

PIONA by GC-VUV: ASTM D8071

Gas Chromatography - Vacuum Ultraviolet Spectroscopy (GC-VUV)

PRESENTED BY

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ASTM D8071-21

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: [D02.04.01](#)

Recommended

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Paraffins, Isoparaffins, Olefins, Naphthenes, Aromatics by Carbon Number from C1 to C15
Methanol, Ethanol, Benzene, Toluene, Ethylbenzene, Xylenes, Naphthalene, Methyl-naphthalenes, Isooctane

Copyright Clearance Center

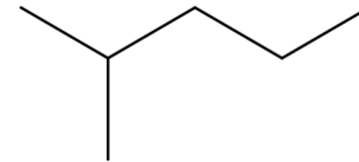
Concentrations Range.

- Paraffins (linear alkanes)



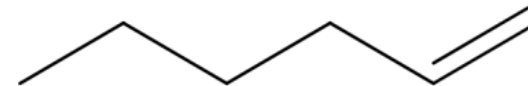
3.5% - 23.1% / Volumn

- Isoparaffins (branched alkanes)



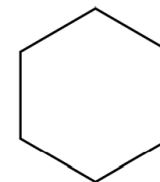
22.6% - 71.9% / Volumn

- Olefins (alkenes)



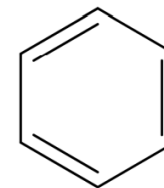
0.01% - 44.0% / Volumn

- Naphthenes (cycloalkanes)




0.6% - 18.4% / Volumn

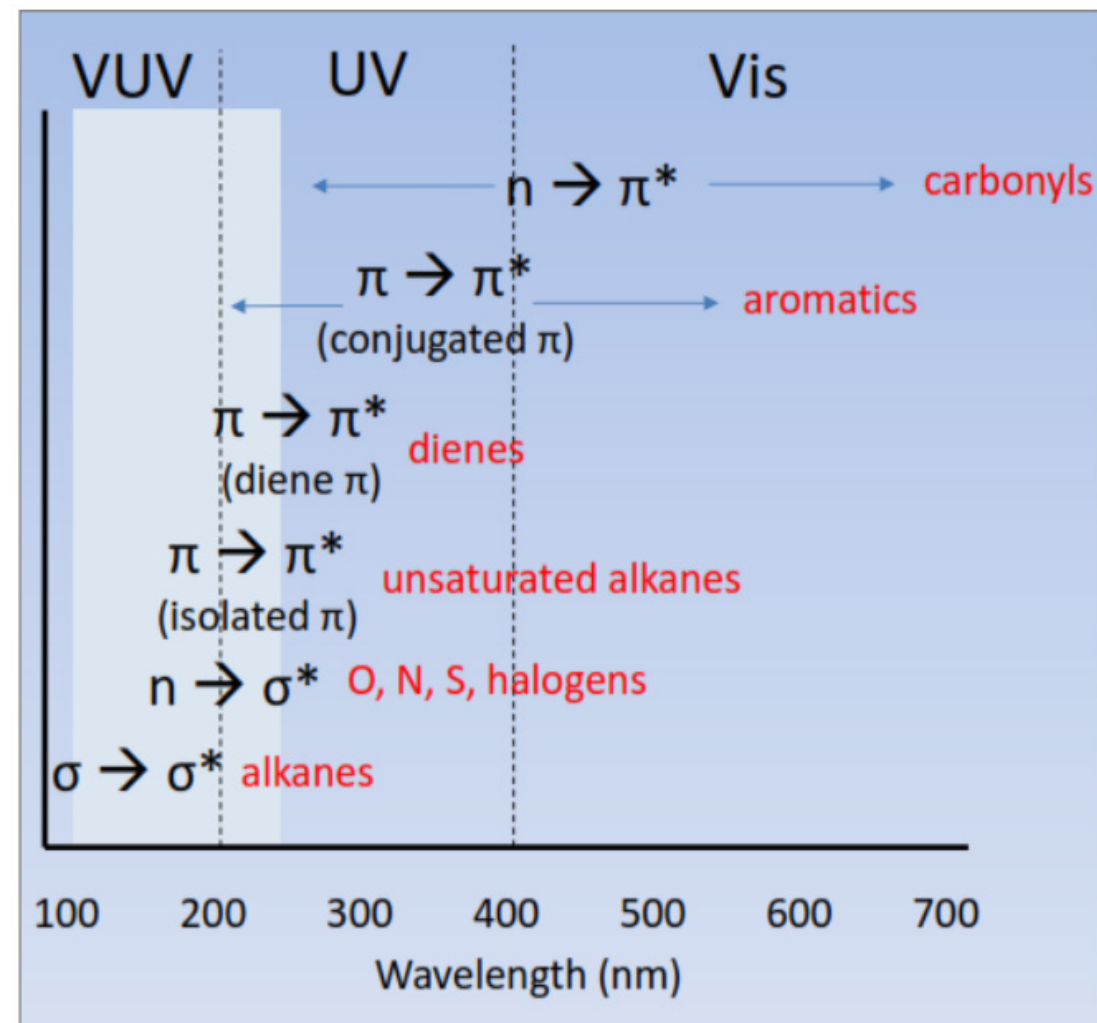
- Aromatics



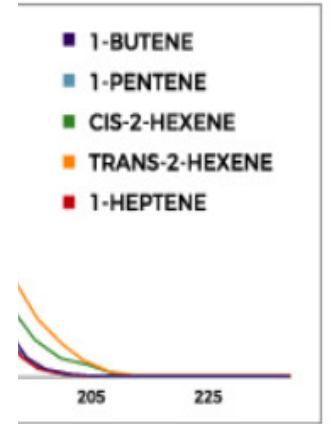
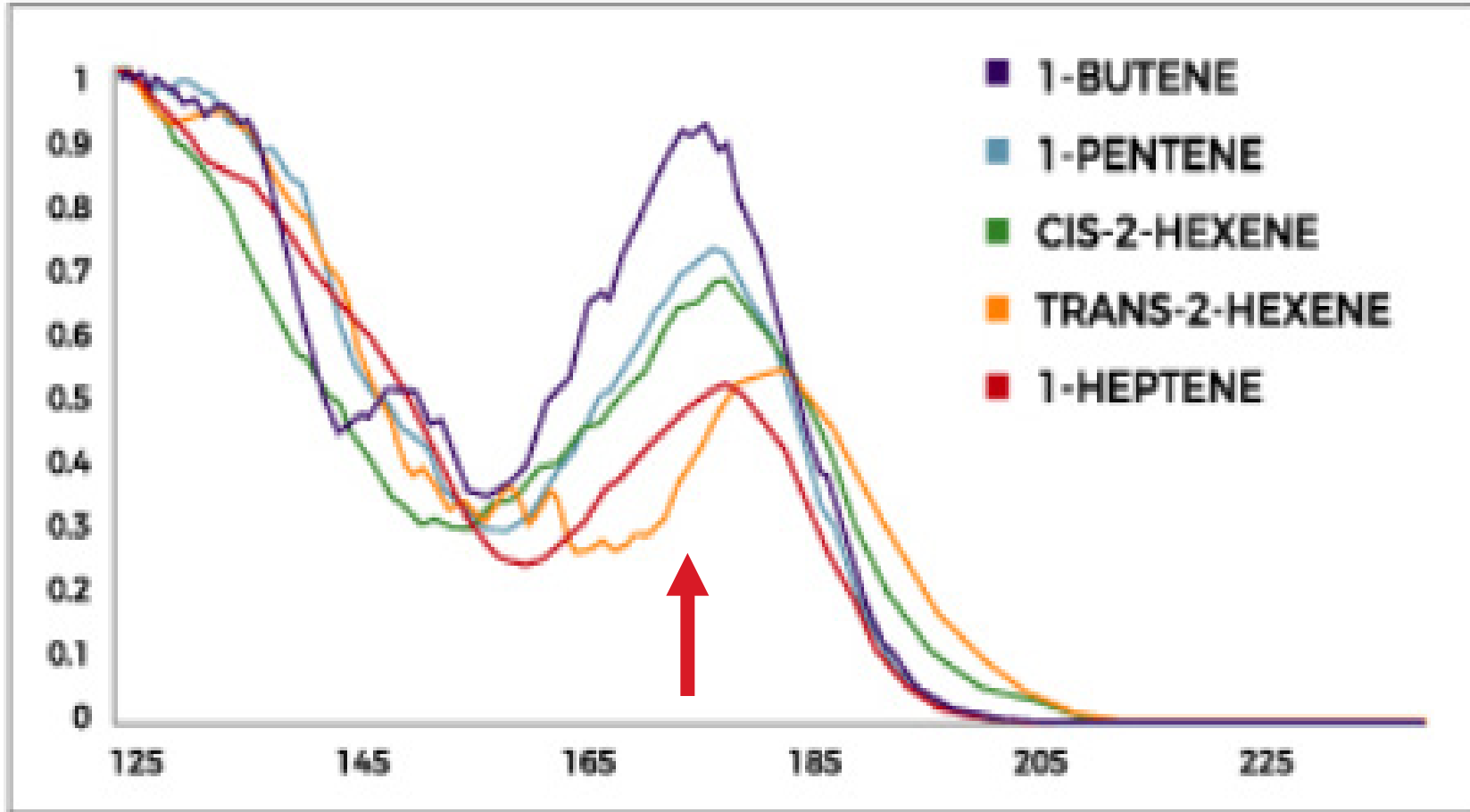
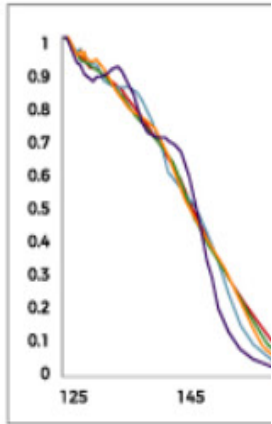
14.7% - 58.1% / Volumn

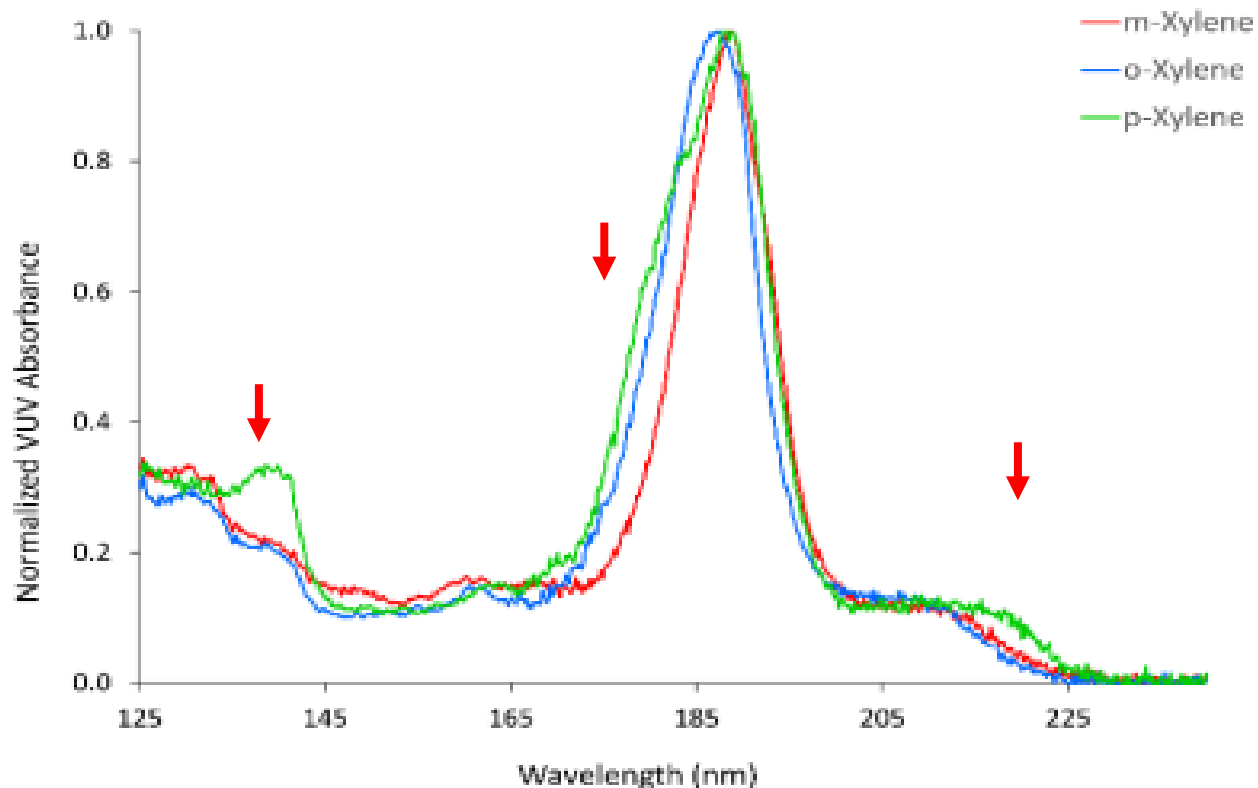
- Absorption spectroscopy in a new spectral region (<200 nm)
 - Previously only measurable using synchrotrons
- A universal technique that provides unique spectral fingerprints
 - High energy, low wavelength exposure produces electronic transitions between $\sigma \rightarrow \sigma^*$, $n \rightarrow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

Structure/Functional group		Transitions	λ_{max}
Alkane	C-C	$\sigma \rightarrow \sigma^*$	165
Alkene	C=C	$\pi \rightarrow \pi^*$	190
Aromatic		$\pi \rightarrow \pi^*$	190
Hydroxyl group	-OH	$n \rightarrow \sigma^*$	180
Carboxyl group	-COOH	$n \rightarrow \pi^*$	205
Nitro group	-NO ₂	$n \rightarrow \pi^*$	271
Amino group	-NH ₂	$n \rightarrow \pi^*$	190

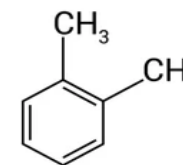


OLEFINS

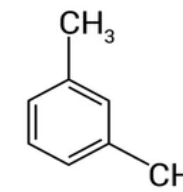




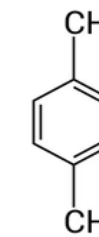
o-xylene



m-xylene

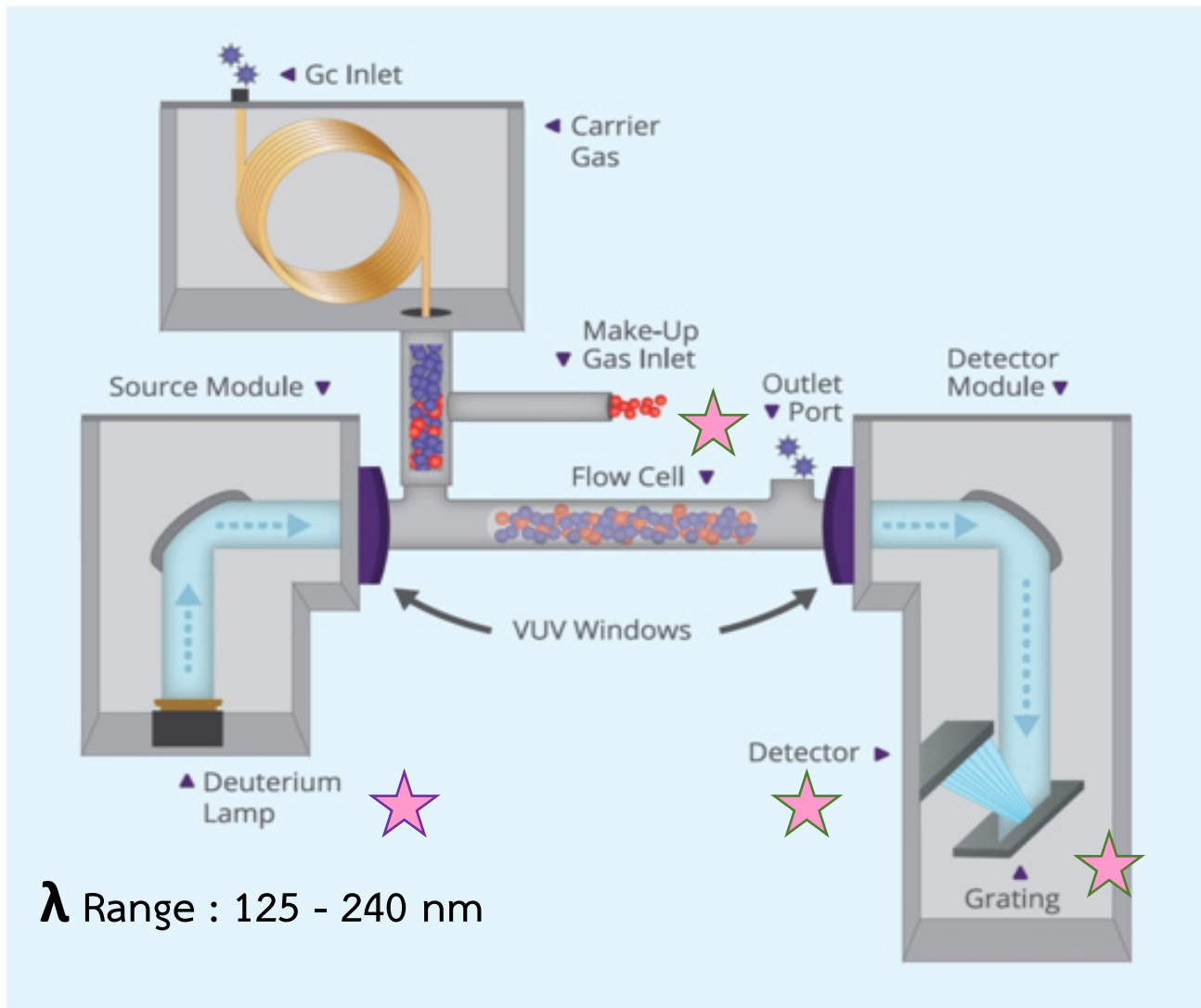


p-xylene



- The distinct VUV spectra of m-xylene, p-xylene and o-xylene. The compounds differ by only the positions of two methyl groups on a benzene ring, and are virtually impossible to distinguish by gas chromatography – mass spectrometry (GC-MS).

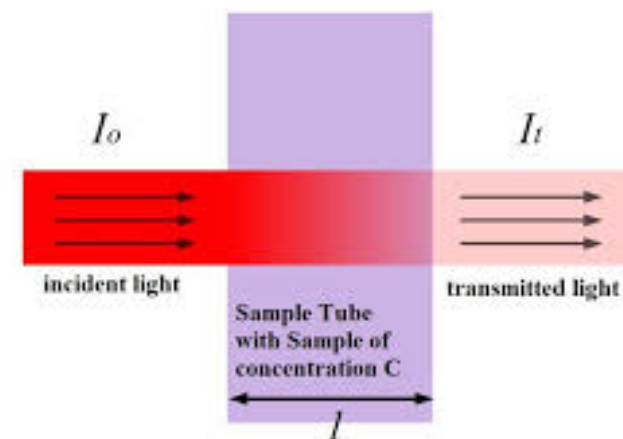
Vacuum Ultraviolet (VUV) System.



Quantitation : Beer-Lambert Law

$$A = \epsilon l c$$

- A is the **absorbance**
- ϵ is the **molar attenuation coefficient** or **absorptivity** of the attenuating species
- l is the optical path length in cm
- c is the **concentration** of the attenuating species



- Trace 1310 GC
 - 1 uL injection
 - Inlet: 250°C, split 300:1
 - Column: Restek Rxi-1ms (30 m x 0.25 mm, 0.25 um)
 - 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 N2
 - Flow cell and transfer line: 275°C
 - Acquisition rate: 4.5 spectra/sec
 - Acquisition range: 125-240 nm



Software Processing (1)

Chromatogram

Detector Response (AU)

Time (min)

Gasoline 87 Octane Number

Click to add or remove plots
 **Changes to the legend are not persistent
 125 - 240 (8071)

R & D Results Report File View Report Export to Excel

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

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

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

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

Report Method C:\Program Files\WUV Analytics\WUV Analyze 130 1953\Demos\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

Chi² Min 1.0000E-9 Chi² Max 1.0000E-1

Chi² delta (%) 60.00 R² 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

- Select Raw Data file.

File from gasoline analysis with GC-VUV

Run File (*.db) or Directory

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

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

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

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Chi² Max 1.0000E-1

Chi² delta (%) 60.00

R² 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

- Retention Index Marker : C4 - C15

The screenshot shows the software interface with the following components:

- Report File:** [Empty field]
- Buttons:** View Report, Export to Excel
- Navigation Tabs:** Input Files, Reverse Search, Create RI File, D8071, Analytes to Include, Advanced, Spectra, Fit Info
- File Selection Fields:**
 - Run File (*.db) or Directory: [Path]
 - Retention Index Markers File:** [Empty field] - **Retention Index markers file** (Callout box)
 - Reference Library File: [Path]
 - Report Method: [Path]
- Analysis Parameters:**
 - Initial Background Time (min): [Empty]
 - Analysis Time (min):
 - Begin: 1.600
 - End: 32.000
 - Time Step: 0.020
 - Methods: PIONA
 - Tiered Search Limit: 3 Analytes
 - Chromatogram Filter: 8071 Filters
 - Chi² Min: 1.0000E-9
 - Chi² Max: 1.0000E-1
 - Chi² delta (%): 60.00
 - R² Limit: 0.4000
 - Abs Threshold: 0.00050
 - BG Threshold: 0.00025
 - BG Scalar: 1.5
 - RI window +/-: 25
- Buttons:** Analyze, Load Parameters, Time Step Status, Save Parameters, Stop Analyzing

- Reference PIONA file absorbance spectra library from VUV.

The screenshot displays the SciSpec software interface. At the top, there are tabs for 'R & D' and 'Results', and a 'Report File' field. Below this is a navigation bar with tabs: 'Input Files', 'Reverse Search', 'Create RI File', 'D8071', 'Analytes to Include', 'Advanced', 'Spectra', and 'Fit Info'. The 'Input Files' section contains several fields: 'Run File (*.db) or Directory' (C:\Program Files\VUV Analytics\VUV Analyze 130 1953\Demos\D8071\Demo VUV-CS.db), 'Retention Index Markers File', 'Reference Library File' (highlighted with a red arrow and a callout box), and 'Report Method' (C:\Program Files\VUV Analytics\VUV Analyze 130 1953\Demos\D8071\18 Report Method.VUV_RM). A large blue callout box with the text 'PIONA compound absorbance spectra library' is overlaid on the 'Reference Library File' field. Below the file selection area is the 'Analysis Parameters' section, which includes: '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), and 'RI window +/-' (25). At the bottom, there are buttons for 'Analyze', 'Load Parameters', 'Time Step Status', 'Save Parameters', and 'Stop Analyzing'.

- Template report

The screenshot displays the software's configuration window for report generation. At the top, there are tabs for 'R & D' and 'Results', and a 'Report File' input field. Below this is a navigation bar with tabs: 'Input Files', 'Reverse Search', 'Create RI File', 'D8071', 'Analytes to Include', 'Advanced', 'Spectra', and 'Fit Info'. The 'Input Files' section contains three file paths with 'Refresh' buttons: 'Run File (*.db) or Directory', 'Retention Index Markers File', and 'Reference Library File'. The 'Report Method' field is highlighted with a blue box and contains the text 'PIONA report method', with a red arrow pointing to it from the left. Below this is the 'Analysis Parameters' section, which includes 'Initial Background Time (min)', 'Analysis Time (min)' (with 'Begin' at 1.800 and 'End' at 32.000), 'Time Step' at 0.020, 'Methods' (set to 'PIONA'), 'Tiered Search Limit' (3 Analytes), 'Chromatogram Filter' (8071 Filters), 'Chi² Min' (1.0000E-9), 'Chi² Max' (1.0000E-1), 'Chi² delta (%)' (60.00), 'R² Limit' (0.4000), 'Abs Threshold' (0.00050), 'BG Threshold' (0.00025), 'BG Scalar' (1.5), and 'RI window +/-' (25). At the bottom, there are buttons for 'Analyze', 'Load Parameters', 'Time Step Status', 'Save Parameters', and 'Stop Analyzing'.

Chromatogram

Detector Response (AU)

Time (min)

Gasoline 87 Octane Number

Click to add or remove plots

**Changes to the legend are not persistent

125 - 240 (8071)

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\WUV Analyze 130 1953\Demos\D8071\Demo VUV-CS.db						<input type="button" value="Refresh"/>	
Analytics\WUV Analyze 130 1953\Demos\D8071\Demo VUV RI.bt						<input type="button" value="Refresh"/>	
Analytics\WUV Analyze 130 1953\Demos\WUV PIONA ASTM D8071 rev 1.1.0.db						<input type="button" value="Refresh"/>	
Report Method C:\Program Files\WUV Analytics\WUV Analyze 130 1953\Demos\D8071\D8071-18 Report Method.VUV_RM						<input type="button" value="Refresh"/> <input type="button" value="Edit / Create ..."/>	

Analysis Parameters

Initial Background (min)

Begin 500 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

Chi² Min 1.0000E-9

Chi² Max 1.0000E-1

Chi² delta (%) 60.00

R² Limit 0.4000

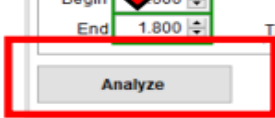
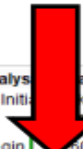
Abs Threshold 0.00050

BG Threshold 0.00025

BG Scalar 1.5

RI window +/- 25

Single File or Batch Processing





Chromatogram

Click to add or remove plots

**Changes to the legend are not persistent

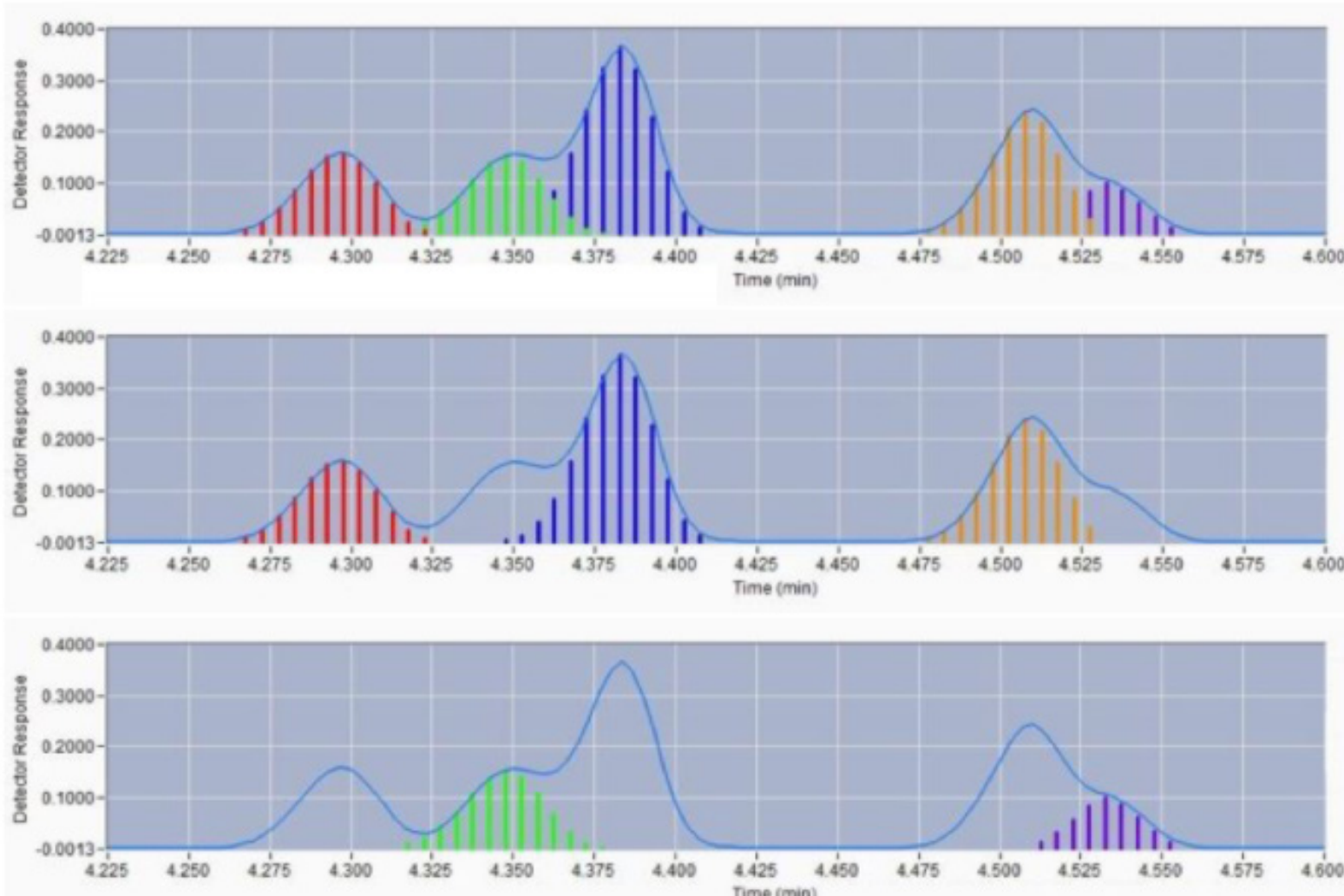
Response		Mass %			Volume %	Amount			Config
P	I	O	N	A	Category	Mass %	RT (min.)	RRF	Density
C1					Paraffin	8.8192			
C2					Isoparaffin	42.5362			
C3					Olefin	9.1821			
C4	1.2604	0.1114	0.0581		Naphthene	8.1559			
C5	3.1375	6.7534	3.7404	0.1456	Aromatic	20.4855			
C6	1.9858	7.3473	2.8238	1.6022	Methanol	0.0000			
C7	1.1744	5.6581	1.0126	2.2271	Ethanol	10.8211	2.370	1.029	0.789
C8	0.5486	18.1335	1.0130	1.6267	Methyl tert-butyl ether	0.0000			
C9	0.3854	2.8188	0.1990	1.3372	iso-octane	7.5817	4.930	0.674	0.692
C10	0.1992	0.8996	0.2441	0.7377	Naphthalene	0.1886	22.429	0.207	1.025
C11	0.0894	0.6189	0.0679	0.4207	Methylnaphthalenes	0.2171	24.810	0.250	1, 1.010
C12	0.0385	0.1390	0.0232	0.0588	Benzene	0.8250	4.029	0.258	0.879
C13		0.0514		0.0350	Toluene	3.9218	7.209	0.267	0.867
C14		0.0047			Ethylbenzene	0.9860	12.730	0.284	0.867
C15					Xylenes	4.7461	13.190	0.284	0.870
C16									
C17									
C18									
C19									
Total	8.8192	42.5362	9.1821	8.1559	20.4855				

C19				
Total	8.8192	42.5362	9.1821	8.1559

LIST POOF FITS

- 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

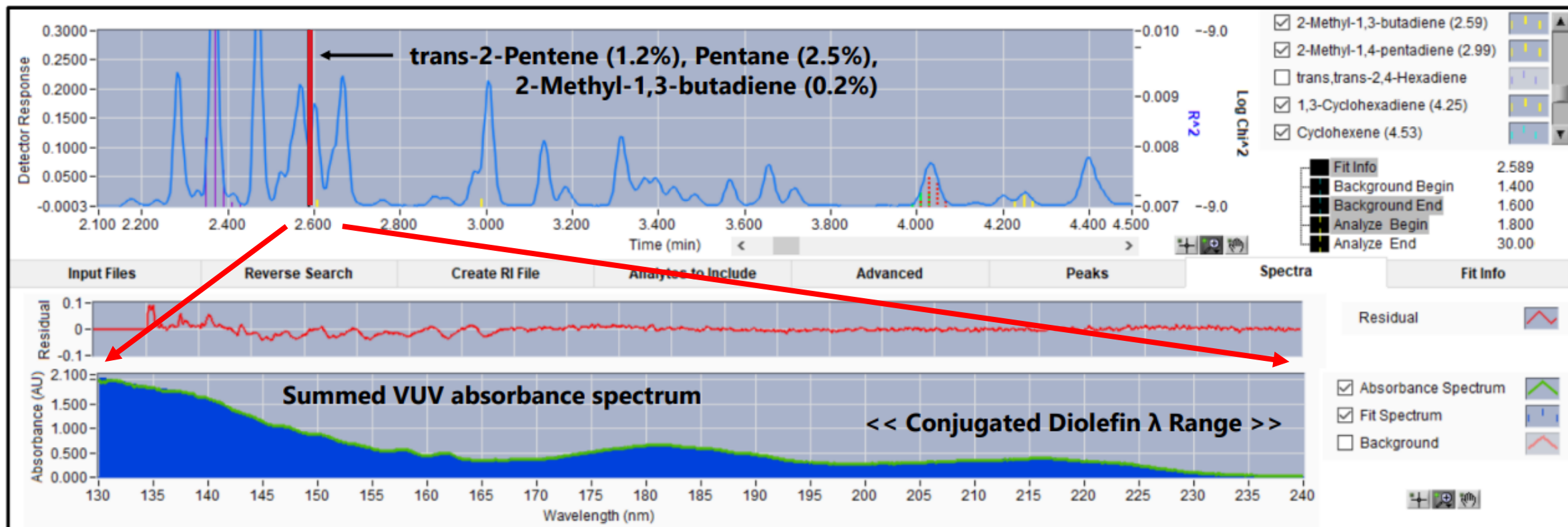
Time Interval Deconvolution (TID)



TID

- Slicing a chromatogram into regularly spaced time intervals, each with a unique summed absorbance spectrum.
- Each slice is then automatically analyzed to determine the contribution of each compound to the measured spectra.
- This means complex chromatograms can be easily, reliably deconvolved and analyzed, without the need for a fixed peak table.

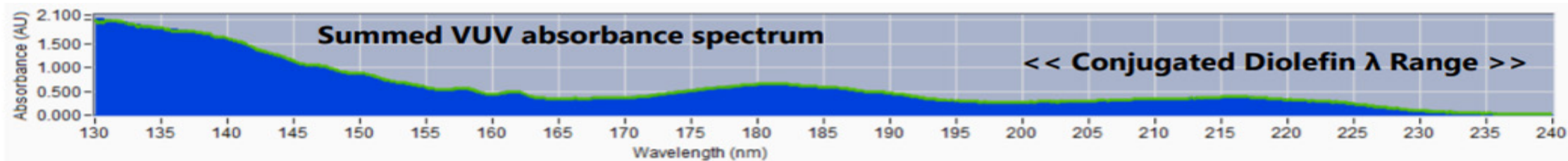
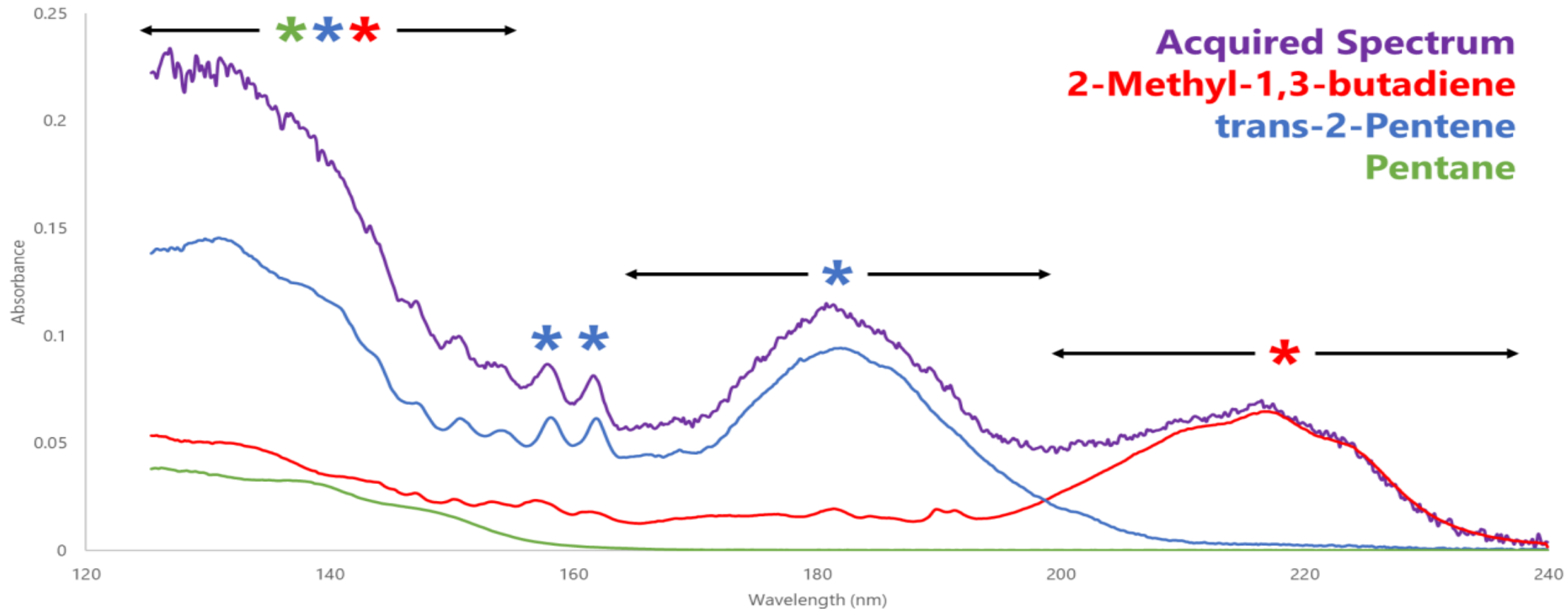
VUV Spectral Deconvolution of Hydrocarbons in Gasoline



Chi² 2: 1.735E-4
R²: 0.9992

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



- **Column : 30m x 0.25mm x 0.25 μ m 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

- **GC-FID (ASTM D6730) : DHA**

- 100m non-polar column, 5% diphenyl “tuning” precolumn
- Speciation of up to 600 compounds in gasoline-range fuels (though not all compounds are identified by name)
- Cryogenic oven start (5°C)
- Run time: 174 minutes
- Requires a trained user to go through data peak by peak.
- Any unexpected coelutions cannot be identified with the FID data, requires MS analysis.

- **Multi-dimensional GC-FID (ASTM D6839) : Reformulyzer**

- Measures PIONA compounds and oxygenates in gasoline and gasoline blend streams
- Physically separates compounds using a series of columns and traps actuated by 6-port valves
- 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.

- ASTM D8071 provides compound class characterisation (PIONA) and individual compounds methanol, ethanol, isooctane, BTEX and naphthalenes. Excellent equivalence with existing methods D5443 & D6839 (Reformulyzer).
- A full equivalence report on 12 sample types is available on request. D8071 also gives correlated values for aromatics (D5769 & D1319), benzene (D3606), olefins (D1319 & D6550), and ethanol (D5599), so it delivers five ASTM methods in one. PIONA-VUV is fast: only 34 minutes runtime.
- GC-VUV for Fuels is a platform developed with value, ease-of-use, and flexibility in mind. Running multiple methods on one VUV Analyzer for Fuels allows you to rapidly switch between different analyses using the same GC, detector, and software. This simplifies operation for the analyst and accelerates analysis time across methods, including: gasoline (ASTM D8071) , jet fuel (ASTM D8267)

ASTM METHOD	D6550	D4815	D5599	D1319	D3606	D5769	D5580	D6729 / D6730	D6839	D8071
TECHNIQUE	SFC	MDGC-FID	GC-OFID	FIA	GC-TCD	GC-MS	MDGC-FID	GC-FID	Reformulyzer®	GC-VUV
Aromatics				X		X	X	X	X	X
Benzene					X	X	X	X	X	X
Olefins X	X			X				X	X	X
Ethanol		X	X					X	X	X
Ethyl Bz.						X	X	X		X
IsoParaffin								X	X	X
Methanol		X	X					X		X
Methyl Naph.								X		X
Naphthalene								X		X
Naphthene								X	X	X
Paraffin								X	X	X
Toluene					X	X	X	X		X

- ✓ Conjugated Diolefin Analysis by GC-VUV
- ✓ Jet Fuel Analysis by GC-VUV ASTM D8267
- ✓ Diesel and Biodiesel by GC-VUV ASTM D8368

