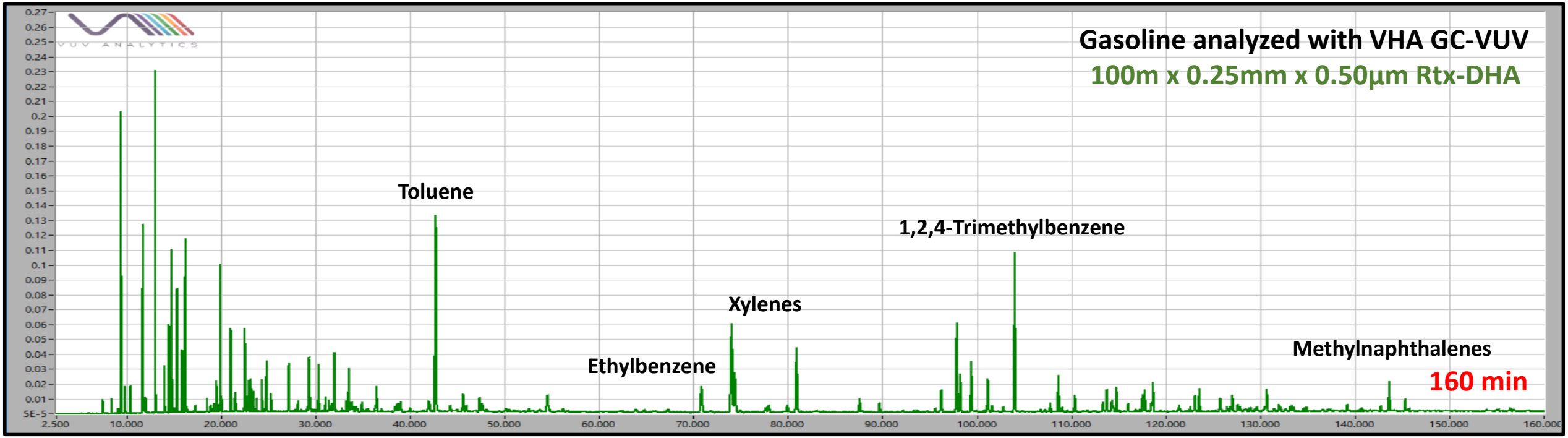
Category	Mass %
2,5-Dimethylheptane	0.0473
Ethylbenzene	0.8470
ctt-1,2,4-Trimethylcyclohexane	0.0000
m-Xylene	2.9707
p-Xylene	1.1242
2-Methyloctane	0.4273
Styrene	0.0000
3-Methyloctane	0.3826
o-Xylene	1.7354
Nonane	0.7974
Isopropylbenzene	0.1543
n-Propylbenzene	0.4698
1-Methyl-3-ethylbenzene	1.9510
1-Methyl-4-ethylbenzene	0.7819
1,3,5-Trimethylbenzene	1.0287
1-Methyl-2-ethylbenzene	0.6209
2-Methylnonane	0.2587
3-Methylnonane	0.2387
1,2,4-Trimethylbenzene	3.4281
Decane	0.4157
1,2,3-Trimethylbenzene	0.7162

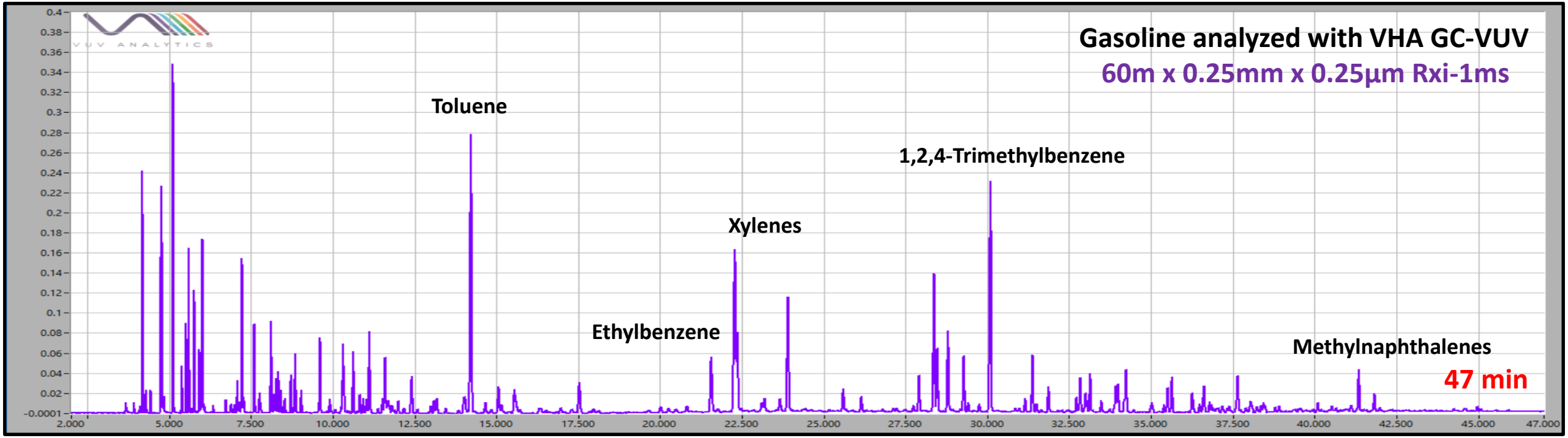
Category	Mass %
Dicyclopentadiene	0.0000
Indene	0.0000
1-Methyl-3-n-propylbenzene	0.3674
1-Methyl-4-n-propylbenzene	0.1724
n-Butylbenzene	0.0000
1,3-Dimethyl-5-ethylbenzene	0.4231
trans-Decalin	0.0000
1-Methyl-2-n-propylbenzene	0.0944
1,4-Dimethyl-2-ethylbenzene	0.2814
1,3-Dimethyl-4-ethylbenzene	0.2362
1,2-Dimethyl-4-ethylbenzene	0.4279
1,2-Dimethyl-3-ethylbenzene	0.0947
Undecane	0.2058
1,2,4,5-Tetramethylbenzene	0.2434
1,2,3,5-Tetramethylbenzene	0.3710
Naphthalene	0.2792
Dodecane	0.1420
Pentamethylbenzene	0.0149
2-Methylnaphthalene	0.4107
1-Methylnaphthalene	0.1688
Tridecane	0.0784

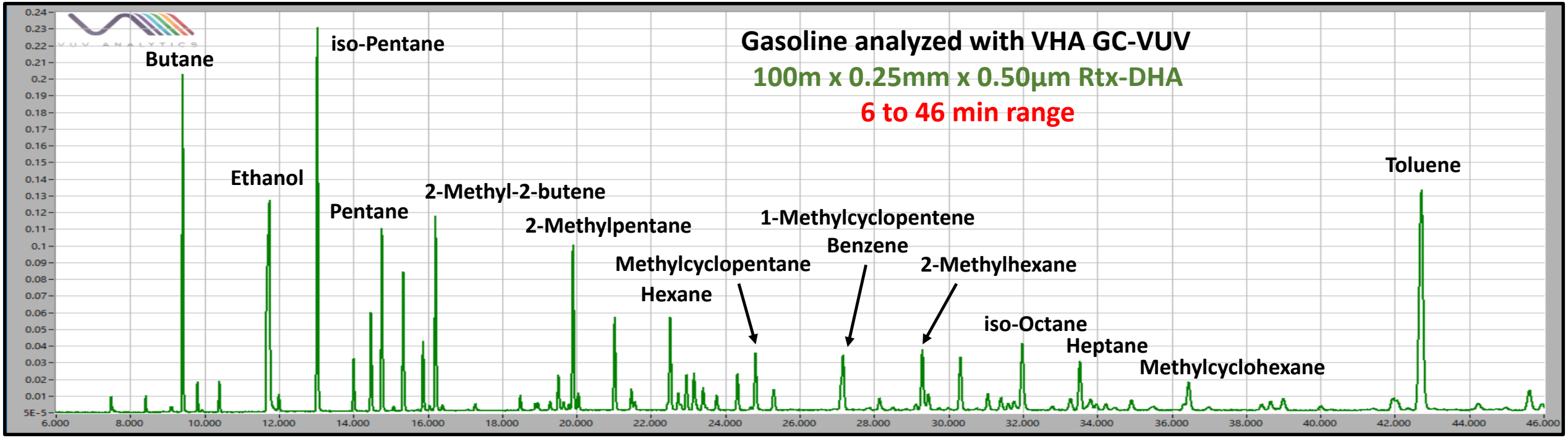
Can We Improve VUV VHA GC Run Time?

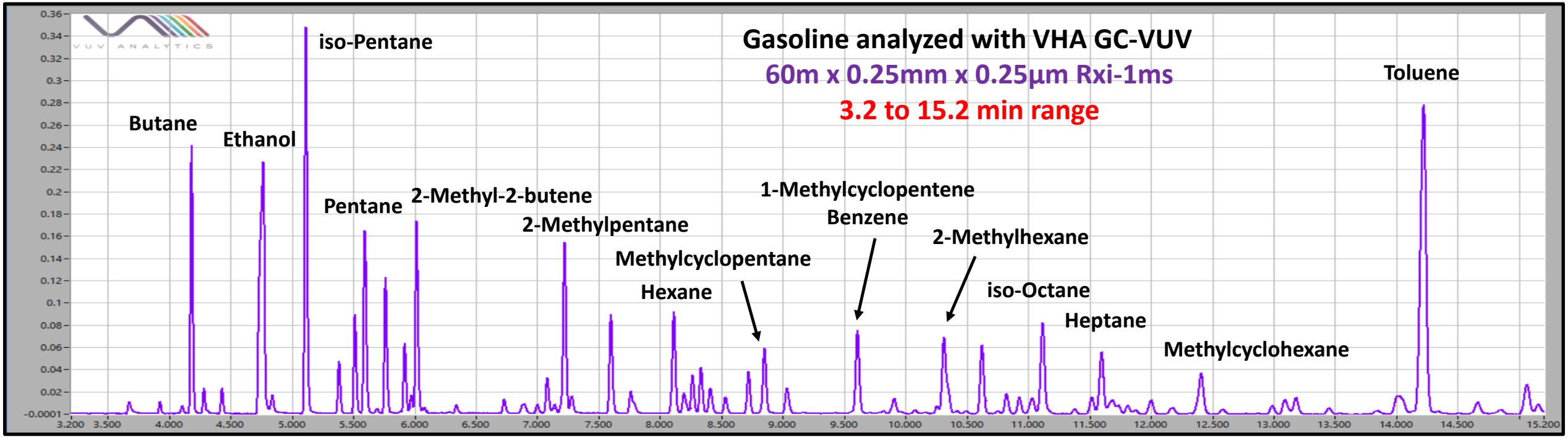
- Shorter GC column
- Thinner column film thickness
- Method translation for a new GC oven program
- Elution order of compounds should be the same
- GREATLY reduced run time
- What about the separations?

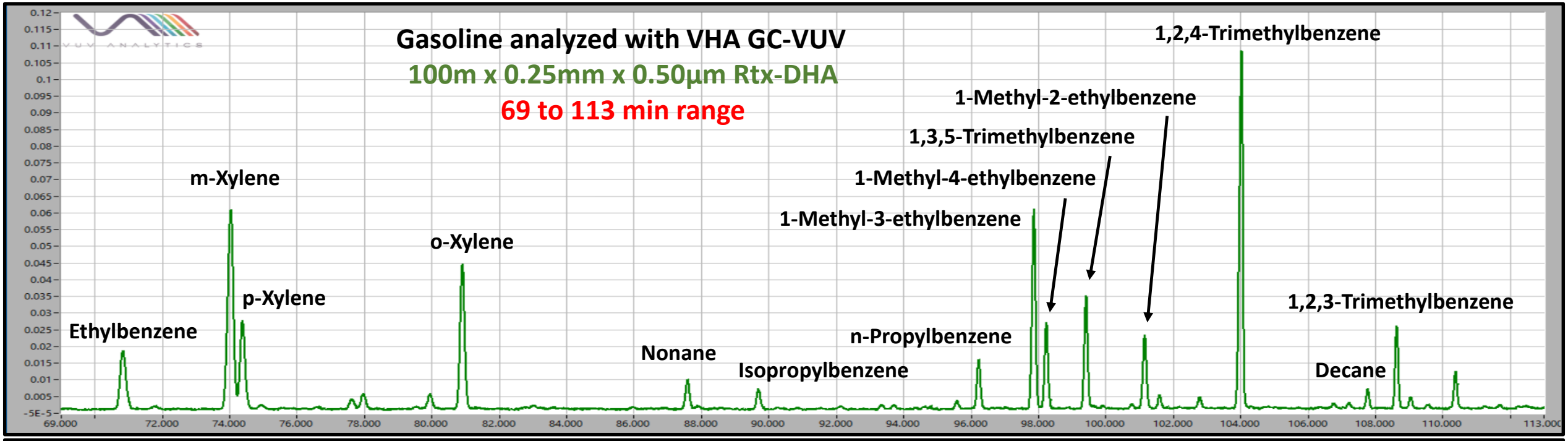


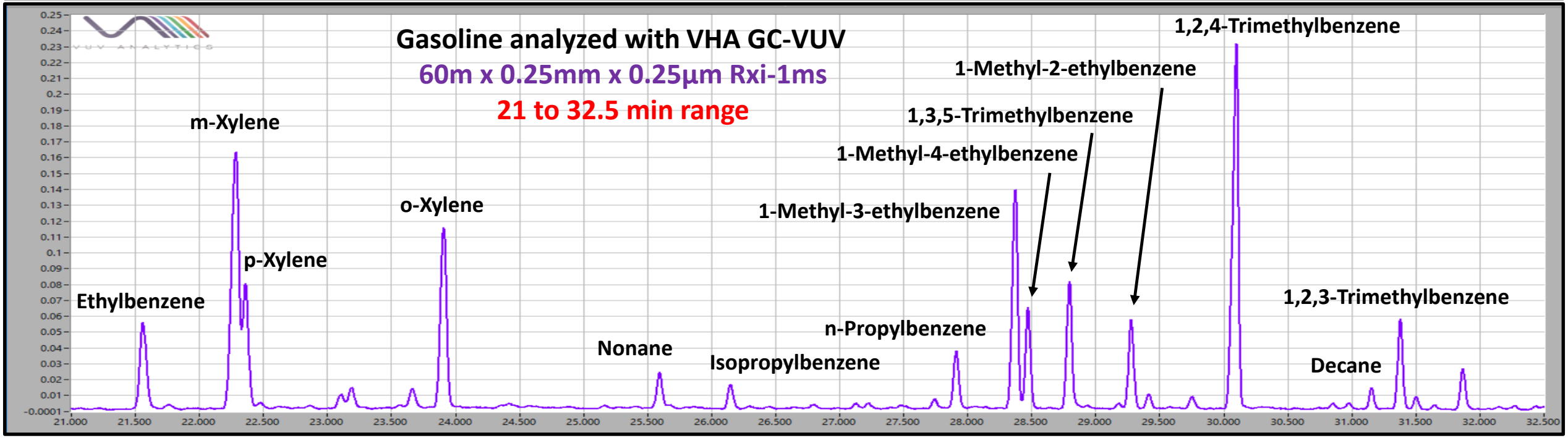

Gasoline analyzed with VHA GC-VUV
100m x 0.25mm x 0.50µm Rtx-DHA
Toluene
1,2,4-Trimethylbenzene
Xylenes
Ethylbenzene
Methylnaphthalenes
160 min

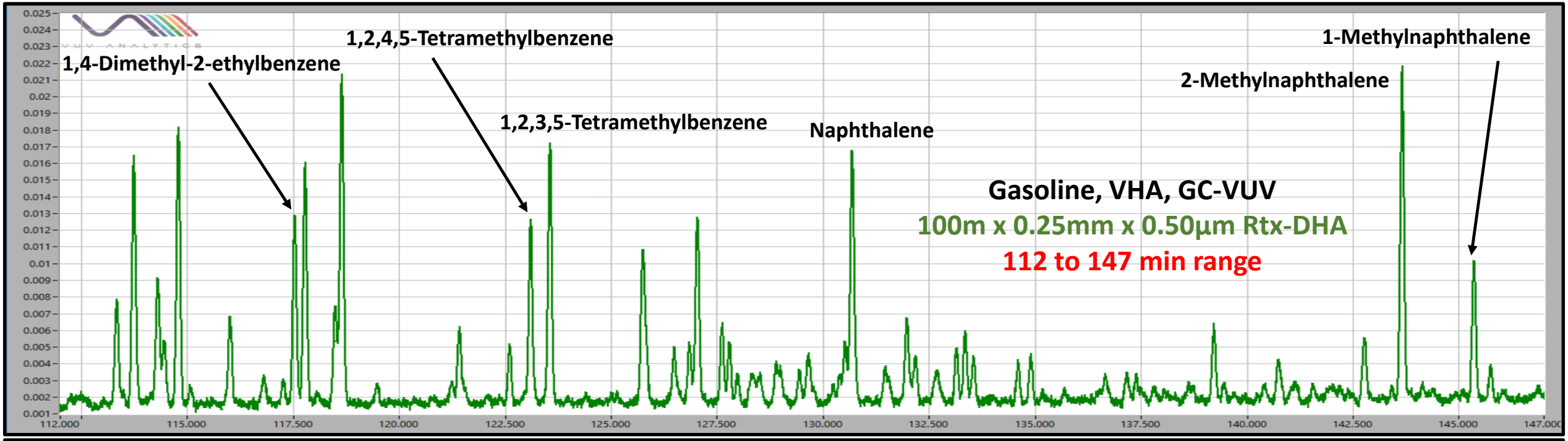

Gasoline analyzed with VHA GC-VUV
60m x 0.25mm x 0.25µm Rxi-1ms
Toluene
1,2,4-Trimethylbenzene
Xylenes
Ethylbenzene
Methylnaphthalenes
47 min

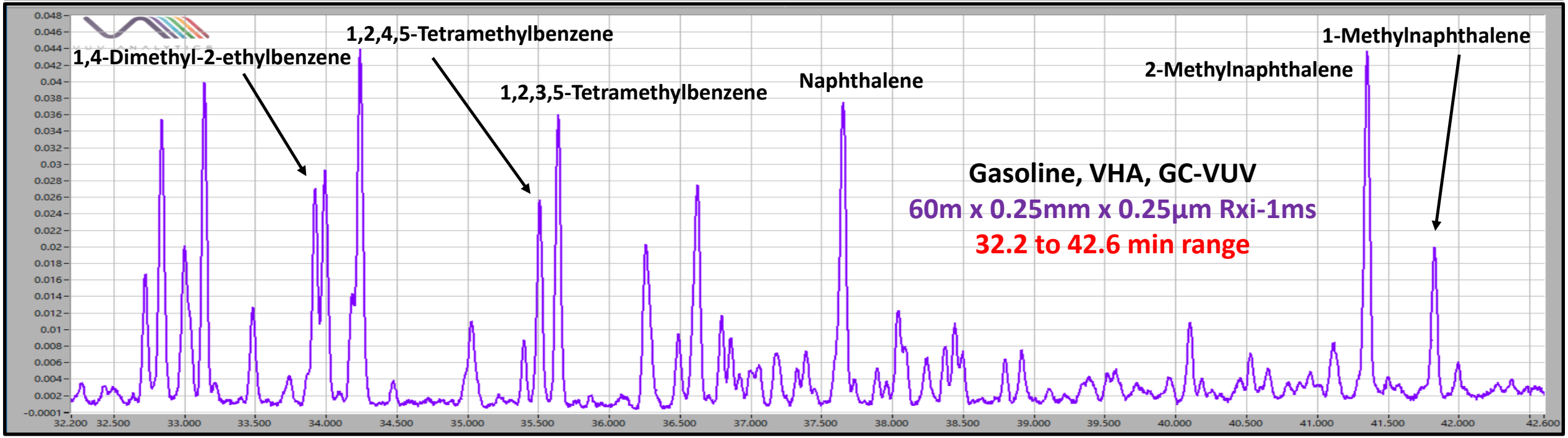

Gasoline analyzed with VHA GC-VUV
100m x 0.25mm x 0.50µm Rtx-DHA
6 to 46 min range
Butane
iso-Pentane
Ethanol
Pentane
2-Methyl-2-butene
2-Methylpentane
1-Methylcyclopentene
Benzene
Methylcyclopentane
2-Methylhexane
Hexane
iso-Octane
Heptane
Methylcyclohexane
Toluene


Gasoline analyzed with VHA GC-VUV
60m x 0.25mm x 0.25µm Rxi-1ms
3.2 to 15.2 min range
Butane
iso-Pentane
Ethanol
Pentane
2-Methyl-2-butene
2-Methylpentane
1-Methylcyclopentene
Benzene
Methylcyclopentane
2-Methylhexane
Hexane
iso-Octane
Heptane
Methylcyclohexane
Toluene


Gasoline analyzed with VHA GC-VUV
100m x 0.25mm x 0.50µm Rtx-DHA
69 to 113 min range
m-Xylene
o-Xylene
p-Xylene
Ethylbenzene
Nonane
Isopropylbenzene
n-Propylbenzene
1-Methyl-3-ethylbenzene
1-Methyl-4-ethylbenzene
1,3,5-Trimethylbenzene
1-Methyl-2-ethylbenzene
1,2,4-Trimethylbenzene
1,2,3-Trimethylbenzene
Decane


Gasoline analyzed with VHA GC-VUV
60m x 0.25mm x 0.25µm Rxi-1ms
21 to 32.5 min range
m-Xylene
o-Xylene
p-Xylene
Ethylbenzene
Nonane
Isopropylbenzene
n-Propylbenzene
1-Methyl-3-ethylbenzene
1-Methyl-4-ethylbenzene
1,3,5-Trimethylbenzene
1-Methyl-2-ethylbenzene
1,2,4-Trimethylbenzene
1,2,3-Trimethylbenzene
Decane


1,4-Dimethyl-2-ethylbenzene
1,2,4,5-Tetramethylbenzene
1,2,3,5-Tetramethylbenzene
Naphthalene
2-Methylnaphthalene
1-Methylnaphthalene
Gasoline, VHA, GC-VUV
100m x 0.25mm x 0.50µm Rtx-DHA
112 to 147 min range


1,4-Dimethyl-2-ethylbenzene
1,2,4,5-Tetramethylbenzene
1,2,3,5-Tetramethylbenzene
Naphthalene
2-Methylnaphthalene
1-Methylnaphthalene
Gasoline, VHA, GC-VUV
60m x 0.25mm x 0.25µm Rxi-1ms
32.2 to 42.6 min range

Mass % Comparison for Gasoline Analyzed with 3 GC-VUV Methods

- ASTM D8071 PIONA
  - 30m x 0.25mm x 0.25µm, no cryo
- ASTM D6730 VUV VHA
  - 100m x 0.25mm x 0.50µm, cryo
- "Fast" VUV VHA
  - 60m x 0.25mm x 0.25µm, cryo

Category	30m D8071	100m VHA	60m VHA
Paraffin	13.7	15.2	13.8
Isoparaffin	27.6	28.5	27.7
Olefin	13.2	12.7	12.3
Naphthene	8.84	6.37	7.75
Aromatic	25.6	24.8	26.9
Di-Aromatic	0.970	0.859	0.994
Ethanol	10.1	11.5	10.6
Iso-octane	1.91	2.08	2.00
Benzene	0.426	0.479	0.441
Toluene	3.51	3.99	3.82
Ethylbenzene	0.875	0.847	0.913
Xylenes	5.55	5.83	5.96
Naphthalene	0.266	0.279	0.345
Methylnaphthalenes	0.590	0.580	0.615

VUV ANALYTICS

Jet Fuel Analysis by GC-VUV

Flying at the Speed of (Ultraviolet) Light

Jet Fuel Analysis – An Overview

- AKA Aviation Turbine Fuel – middle distillate
  - Kerosene-type (e.g. Jet A, A-1): C8-C18(C22)
  - Wide-cut (e.g. Jet B): C5-C16
- Strict upper limits on total aromatics (25%) and total di-aromatics (3%)
- No real “PIONA” analysis (matrix too complex)

FIA – Overview and Issues

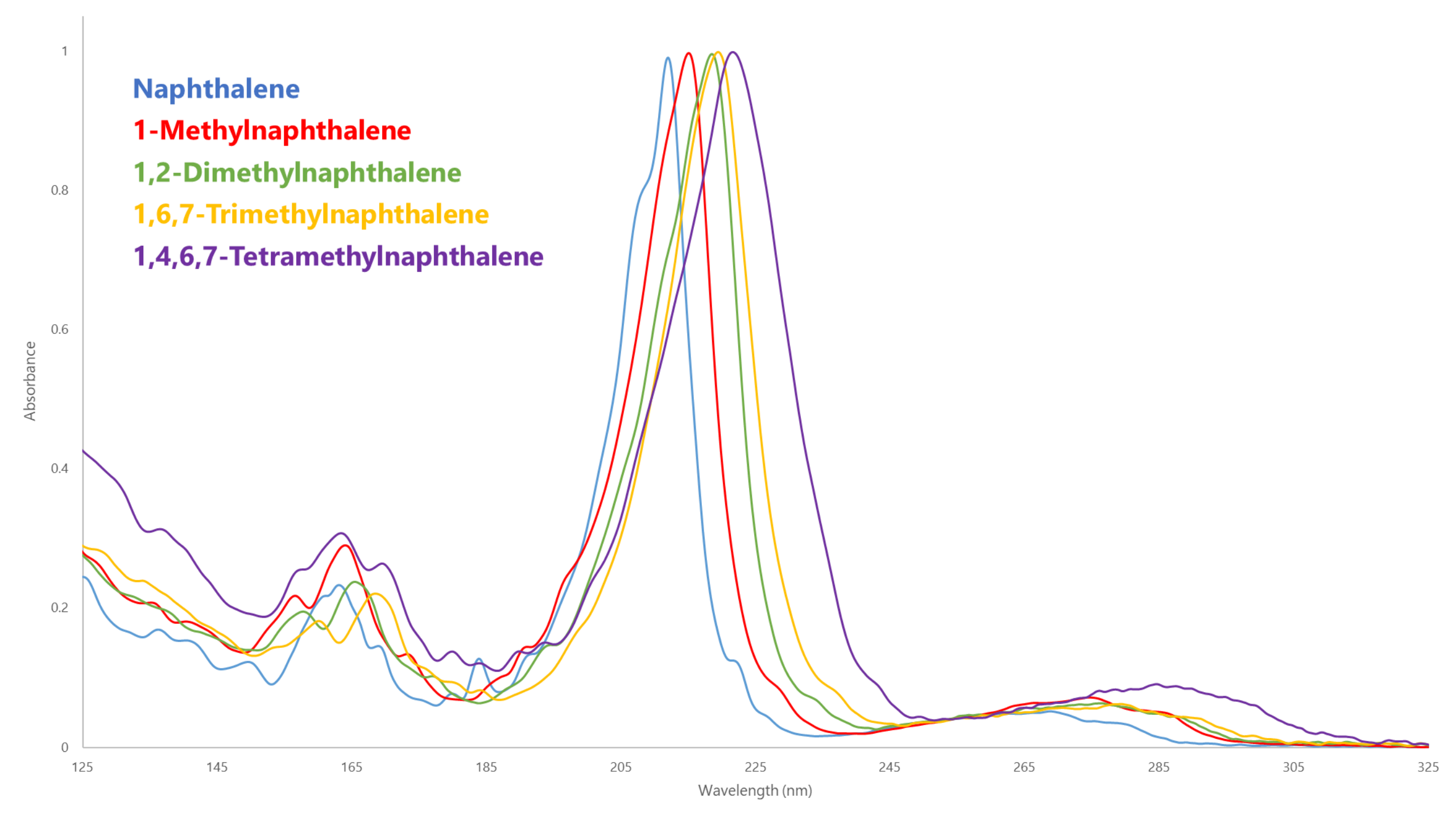
- ASTM D1319-14 – Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption
  - Silica gel fractionation not always clean cut between saturates, olefins, and aromatics
  - Performance issues with newer dye batches
  - Sole manufacturer of the dye no longer exists
  - FIA dye more valuable than gold???

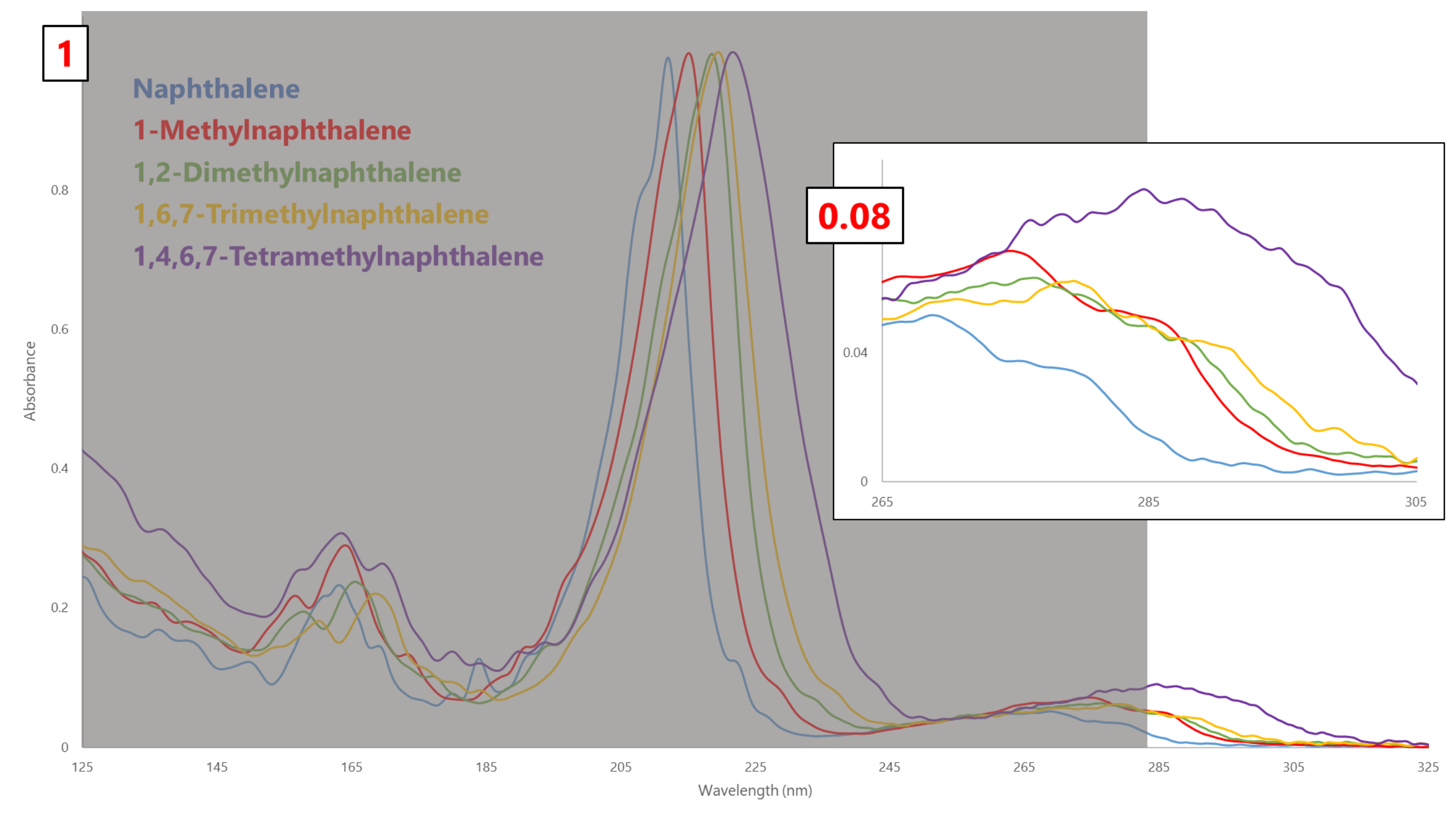
Issues with ASTM D1840 Method Wavelength

- ASTM D1840 must use 285 nm for all absorbance measurements to eliminate the interference from mono-aromatics
- The relative absorbance for di-aromatics at <250 nm is greater than 10x the absorbance at 285 nm!
- The lower absolute response at 285 nm can lead to a large error range

4. Summary of Test Method

4.1 The total concentration of naphthalenes in jet fuels is determined by measurement of the absorbance at 285 nm of a solution of the fuel at known concentration.


Naphthalene
1-Methylnaphthalene
1,2-Dimethylnaphthalene
1,6,7-Trimethylnaphthalene
1,4,6,7-Tetramethylnaphthalene
Absorbance
1
0.8
0.6
0.4
0.2
0
125
145
165
185
205
225
245
265
285
305
325
Wavelength (nm)


1
Naphthalene
1-Methylnaphthalene
1,2-Dimethylnaphthalene
1,6,7-Trimethylnaphthalene
1,4,6,7-Tetramethylnaphthalene
0.08
Absorbance
0
0.2
0.4
0.6
0.8
0.04
0
265
285
305
125
145
165
185
205
225
245
265
285
305
325
Wavelength (nm)

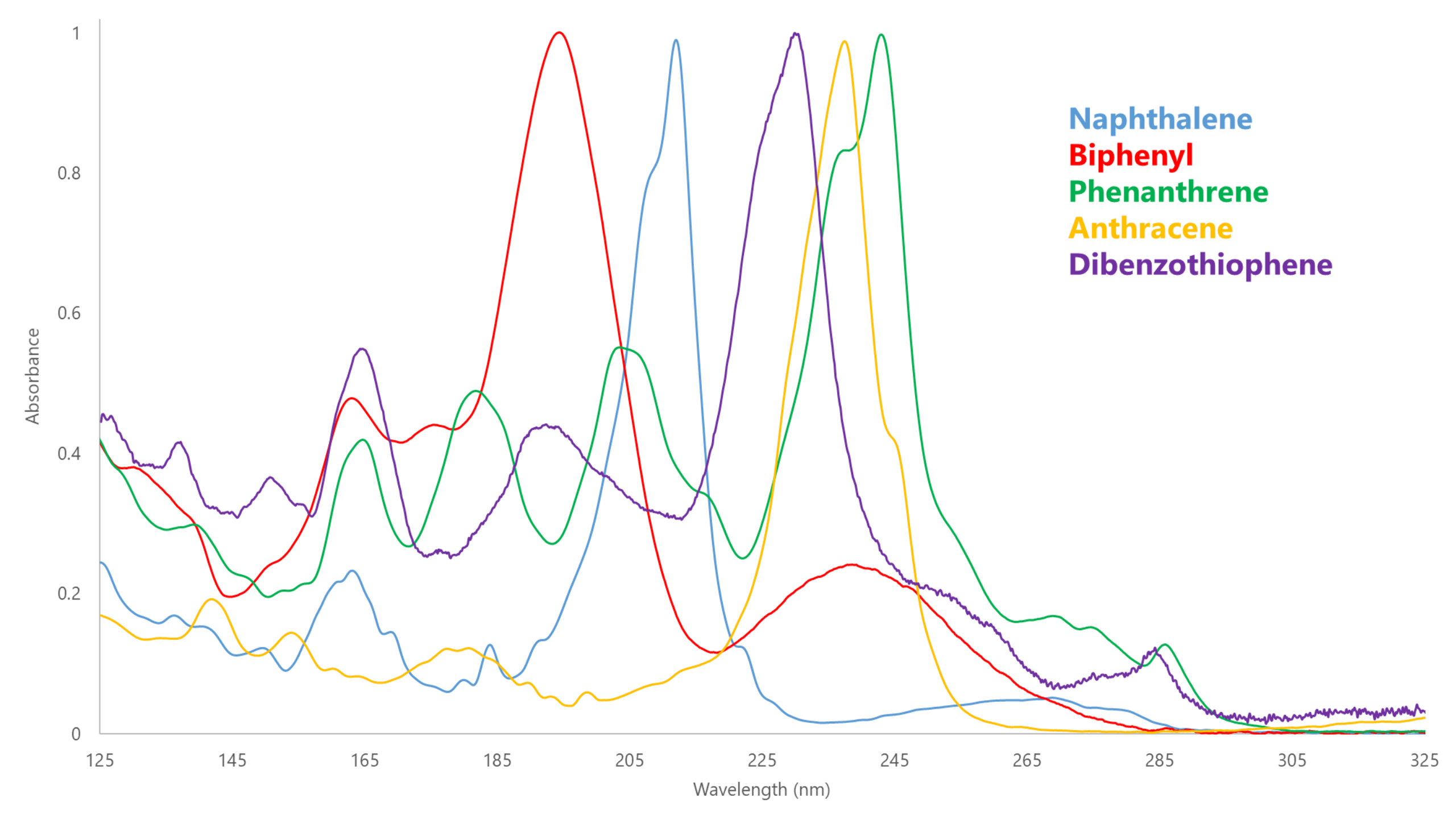
Interferences in ASTM D1840 Di-Aromatic Determination

6. Interferences

6.1 Interferences add to the apparent naphthalene content. Phenanthrenes, dibenzothiophenes, biphenyls, benzothiophenes, and anthracenes interfere if present. The end point limitation of 315 °C will minimize this interference except for benzothiophenes and biphenyls. The contribution to measured naphthalene content by the presence of 1 % of such interfering compounds can be estimated from Table 1.

TABLE 1 Interfering Compounds

Type of Interfering Compound	Error in Percentage of Naphthalenes Caused by 1 % Interfering Compound
Phenanthrenes	2
Dibenzothiophenes	2
Biphenyls	1
Benzothiophenes	0.6
Anthracenes	0.1


Naphthalene
Biphenyl
Phenanthrene
Anthracene
Dibenzothiophene
Absorbance
Wavelength (nm)
1
0.8
0.6
0.4
0.2
0
125
145
165
185
205
225
245
265
285
305
325

Caveats for Analyzing Jet Fuel using GC-VUV

- Olefins typically not present in jet fuel
  - However, their absorbance spectra have response in both the saturate (125-160 nm) and aromatic (170-200 nm) regions
  - Any reported values are likely S/A coelutions; therefore all olefin spectra removed from spectra library
- Classification of saturates nearly impossible at higher C#
  - Number of isomers increases dramatically with C#
  - At higher C# (>C_{10}), absorbance spectra of isoparaffins and naphthenes are too similar to distinguish in a complex sample

C#	P/I Isomers
9	35
12	355
15	4347
18	60523

Why Can We Analyze Jet Fuel So Quickly?

- The requisite spectral data is simplified
  - At higher C# (>C_{10}), absorbance spectra of isoparaffins and naphthenes are too similar to distinguish in a complex sample → ***all saturates quantified together***
  - Mono- and di-aromatics matched using representative absorbance spectra → ***specific compound identification not necessary***
- Distinct wavelength regions of maximum absorbance → ***easy spectral deconvolution***
  - Saturates (125-160 nm)
  - Mono-aromatics (175-205 nm)
  - Di-aromatics (205-240 nm)

GC-VUV Conditions for Jet Fuel Analysis

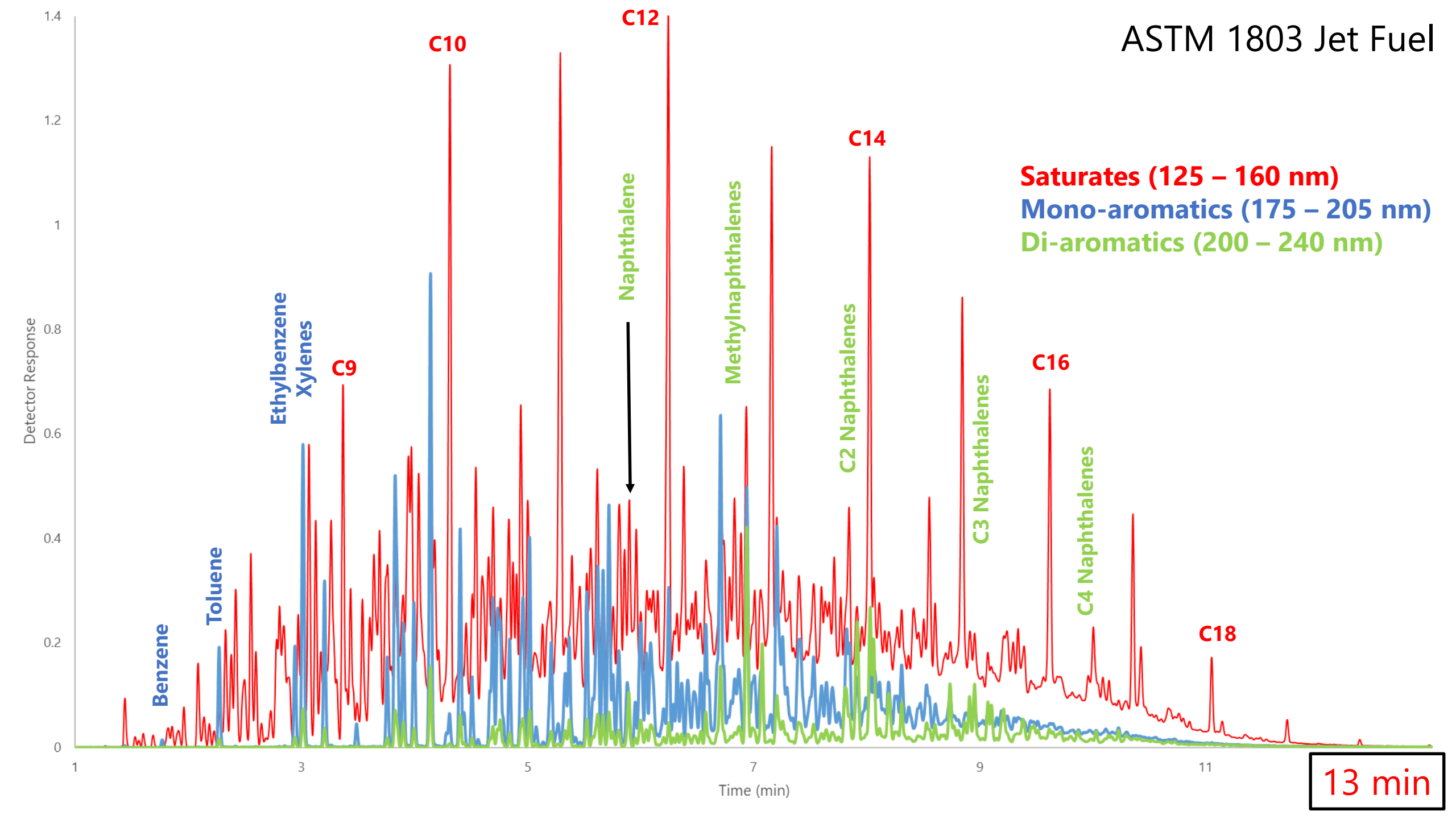
- Agilent 6890 GC
  - 1 µL injection
  - Inlet: 250°C, split 100:1
  - Column: Restek Rxi-1ms (30 m x 0.25 mm, 0.25-µm)
  - Flow: **2 mL/min helium**, constant flow
  - Oven: **50°C, hold 0.1 min; 15°C/min to 260°C** (run time – **14.1 min**)

- VUV Analytics VGA-100
  - Makeup gas: 0.23 psi N_2
  - Flow cell and transfer line: 275°C
  - Acquisition rate: **7 spectra/sec**
  - Acquisition range: 125-240 nm

GC-VUV Conditions for Jet Fuel Analysis

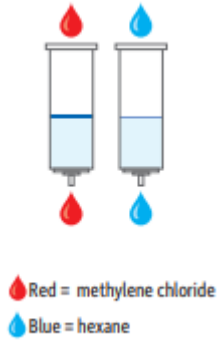
- Agilent 6890 GC
  - 1 µL injection
  - Inlet: 250°C, split 100:1
  - Column: Restek Rxi-1ms (30 m x 0.25 mm, 0.25-µm)
  - Flow: **2 mL/min helium**, constant flow
  - Oven: **50°C hold 0.5 min; 15°C/min to 200°C** (run time – **14.1 min**)
- VUV Analytics VGA-100
  - Makeup gas: 0.23 psi N_2
  - Flow cell and transfer line: 275°C
  - Acquisition rate: **7 spectra/sec**
  - Acquisition range: 125-240 nm

SAME CONFIGURATION AS ASTM D8071

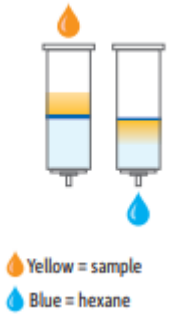

ASTM 1803 Jet Fuel
Saturates (125 – 160 nm)
Mono-aromatics (175 – 205 nm)
Di-aromatics (200 – 240 nm)
Benzene
Toluene
Ethylbenzene
Xylenes
C9
C10
C12
Naphthalene
Methylnaphthalenes
C14
C2 Naphthalenes
C3 Naphthalenes
C16
C4 Naphthalenes
C18
Detector Response
Time (min)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1
3
5
7
9
11
13 min

Fractionation of Jet Fuels

Conditioning



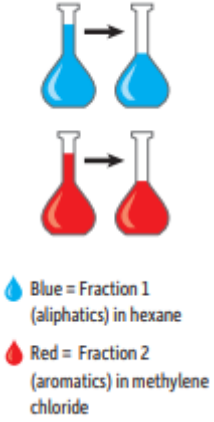
Sample Loading



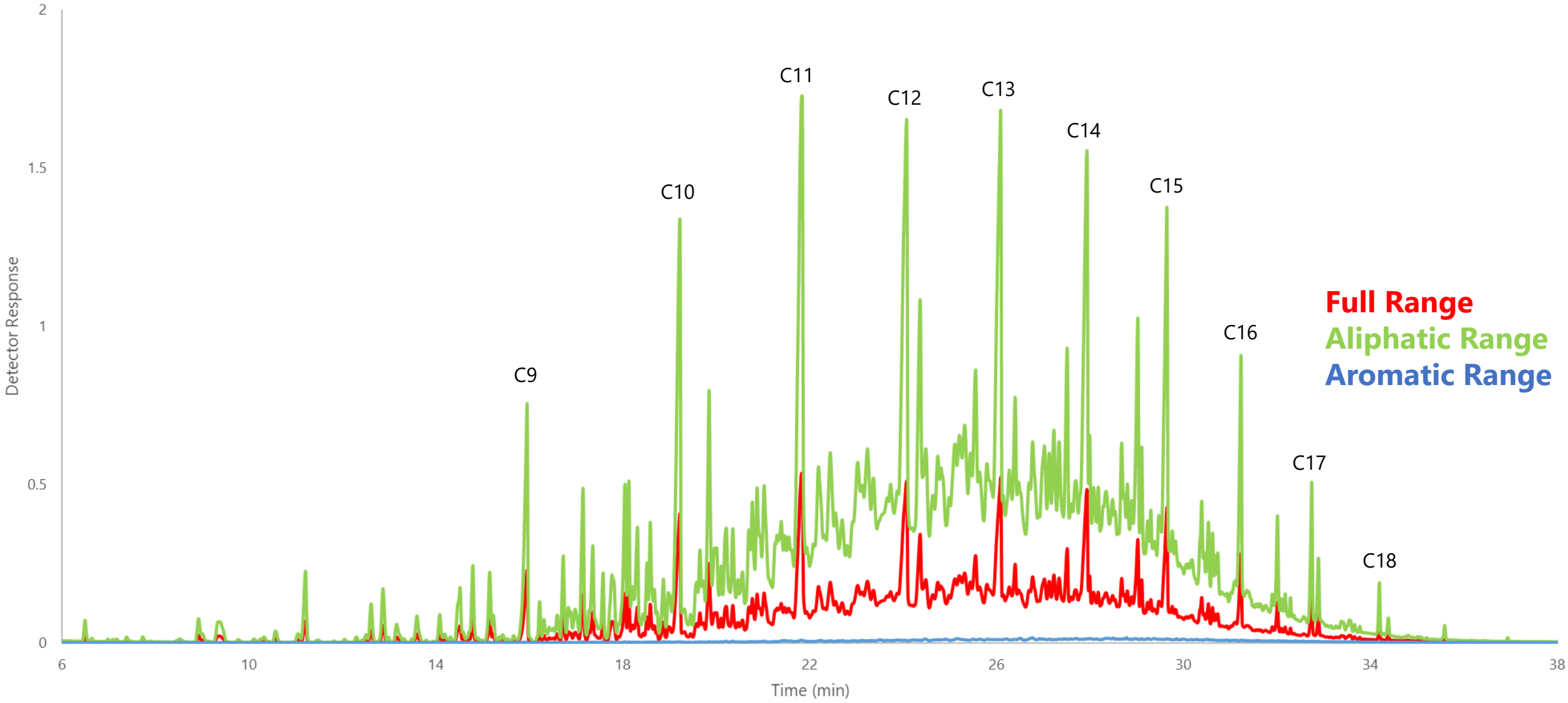
Aliphatic Elution

Aromatic Elution

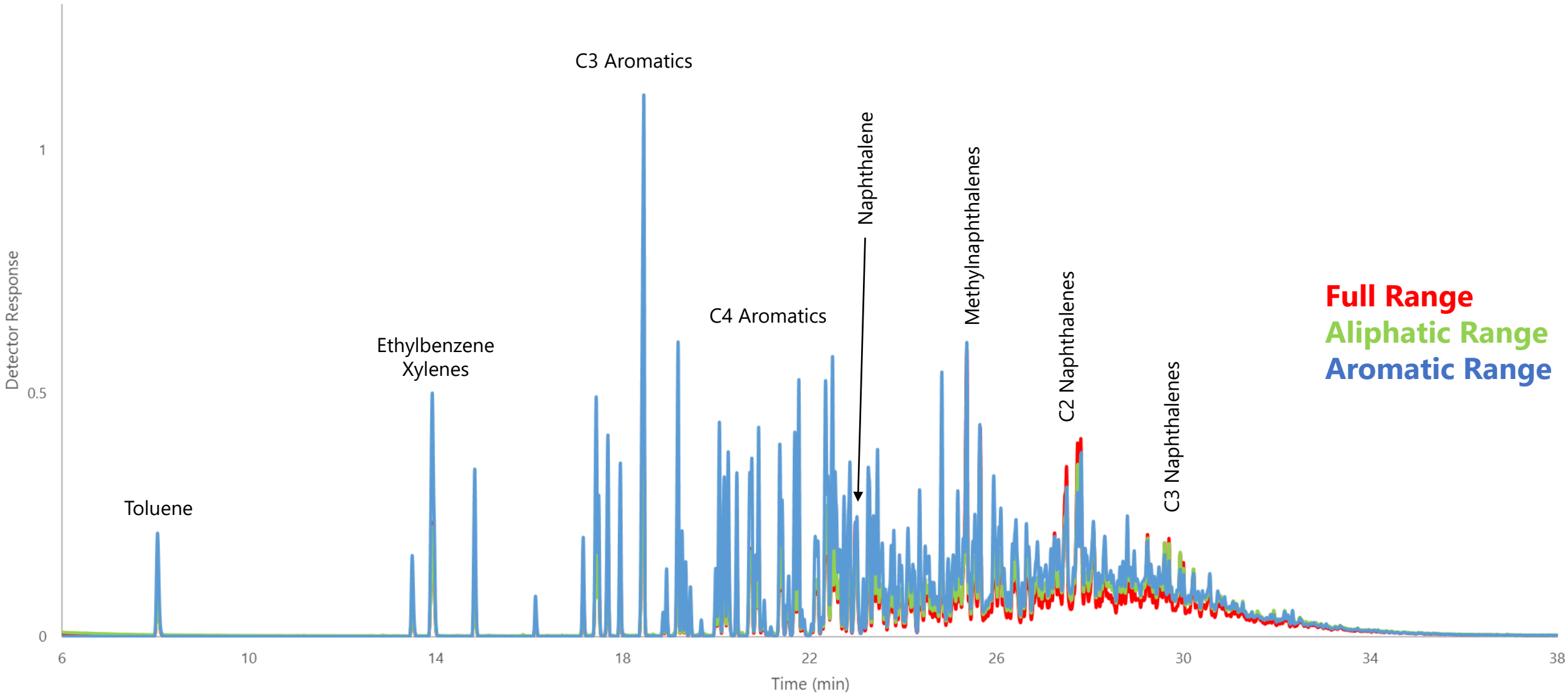
Concentration

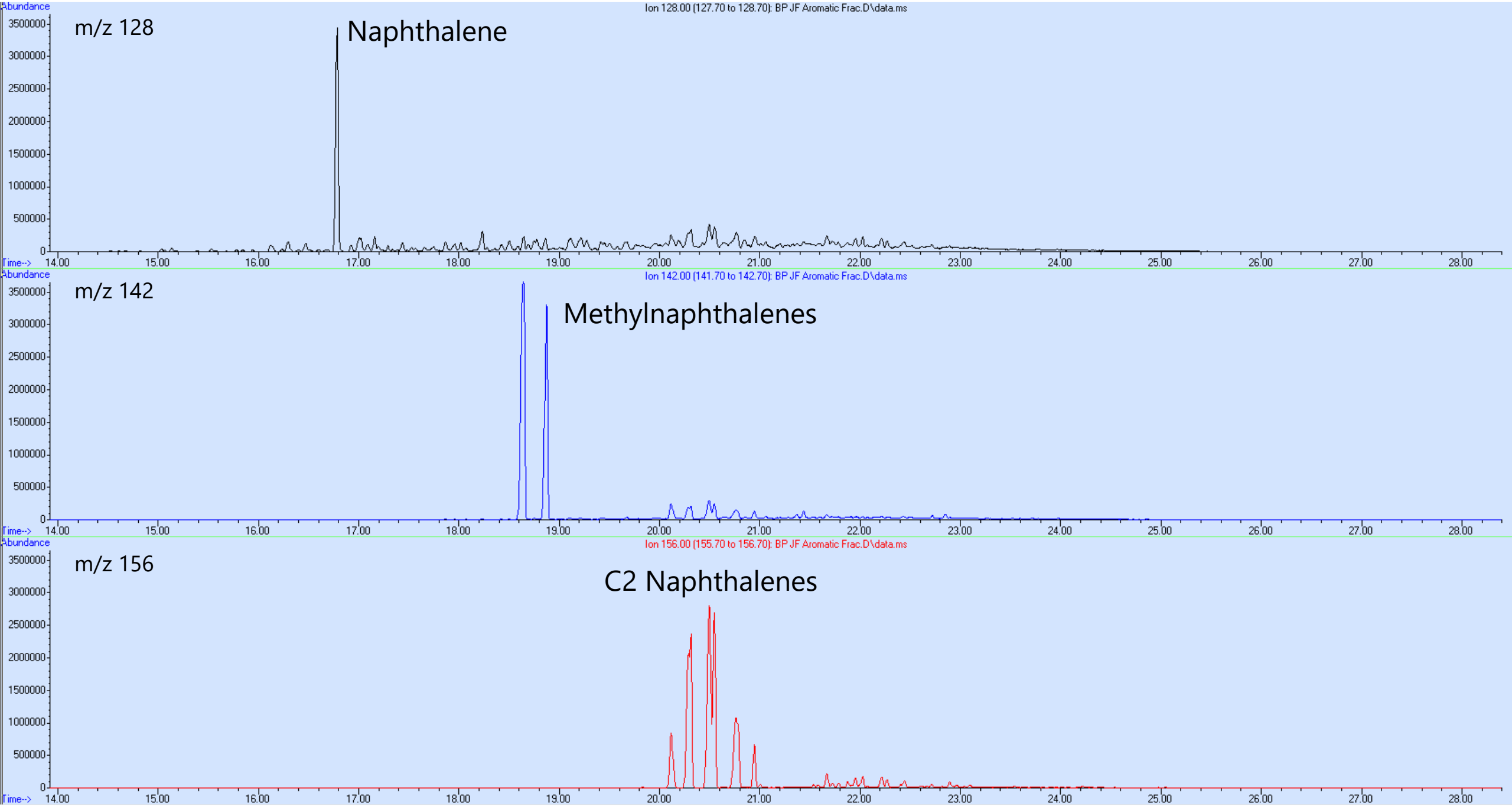


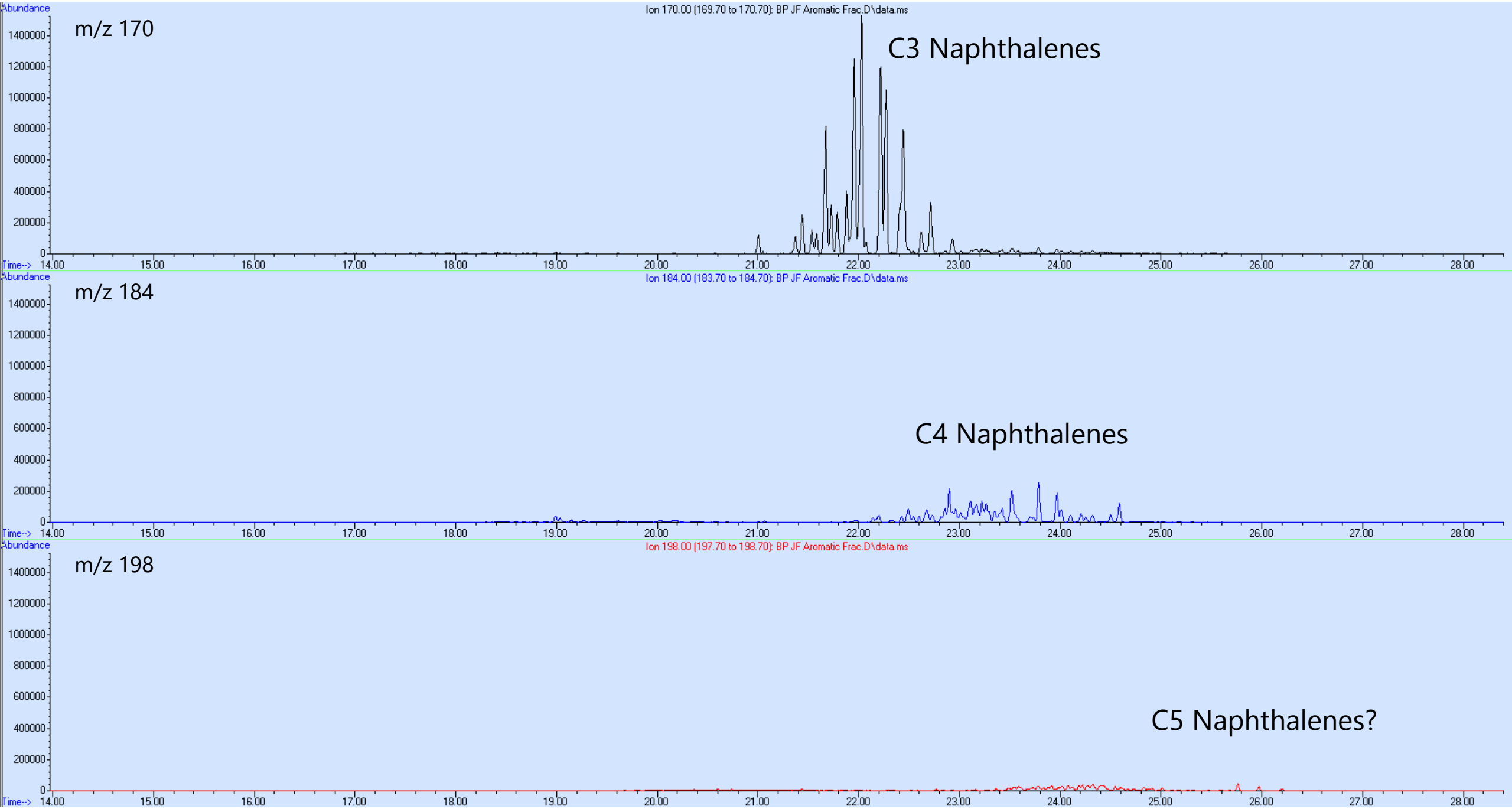
Jet Fuel – Aliphatic Fraction

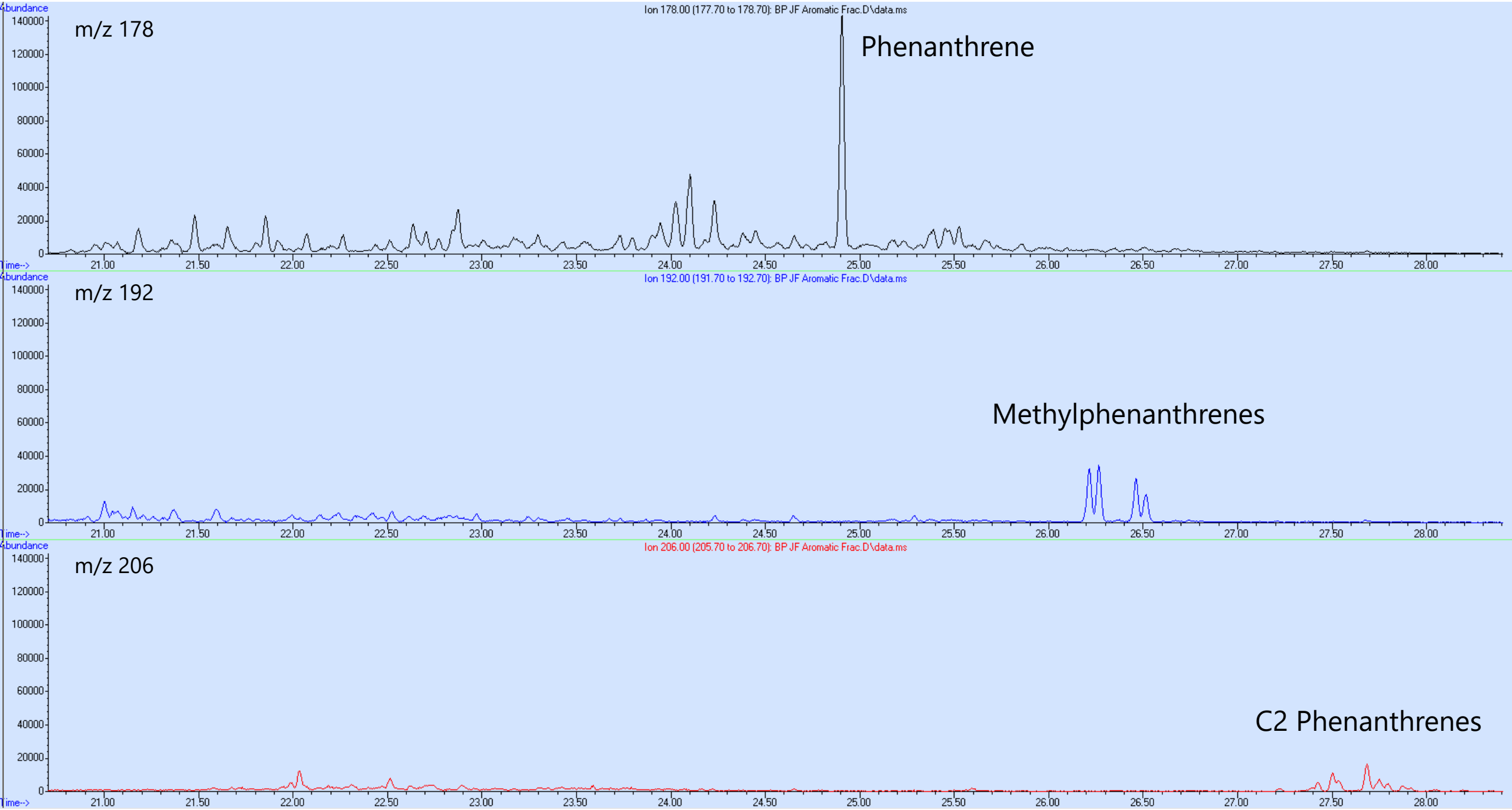


Jet Fuel – Aromatic Fraction

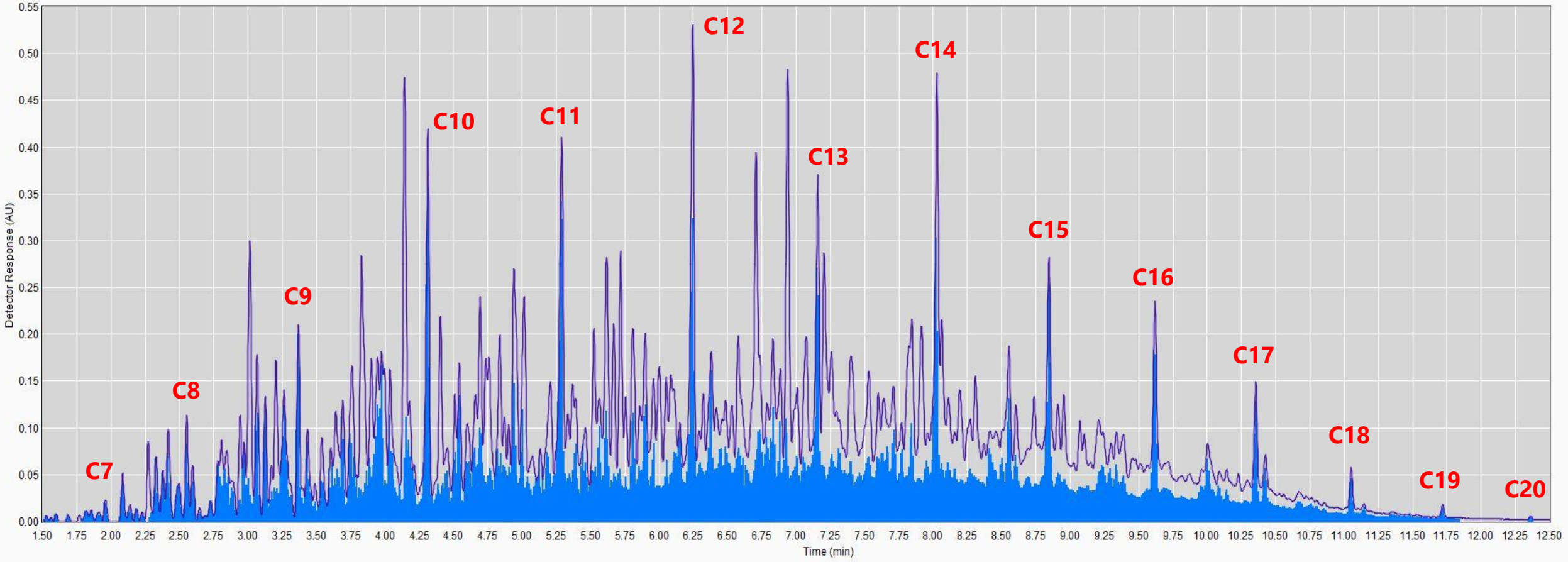



Abundance
Ion 128.00 (127.70 to 128.70): BP JF Aromatic Frac.D\data.ms
m/z 128
Naphthalene
Time-->
Abundance
Ion 142.00 (141.70 to 142.70): BP JF Aromatic Frac.D\data.ms
m/z 142
Methylnaphthalenes
Time-->
Abundance
Ion 156.00 (155.70 to 156.70): BP JF Aromatic Frac.D\data.ms
m/z 156
C2 Naphthalenes
Time-->

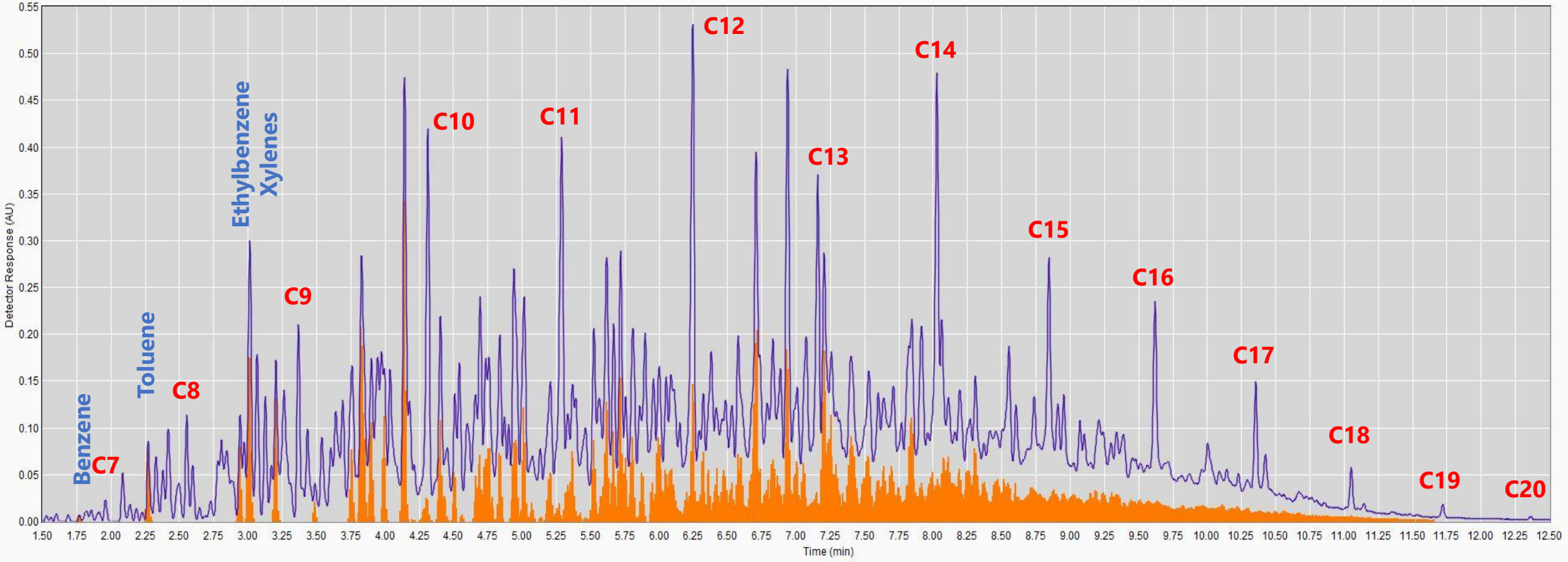

Abundance
Ion 170.00 (169.70 to 170.70): BP JF Aromatic Frac.D\data.ms
m/z 170
C3 Naphthalenes
Time-->
Abundance
Ion 184.00 (183.70 to 184.70): BP JF Aromatic Frac.D\data.ms
m/z 184
C4 Naphthalenes
Time-->
Abundance
Ion 198.00 (197.70 to 198.70): BP JF Aromatic Frac.D\data.ms
m/z 198
C5 Naphthalenes?
Time-->


Abundance
Ion 178.00 (177.70 to 178.70): BP JF Aromatic Frac.D\data.ms
m/z 178
Phenanthrene
Time-->
Abundance
Ion 192.00 (191.70 to 192.70): BP JF Aromatic Frac.D\data.ms
m/z 192
Methylphenanthrenes
Time-->
Abundance
Ion 206.00 (205.70 to 206.70): BP JF Aromatic Frac.D\data.ms
m/z 206
C2 Phenanthrenes
Time-->

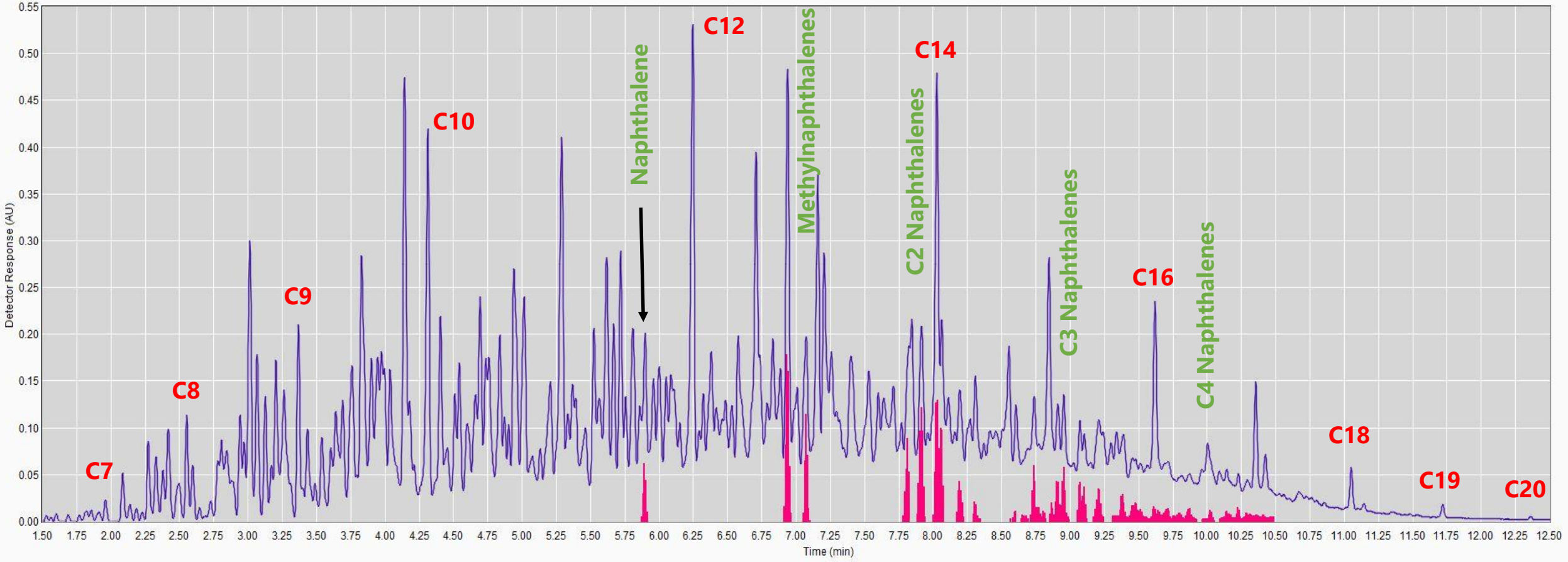
Jet Fuel Analysis – Total Saturates

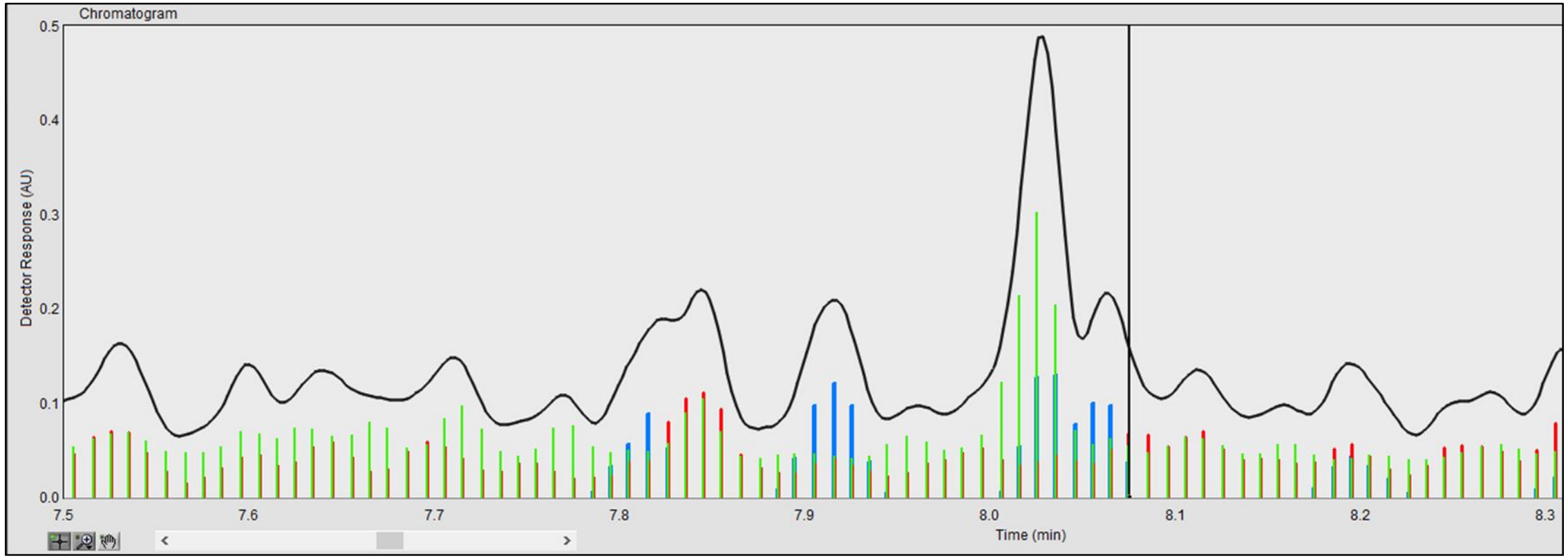


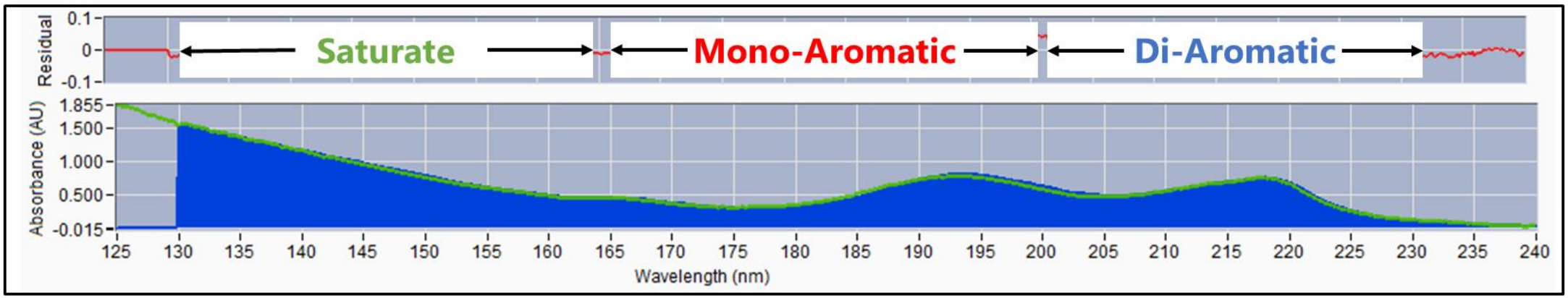
Jet Fuel Analysis – Total Mono-Aromatics



Jet Fuel Analysis – Total Di-Aromatics

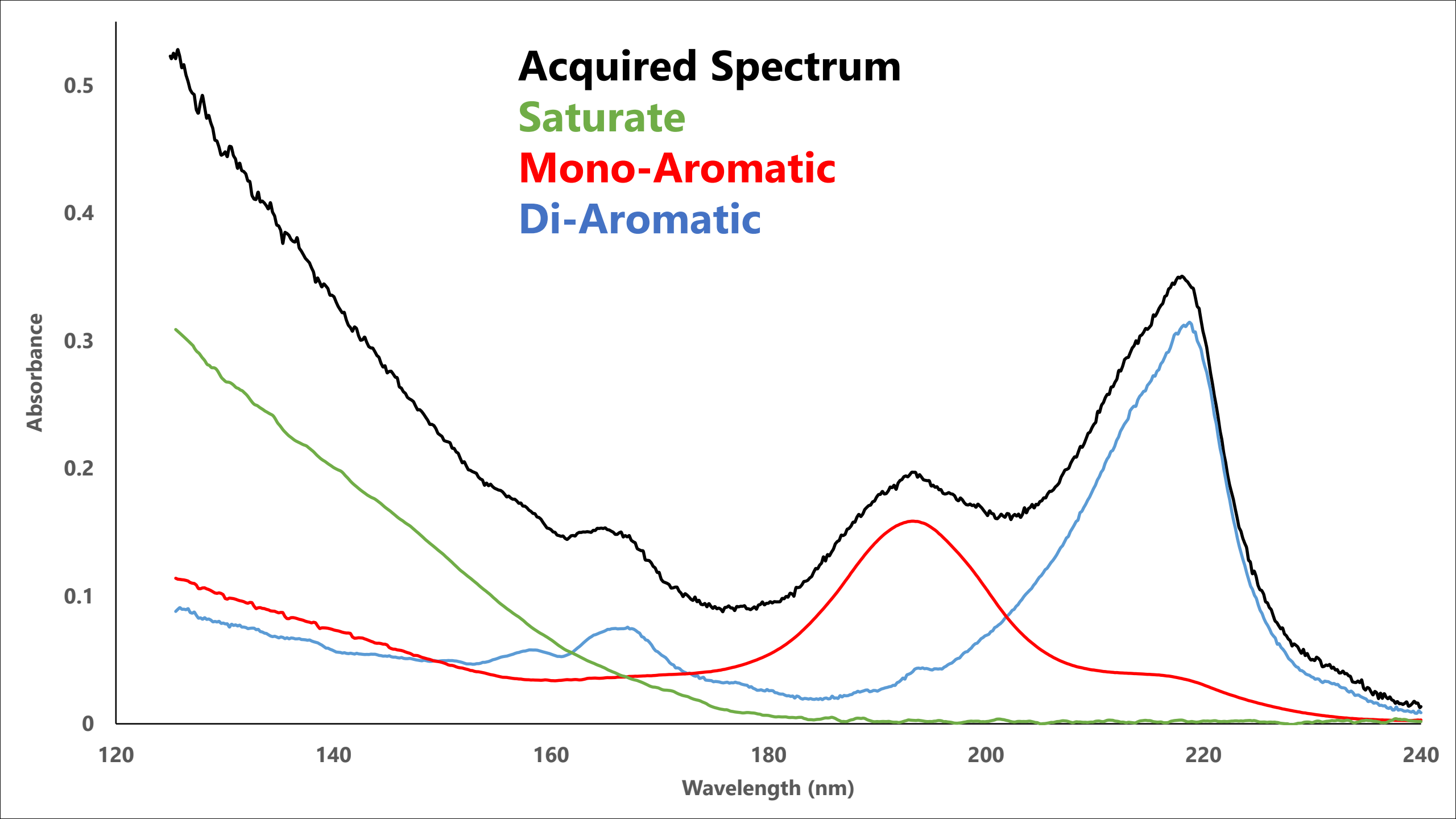




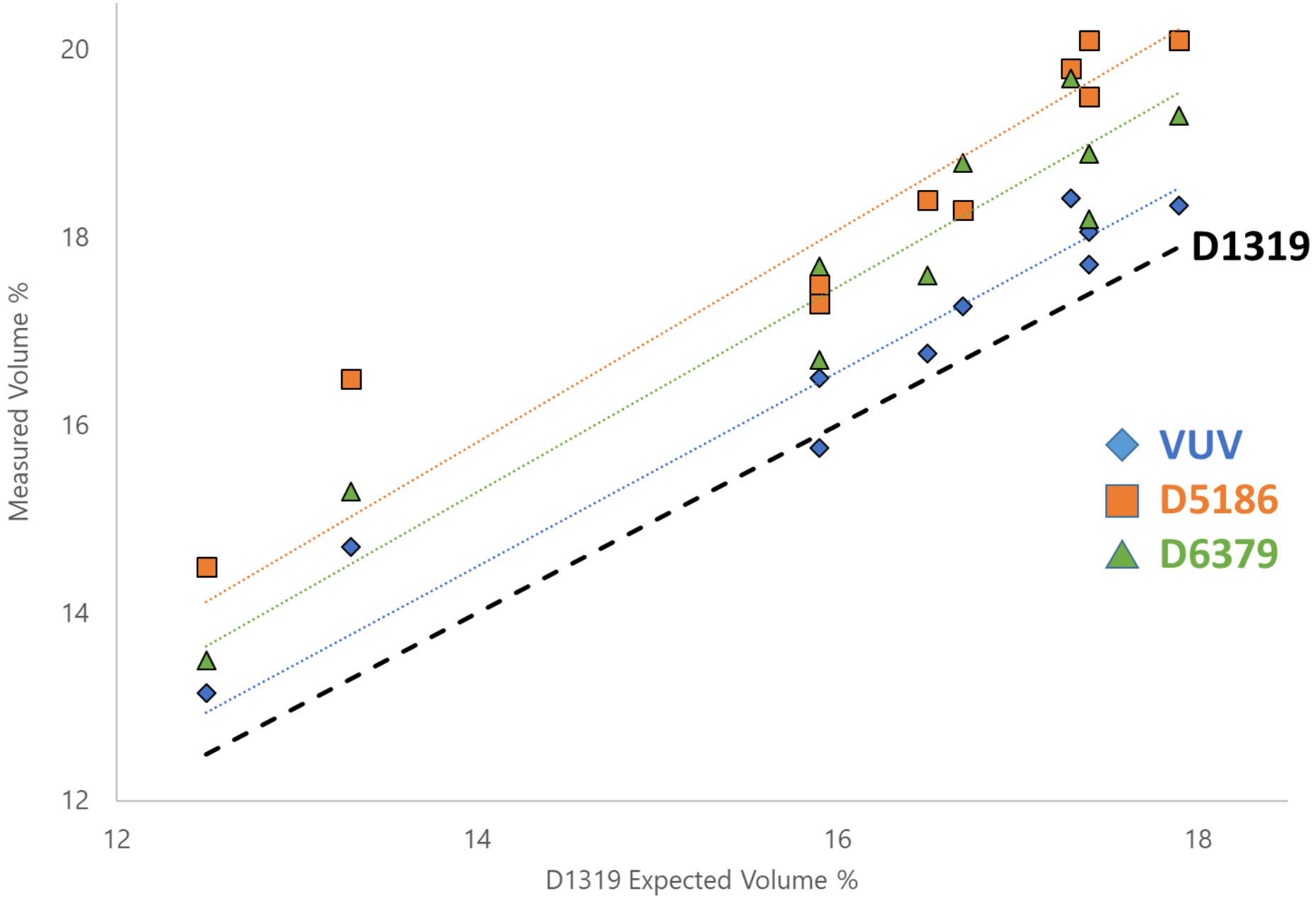


Analyte Table

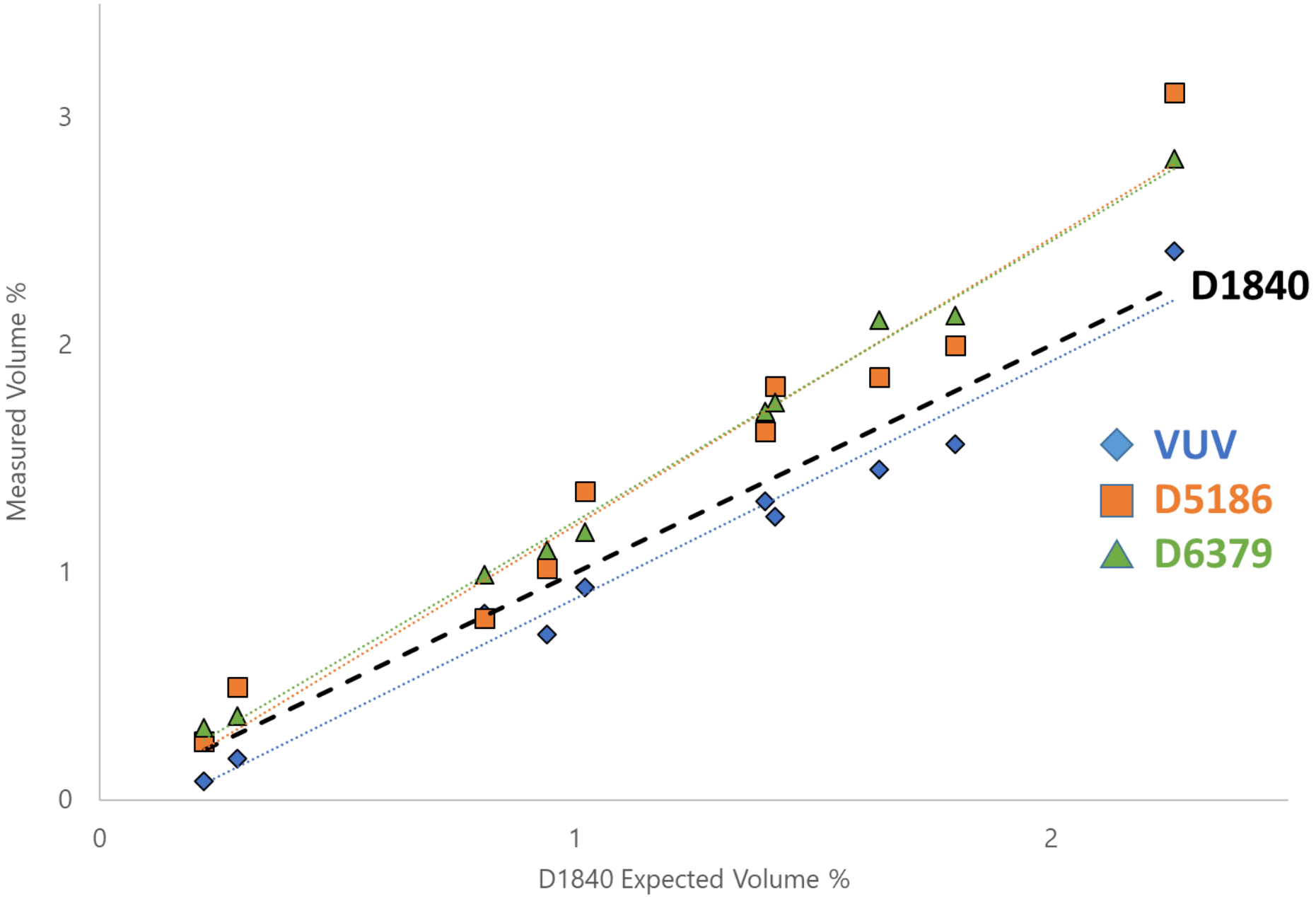
RRF Display	Analyte Name	Analyte Category	Fit Values	Spectra Ave.	Response (Sum, 4 Scans)	Ret. Index
Total Aromatics		Mono-Aromatic	0.7298	0.3713	0.2710	1400.0
Total Di-Aromatics		Di-Aromatic	0.5872	0.2555	0.1500	1418.0
Total Saturates		Saturate	1.0999	0.1984	0.2177	1390.0


Acquired Spectrum
Saturate
Mono-Aromatic
Di-Aromatic
Absorbance
0.5
0.4
0.3
0.2
0.1
0
120
140
160
180
200
220
240
Wavelength (nm)

Total Aromatics



Total Di-Aromatics



Inter-Run Precision of Jet Fuel

Total Saturates				Total Aromatics				Total Di-Aromatics			
Sample	Average	Std Dev	%RSD	Sample	Average	Std Dev	%RSD	Sample	Average	Std Dev	%RSD
AITF T277	82.2	0.03	**0.03**	AITF T277	17.8	0.03	**0.15**	AITF T277	1.88	0.003	**0.14**
ASTM 1703	80.9	0.02	**0.02**	ASTM 1703	19.1	0.02	**0.08**	ASTM 1703	0.87	0.004	**0.48**
ASTM 1711	87.6	0.01	**0.02**	ASTM 1711	12.4	0.01	**0.12**	ASTM 1711	2.11	0.006	**0.26**
CL18 3008	82.2	0.08	**0.10**	CL18 3008	17.8	0.08	**0.45**	CL18 3008	1.12	0.01	**1.21**
CL18 3011	84.4	0.02	**0.03**	CL18 3011	15.6	0.02	**0.13**	CL18 3011	0.10	0.003	**3.34**
CL18 3012	86.9	0.02	**0.03**	CL18 3012	13.1	0.02	**0.17**	CL18 3012	0.99	0.006	**0.59**

Conclusions

- PIONA analysis of gasoline
  - Fast and accurate, spectral deconvolution is very powerful
  - ASTM D8071 (IP# coming soon!), ILS complete
- Conjugated diolefins in gasoline
  - Can be analyzed as part of D8071; LODs as low as 0.01%
- VUV VHA
  - Prototype, but results match well with D8071
- Analysis of jet fuel
  - Data correlates well with existing methods, high precision
  - ILS complete, ASTM and IP #s coming very soon!