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: D02.04.0L

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

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

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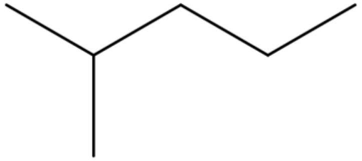
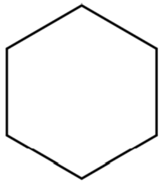
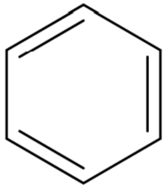
ASTM D8071 scope : PIONA

ASTM D8071

Concentrations Range.

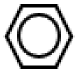
- Paraffins (linear alkanes)  3.5% - 23.1% / Volumn
- Isoparaffins (branched alkanes)  22.6% - 71.9% / Volumn
- Olefins (alkenes)  0.01% - 44.0% / Volumn
- Naphthenes (cycloalkanes)  0.6% - 18.4% / Volumn
- Aromatics  14.7% - 58.1% / Volumn

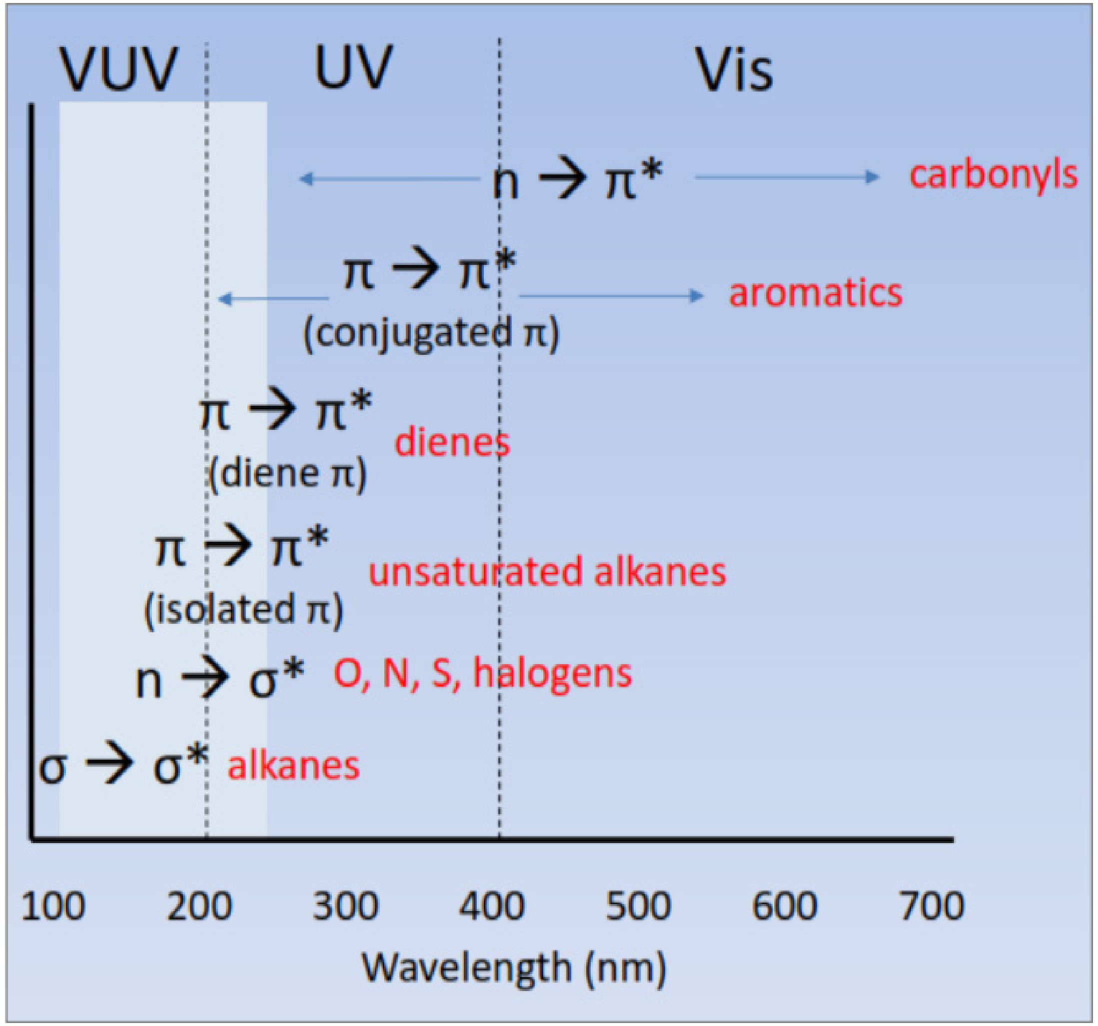
Vacuum Ultraviolet (VUV) Absorption Spectroscopy

VUV ANALYTICS

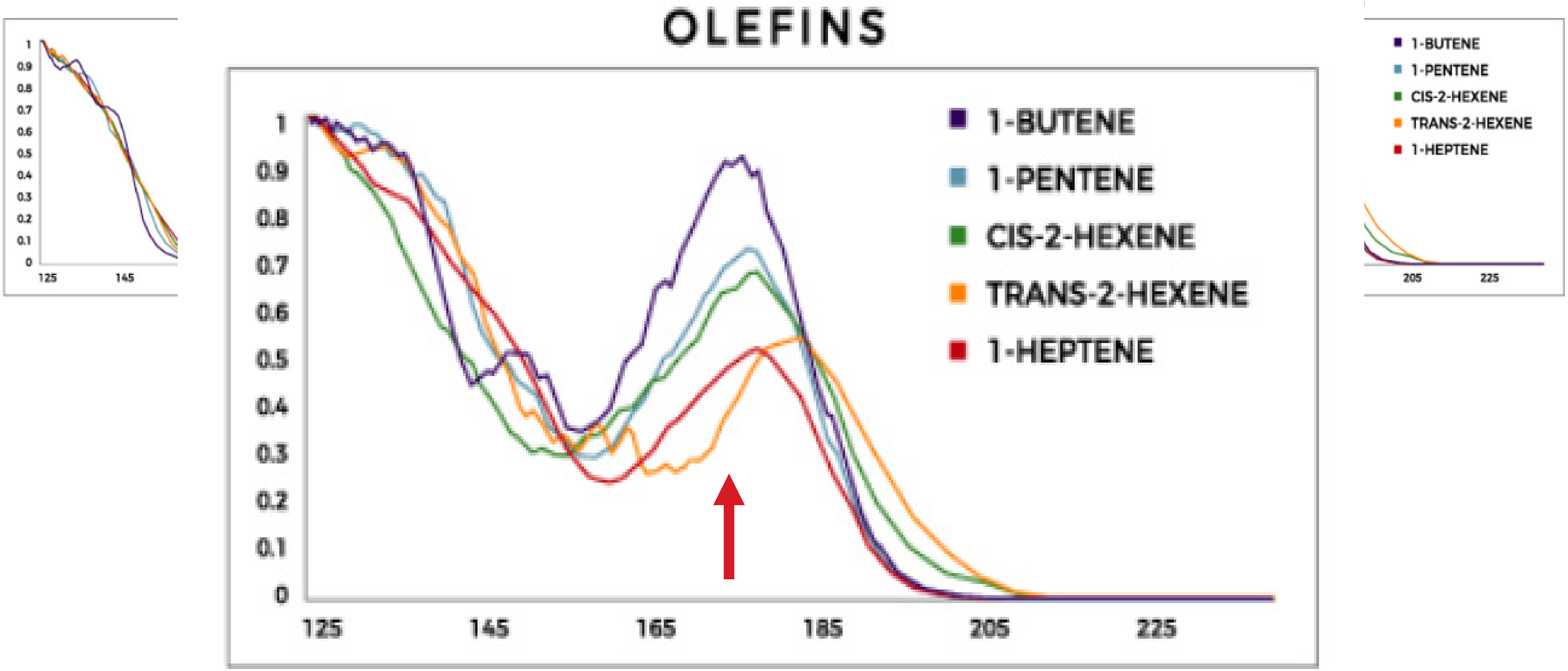
- Absorption spectroscopy in a new spectral region (<200 nm)
  - Previously only measurable using synchrotrons
- A universal technique that provides unique spectral fingerprints
  - High energy, low wavelength exposure produces electronic transitions between $\sigma \rightarrow \sigma^*$, $n \rightarrow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

Structure vs Transitions

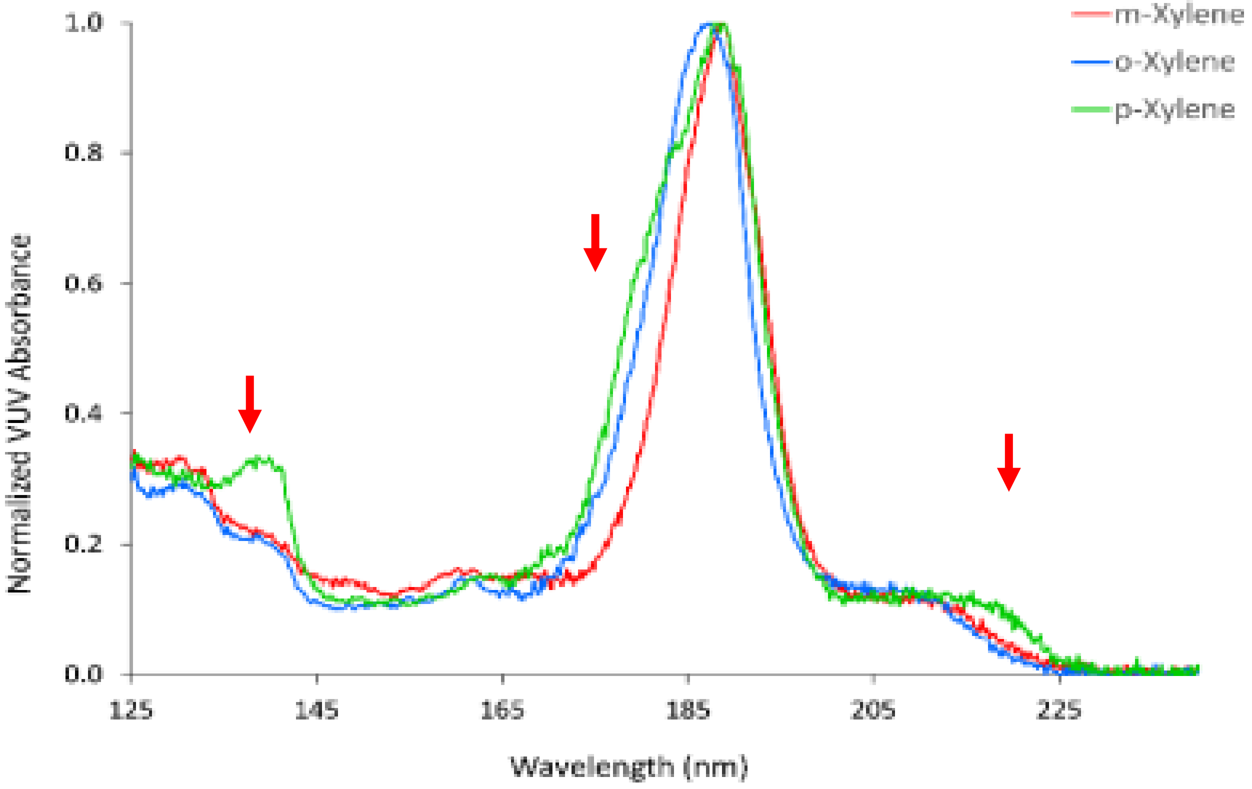
Structure/Functional group		Transitions	λmax
Alkane	C-C	$\sigma \rightarrow \sigma^*$	165
Alkene	C=C	$\pi \rightarrow \pi^*$	190
Aromatic		$\pi \rightarrow \pi^*$	190
Hydroxyl group	- OH	$n \rightarrow \sigma^*$	180
Carboxyl group	- COOH	$n \rightarrow \pi^*$	205
Nitro group	- NO2	$n \rightarrow \pi^*$	271
Amino group	- NH2	$n \rightarrow \pi^*$	190

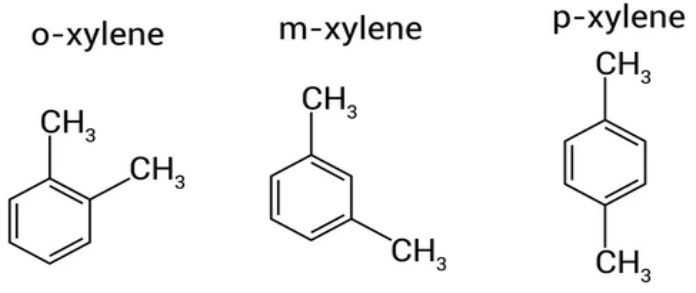


Spectral fingerprints..



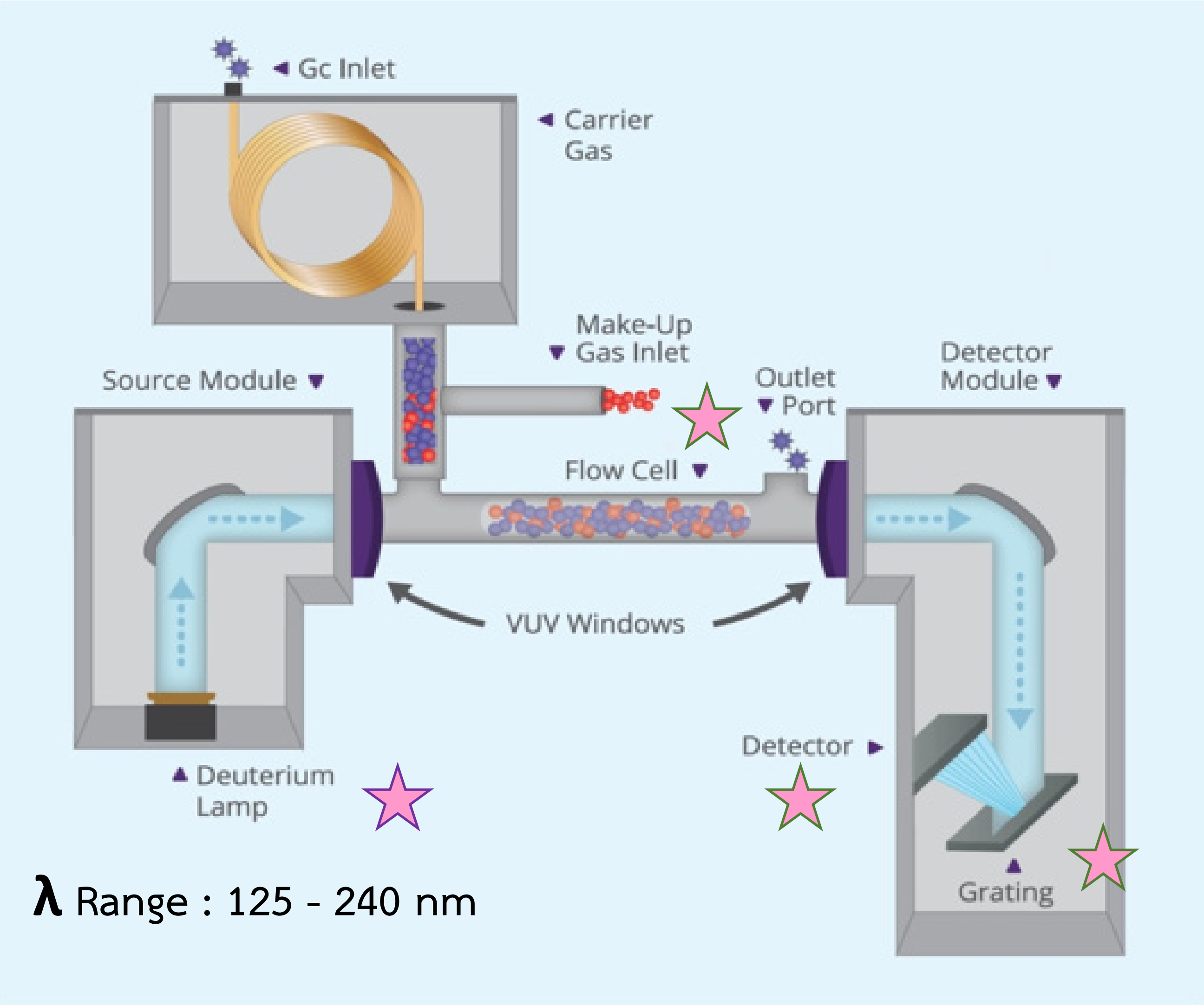
Spectral fingerprints : Isomer





- 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).

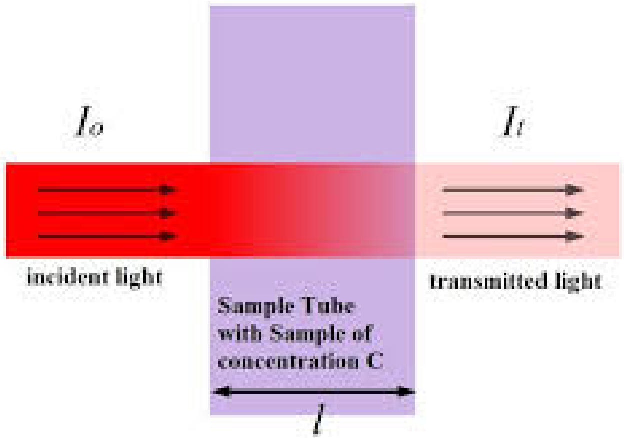
Vacuum Ultraviolet (VUV) System.



Quantitation : Beer-Lambert Law

$$A = \varepsilon \ell c$$

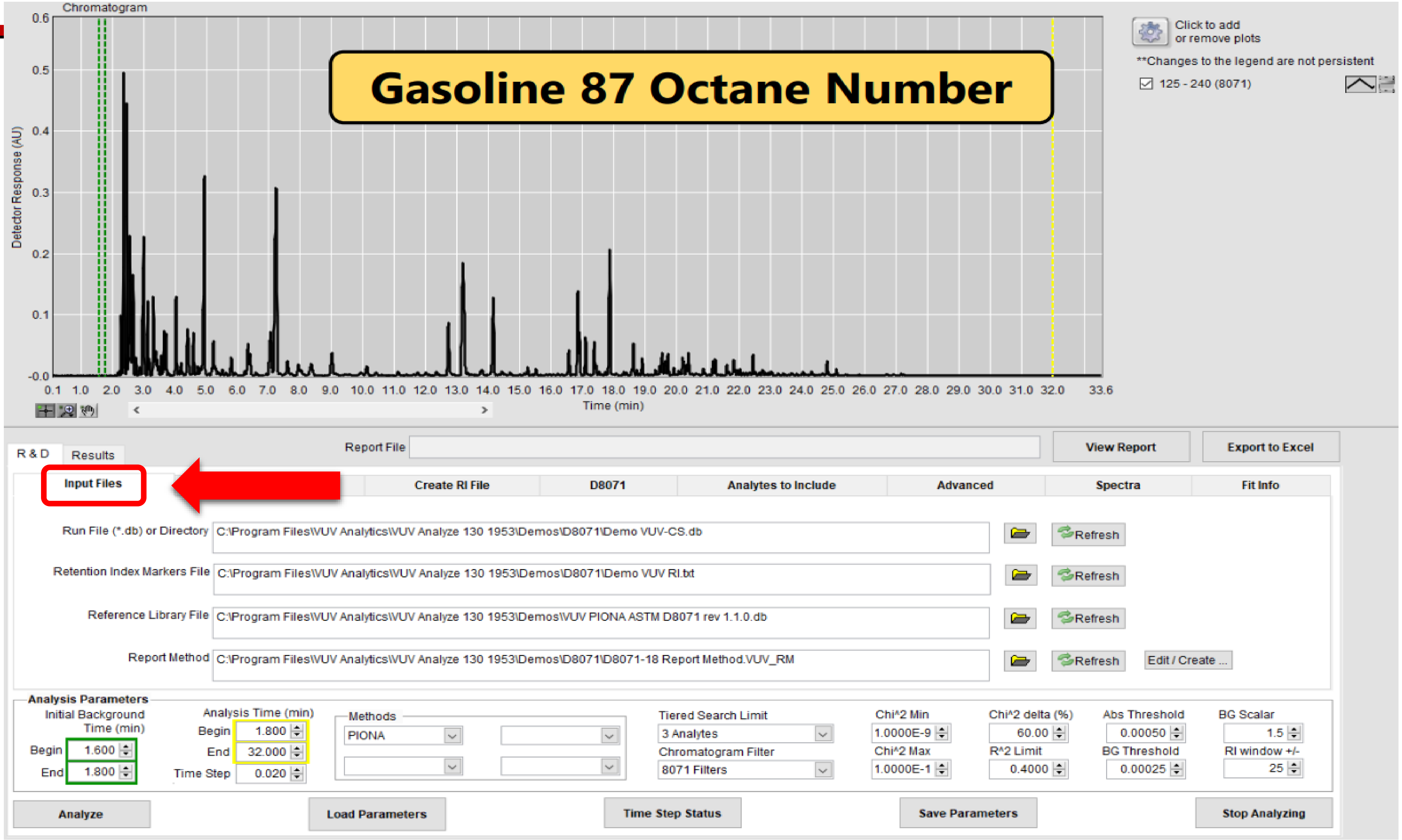
- A is the absorbance
- ε is the molar attenuation coefficient or absorptivity of the attenuating species
- ℓ is the optical path length in cm
- c is the concentration of the attenuating species



ASTM D8071 Run Conditions

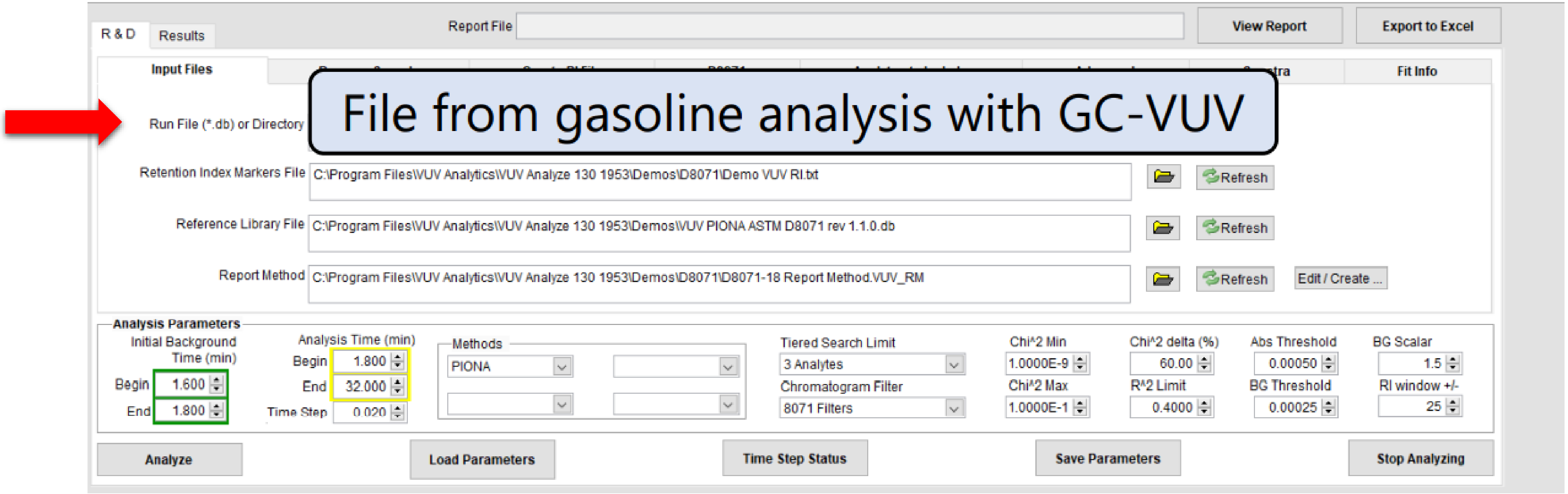
- **Trace 1310 GC**
  - 1 uL injection
  - Inlet: 250°C, split 300:1
  - Column: Restek Rxi-1ms (30 m x 0.25 mm, 0.25 um)
  - Flow: 1 mL/min helium, constant flow
  - Oven: 35°C, hold 10 min; 7°C/min to 200°C (run time – 33.6 min)
- **VUV Analytics VGA-100**
  - Makeup gas: 0.40 psi N2
  - Flow cell and transfer line: 275°C
  - Acquisition rate: 4.5 spectra/sec
  - Acquisition range: 125-240 nm

Software Processing (1)



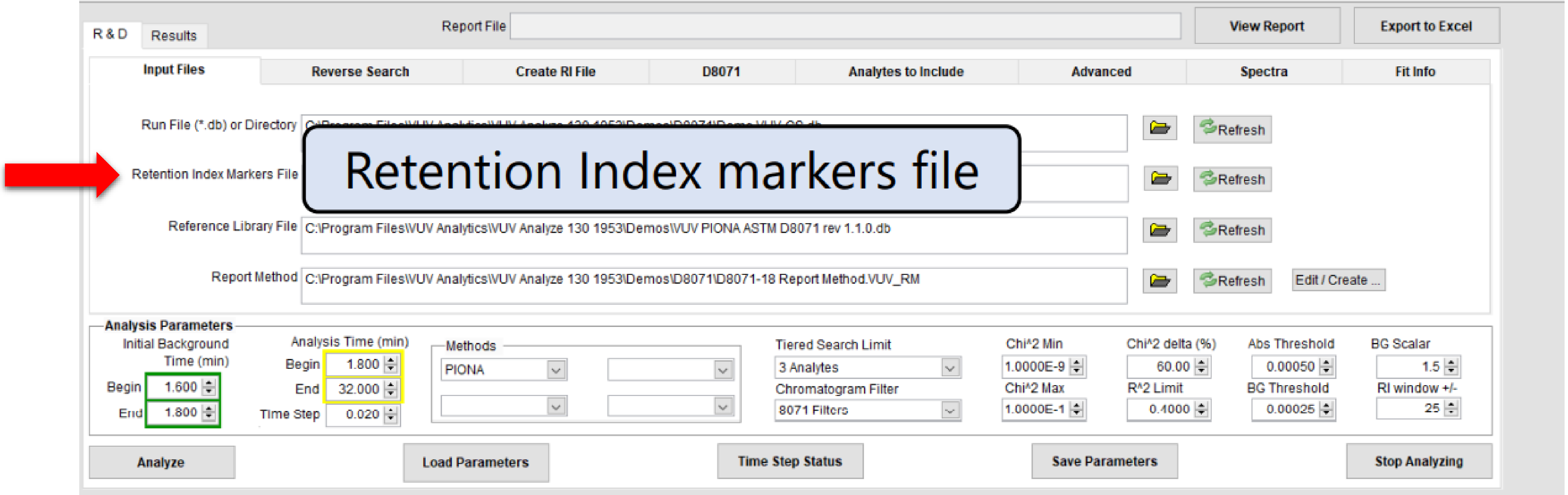
Software Processing (2)

- Select Raw Data file.



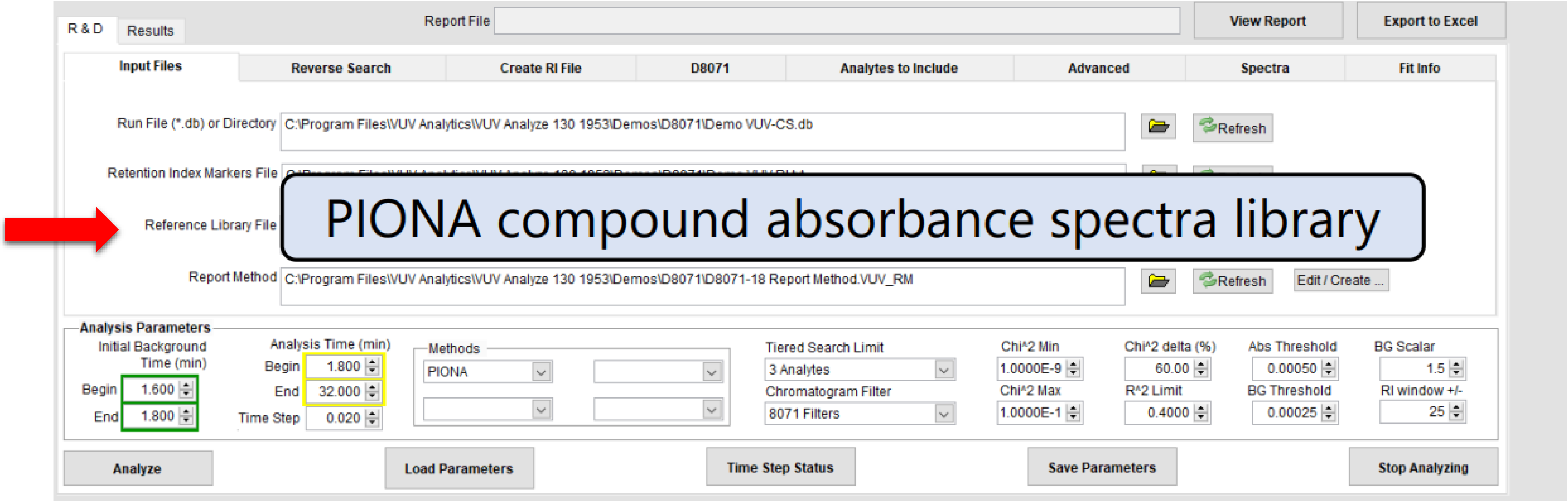
Software Processing (3)

- Retention Index Marker : C4 - C15



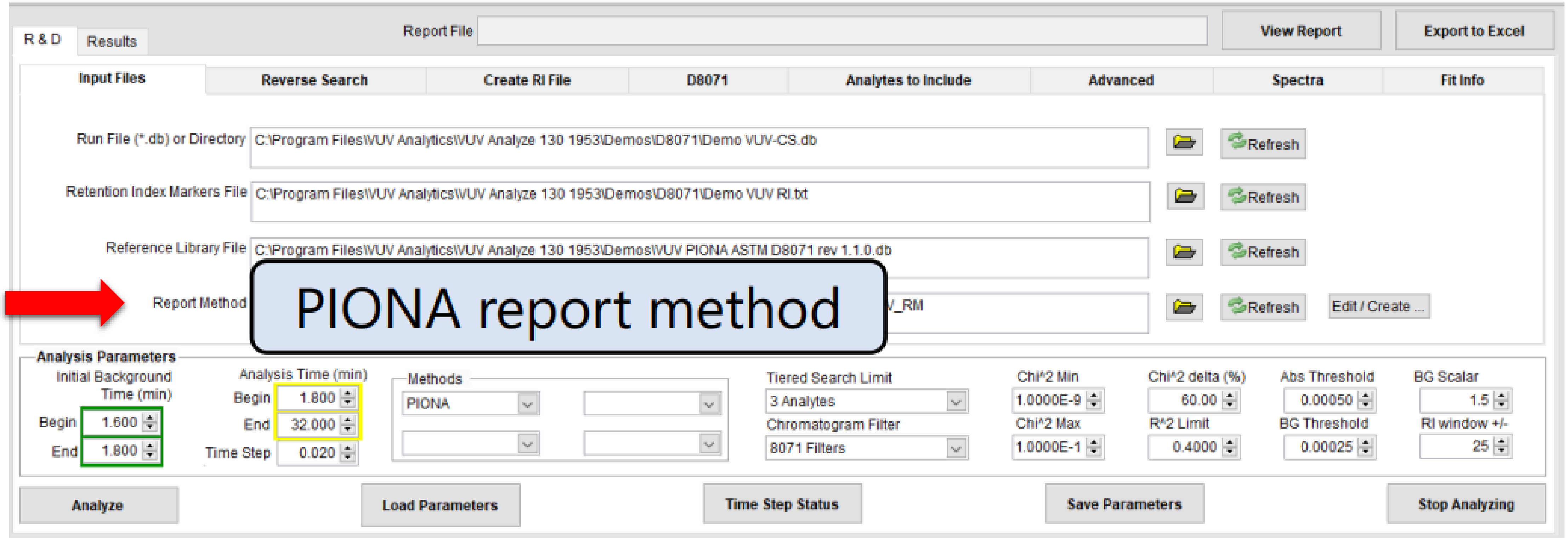
Software Processing (4)

- Reference PIONA file absorbance spectra library from VUV.

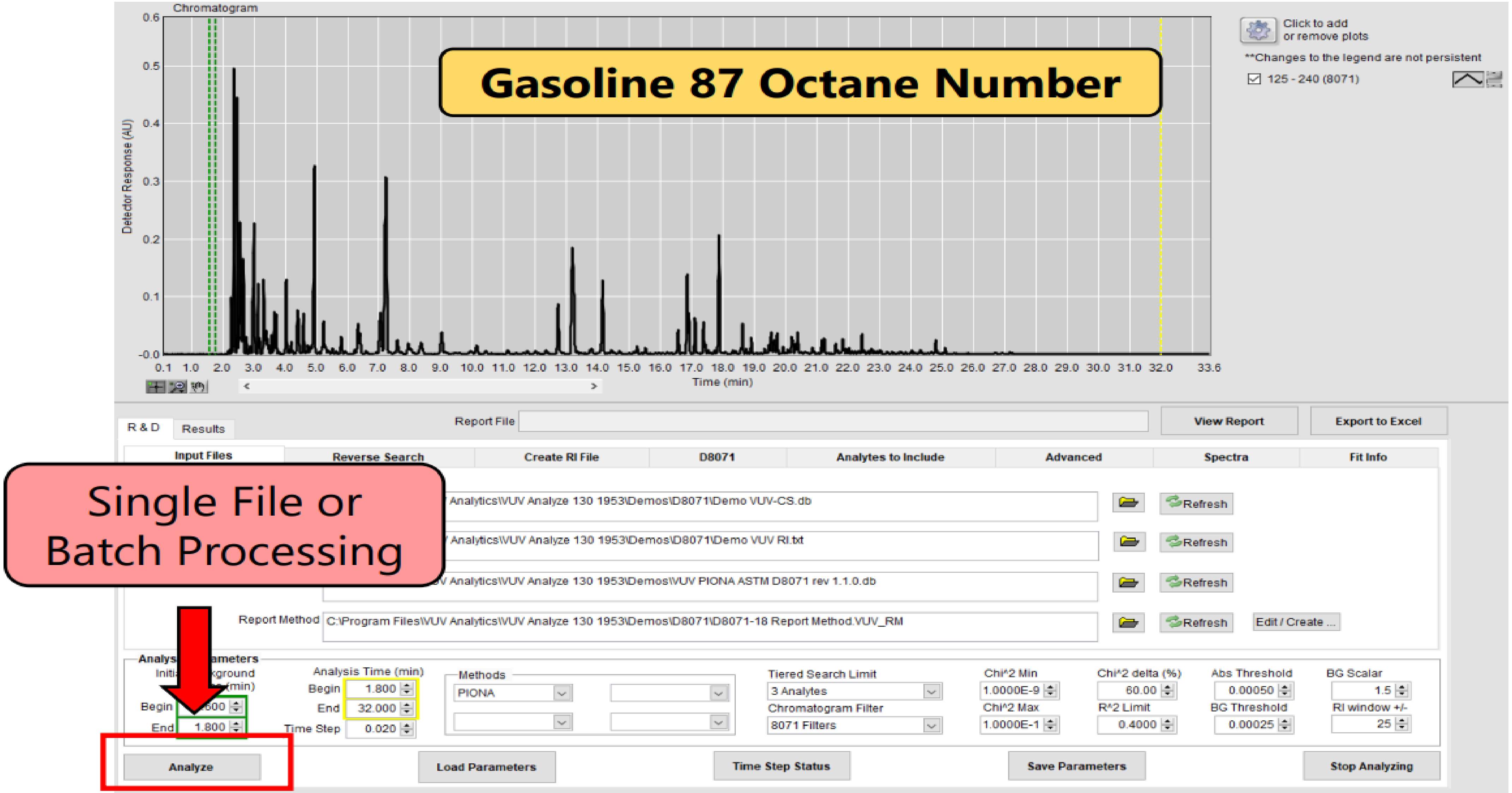


Software Processing (5)

- Template report



Software Processing (6)



Software Processing (7)

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

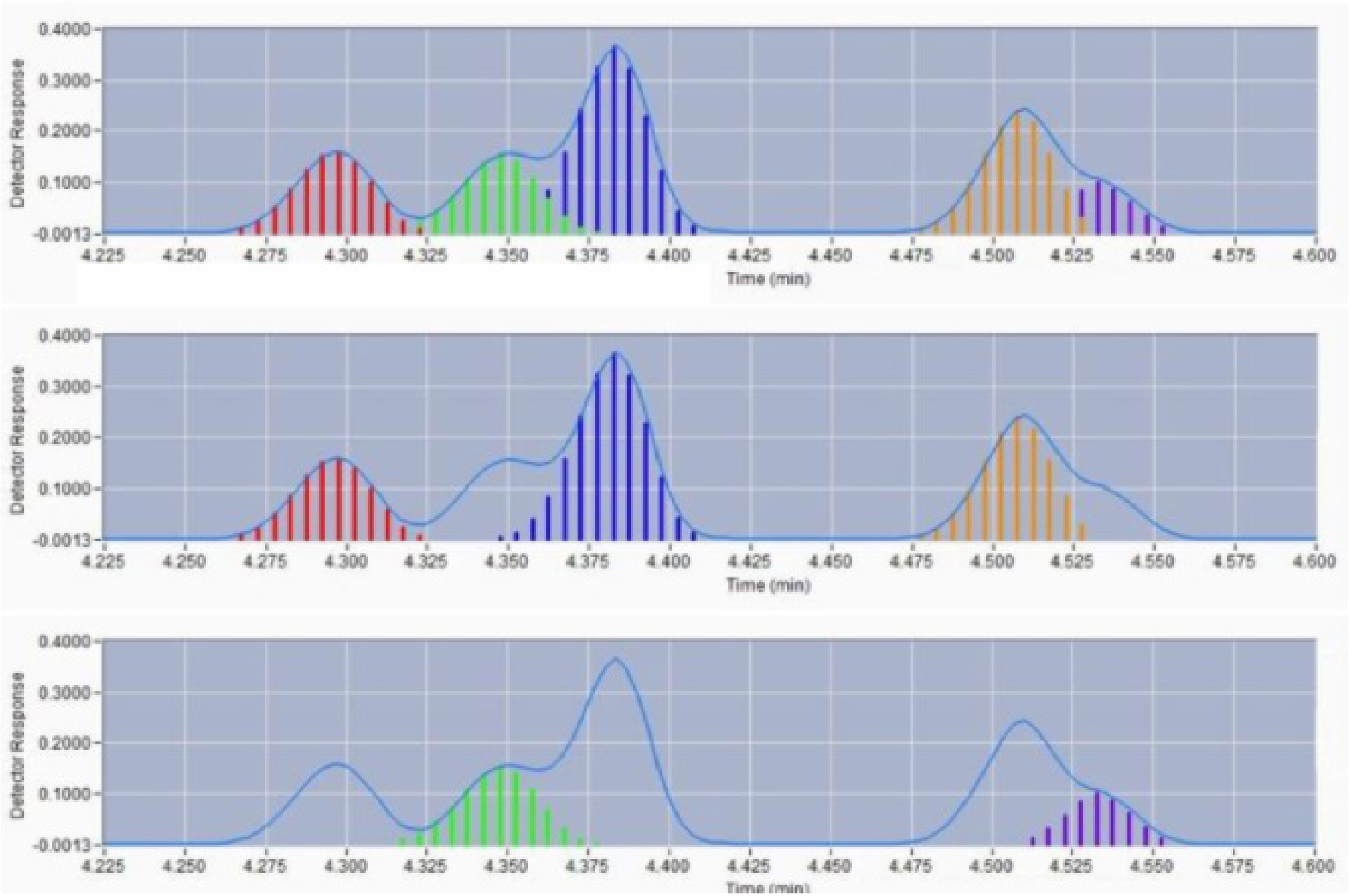
C19
Total 8.8192 42.5362 9.1821 8.1559 20.4855

List Poor Fits

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

Time Interval Deconvolution (TID)



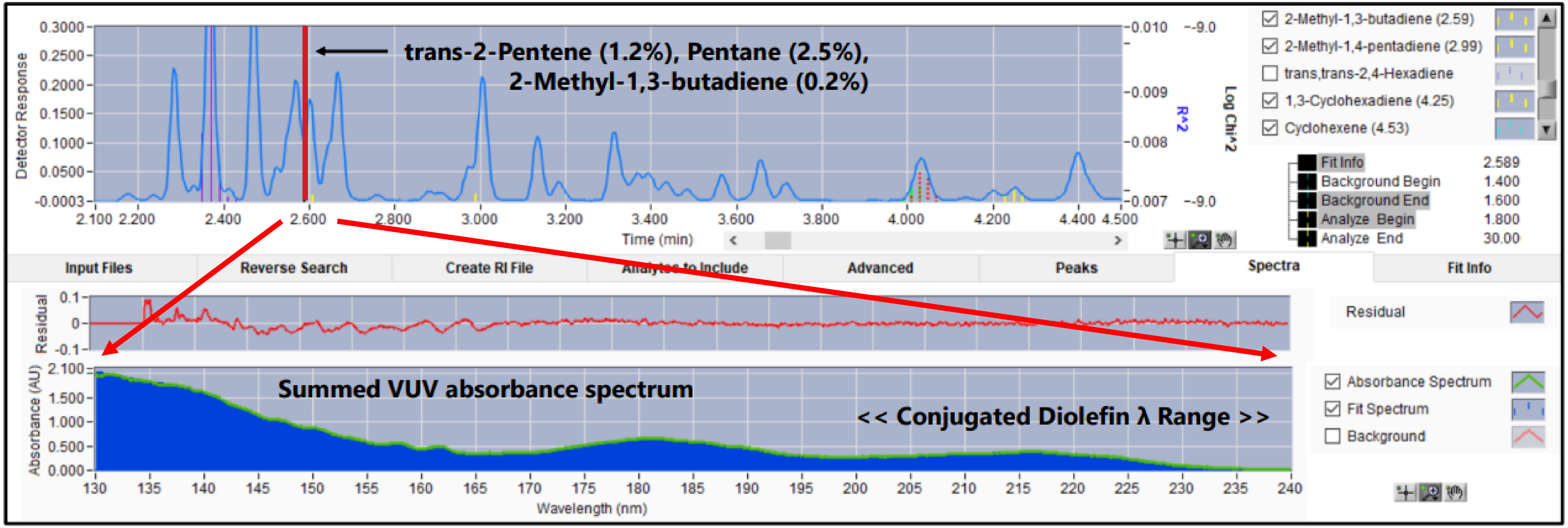
TID

- 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



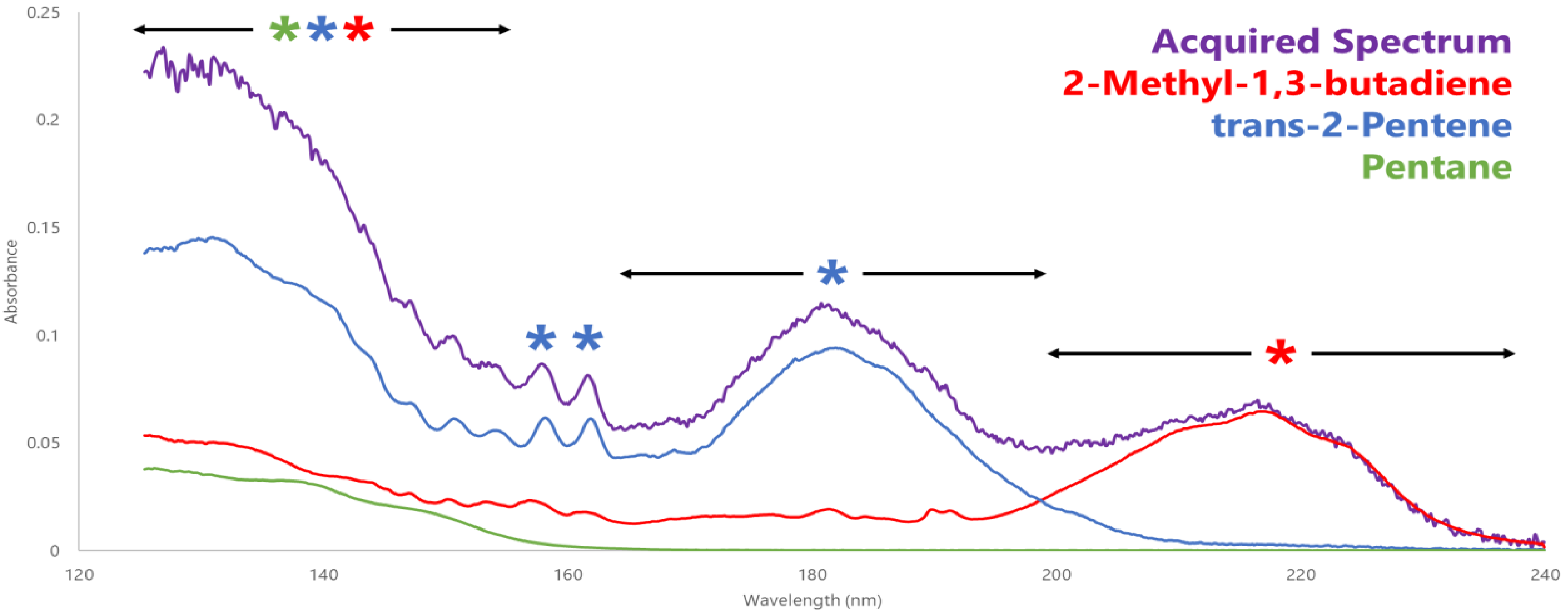
Analyte Table

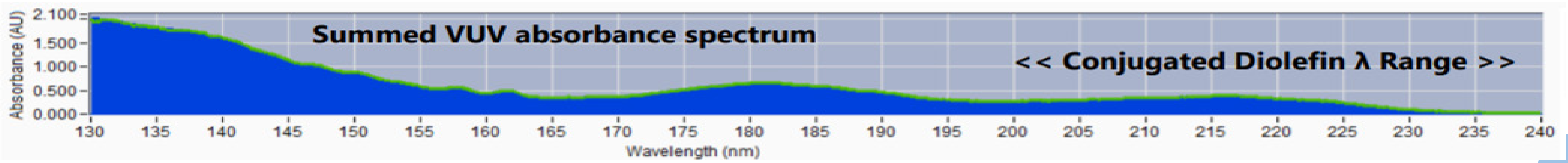
Chi^2 2: 1.735E-4

R^2: 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





PIONA by GC-VUV follow ASTM D8071

- **Column : 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

Traditional Gasoline Analysis : DHA

- **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.

Traditional Gasoline Analysis : Reformulyzer

- **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.

Conclusion...

- ASTM D8071 provides compound class characterisation (PIONA) and individual compounds methanol, ethanol, isooctane, BTEX and naphtalenes. 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	Reformu-lyzer®	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