Možnosti stanovení složek bioplynů, rozpouštědel a degradačních produktů polymerů plynovou chromatografií s detekcí ve vakuové UV oblasti

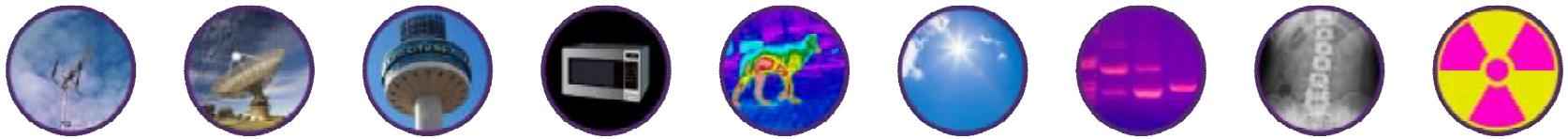
Ing. Tomáš Korba

AMEDIS, Praha

The Commercialization of Light

The Electromagnetic Spectrum

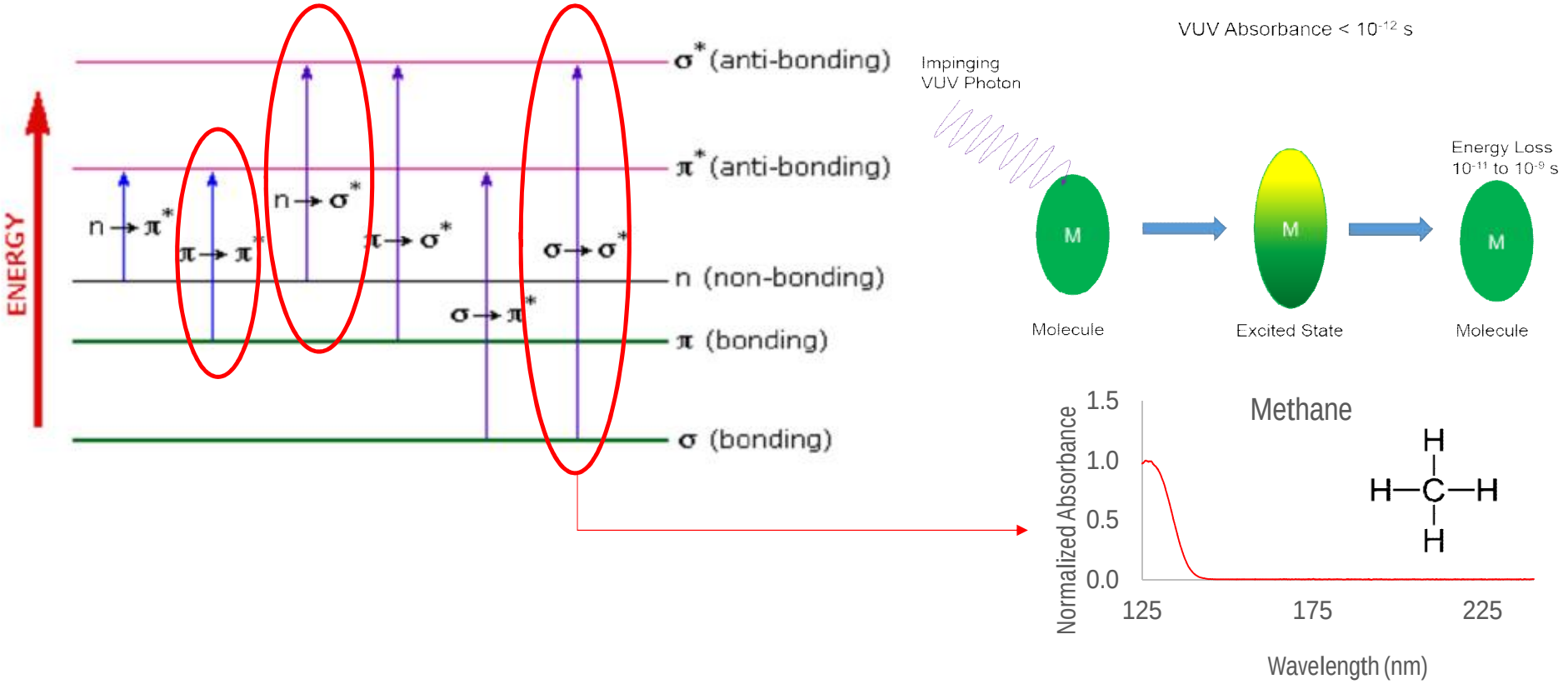
✓ : Commercialized



Radiation Type	Radio		Microwave	Infrared	Visible	Ultraviolet	X-ray	Gamma ray
Wavelength (m)	10^{3}		10^{-2}	10^{-5}	0.5×10^{-6}	10^{-8}	10^{-10}	10^{-12}
	MRI	NMR	Microwave Spectroscopy	FTIR	Microscopy		Crystallography	Radiation Detector Nuclear Med
			Microwave Oven	THz Scanner	HPLC-DAD		XRF Imaging	

VUV ANALYTICS

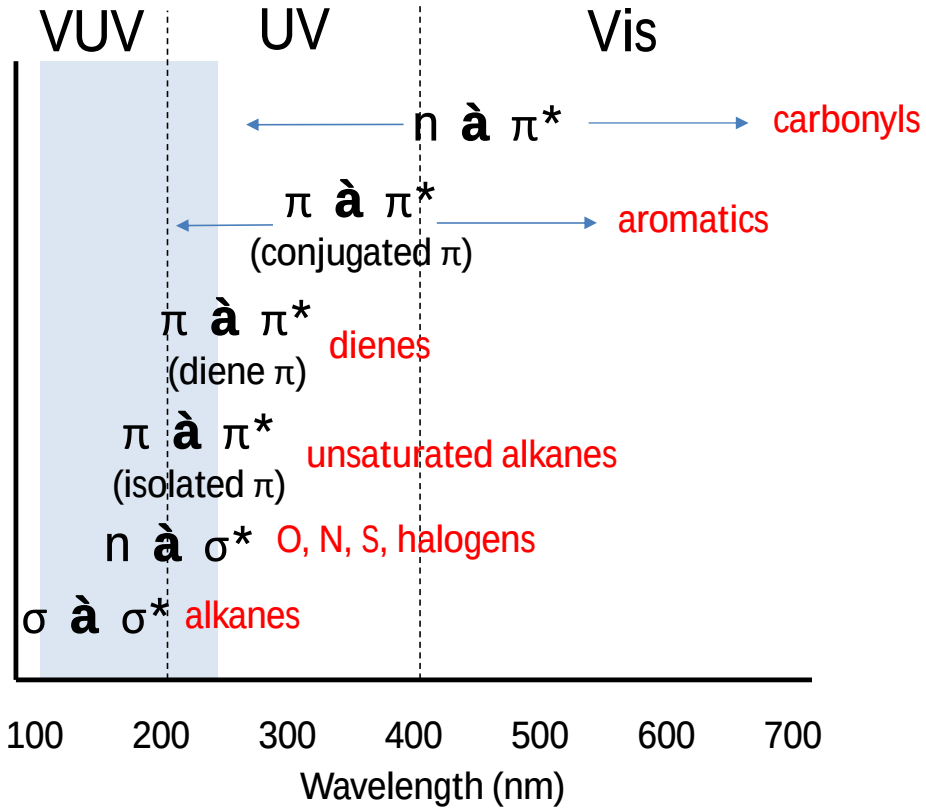
Overview of Molecular Spectroscopy



**Exciting the electron cloud, probing the electronic state of the molecule*

VUV ANALYTICS

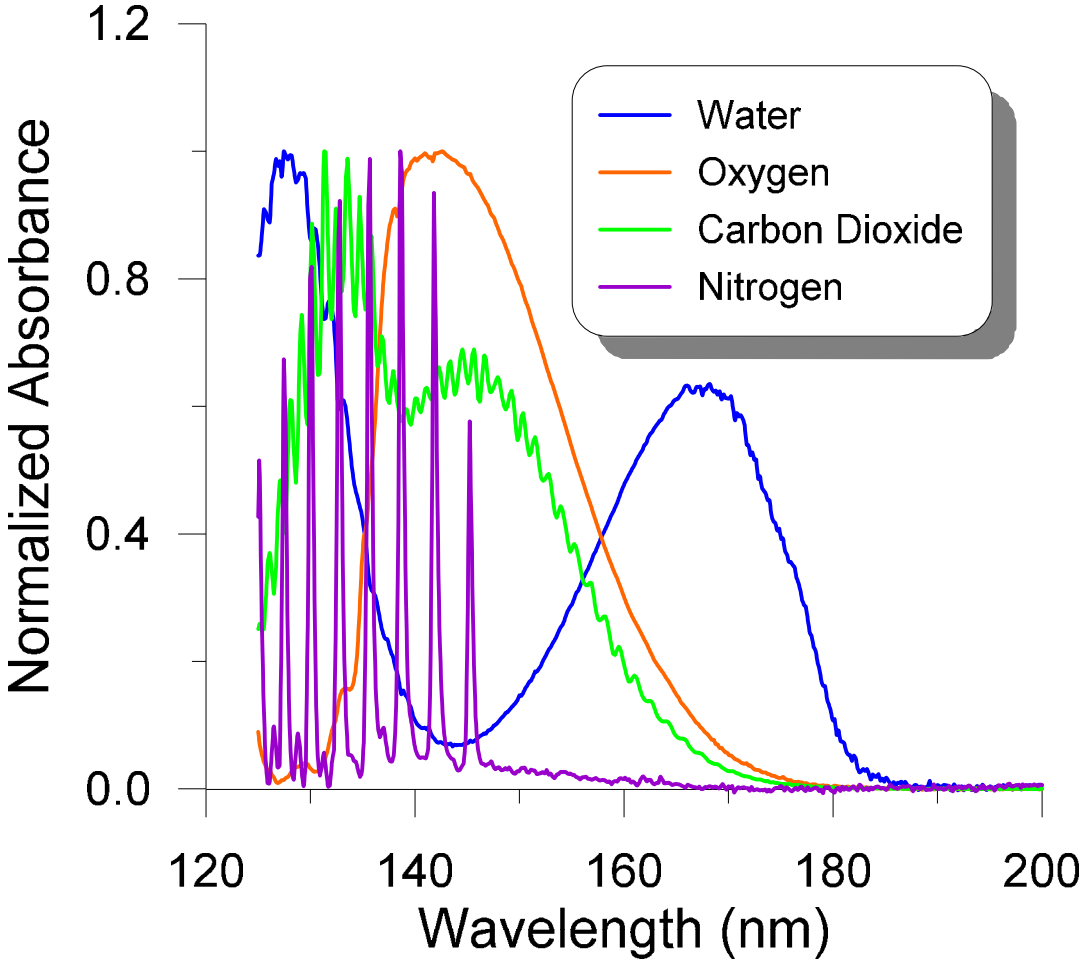
Vacuum Ultraviolet Detector for GC



VUV ANALYTICS

Schug et al., *Anal. Chem*. 2014, *86*, 8329-8335.

VUV: A Gap in The Analytical Toolbox



"The excitation energies associated with electrons forming most single bonds are sufficiently high that absorption occurs in the so-called vacuum ultraviolet region (λ<185nm), where components in the atmosphere also absorb strongly. Because of experimental difficulties associated with the vacuum ultraviolet region, most spectrophotometric investigations of organic compounds have involved longer wavelengths than 185nm."

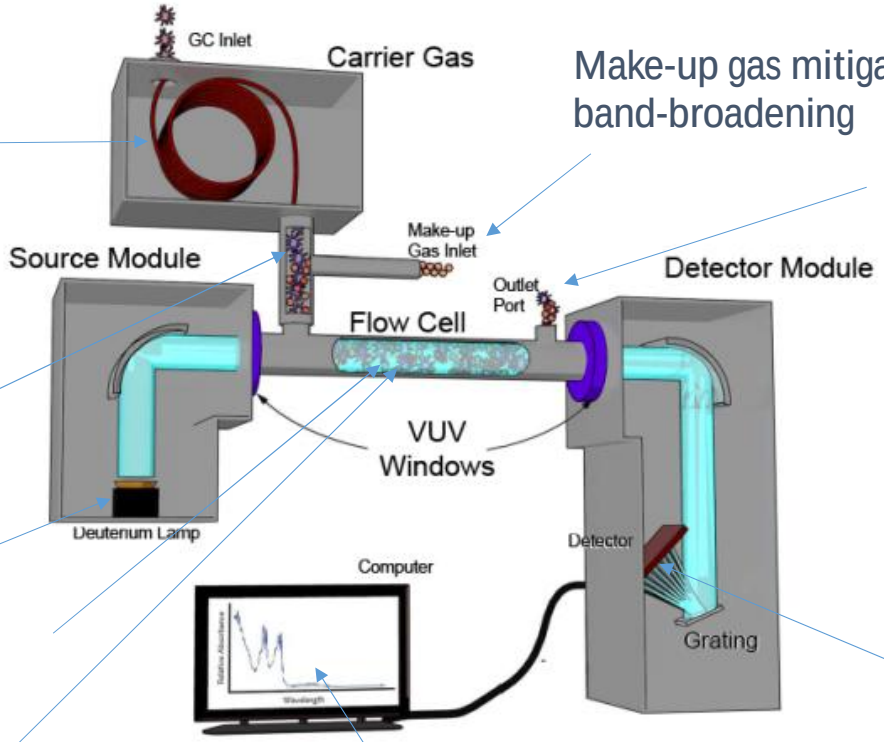
Principals of Instrumental Analysis,
by Douglas Skoog, Sixth Edition, 2006

VUV ANALYTICS

Characteristics of VGA-100 (VGA-101)

VUV ANALYTICS

Carrier and make-up gases (He, H_2, N_2, Ar) largely VUV transparent. No vacuum required!!



Make-up gas mitigates/alleviates band-broadening

Nondestructive

Heated transfer line (up to 320 °C (420 °C))

VUV/UV source lamp (D_2); stable signal and robust

Thermostatted flow cell (up to 320 °C (420 °C))

Full range 120 – 240 nm (430 nm) data acquisition at up to 100 Hz

Post-run processing for universal or selective detection; library spectral matching; etc.

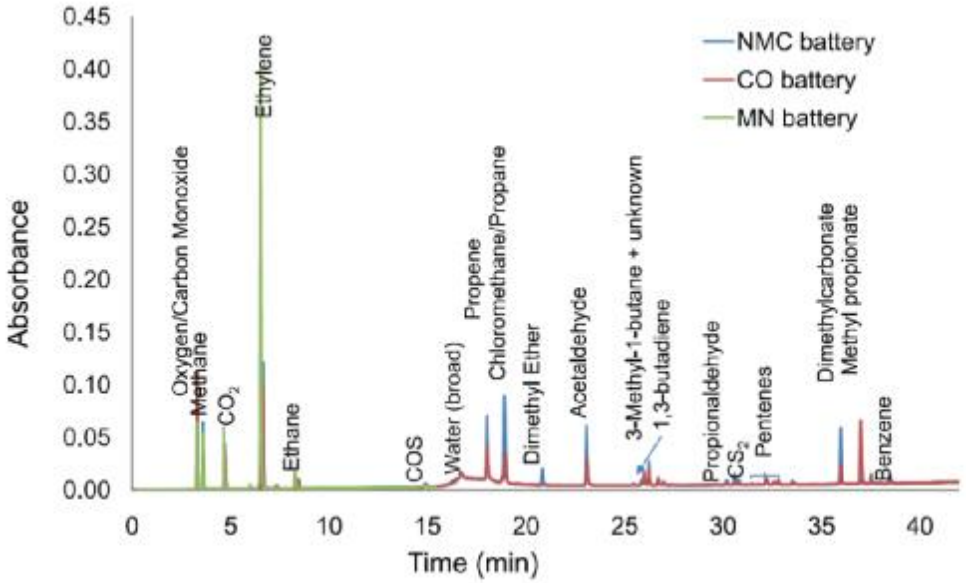
Analyte-specific absorption based on Beer's Law principles; Qualitative and quantitative analysis (wide linear range)

Schug et al., *Anal. Chem*. 2014, *86*, 8329-8335.

Key Features of GC-VUV

- Universal and selective detection
- Unique, class similar spectra
- Optical differentiation of isomers
- Deconvolution of coeluting analytes
- Automated classification and speciation of mixtures
- Good quantitative performance

Permanent gas analysis



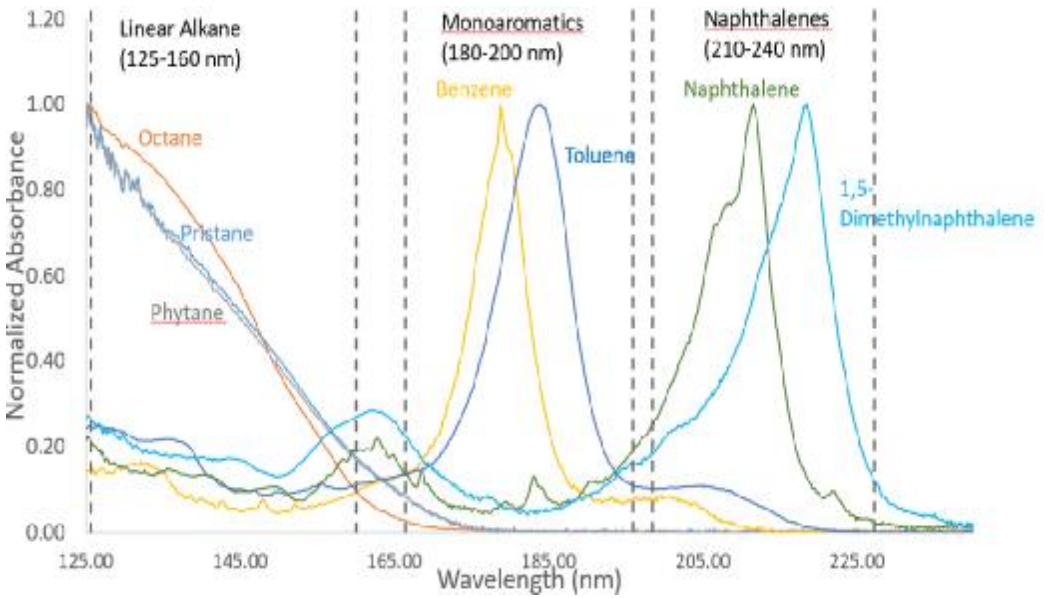
Thermal runaway of Li-ion and Li-M batteries

Bai et al., *J. Chromatogr A* 2015, *1388*, 244-250.

Key Features of GC-VUV

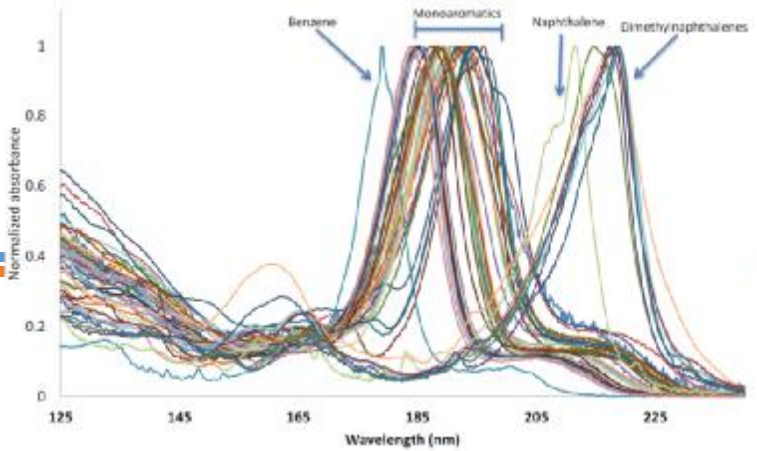
- Universal and selective detection
- Unique, class similar spectra
- Optical differentiation of isomers
- Deconvolution of coeluting analytes
- Automated classification and speciation of mixtures
- Good quantitative performance

Alkanes vs. Aromatics



Weathered diesel analysis

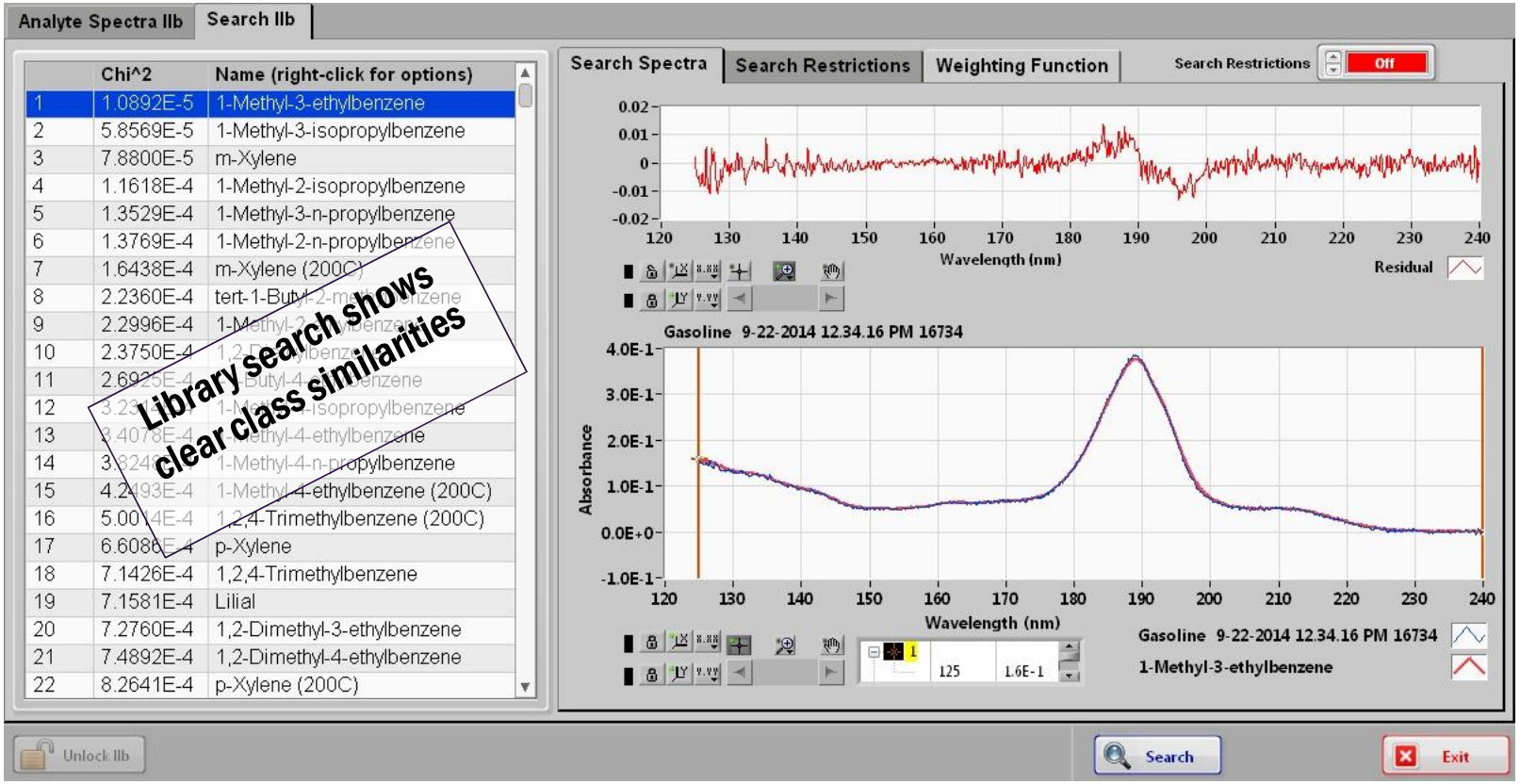
- Aromatics and substituted aromatics



Note: The absorbance of e.g benzene at 180 nm is 10 000 more intense than at the typical 254 nm in HPLC

Bai et al., *Revised*

Library search and Unambiguous Compound Identification

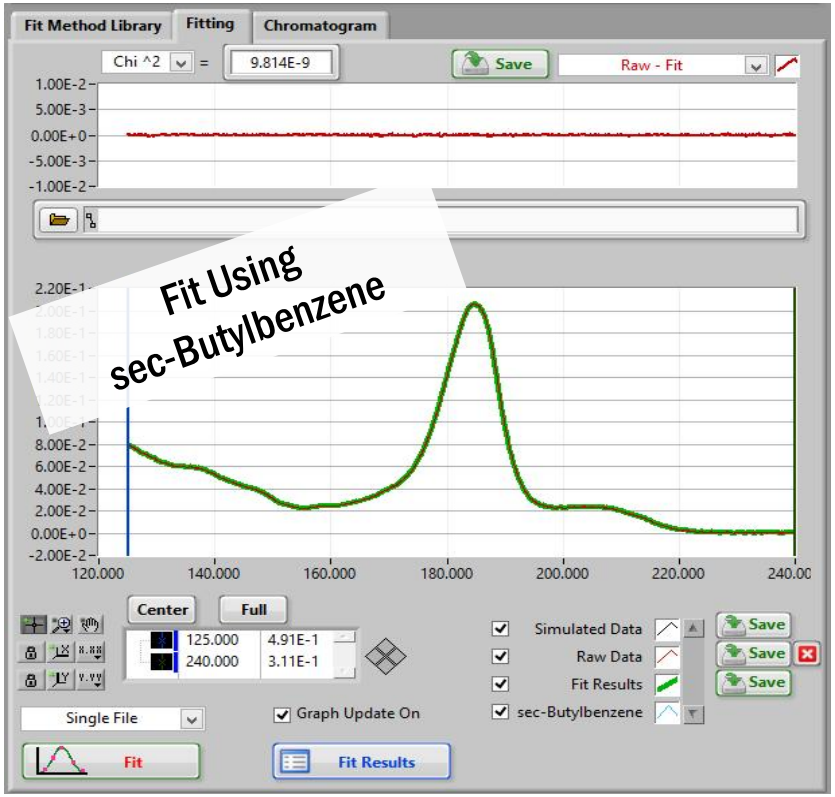


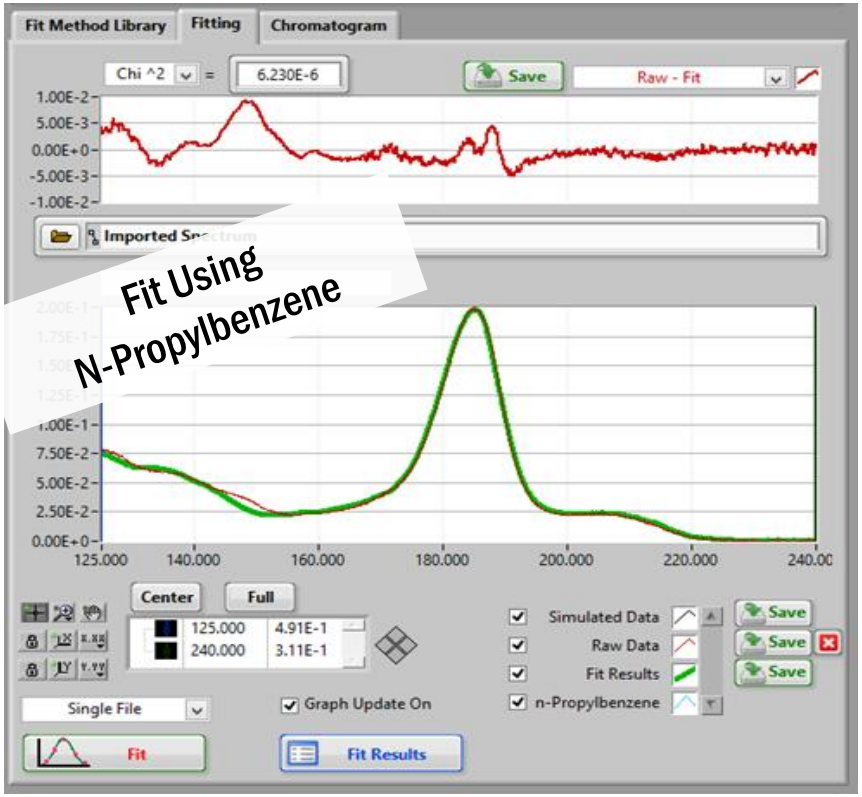
Spectra are very robust;
No ghost components in the library match list

VUV ANALYTICS

Similar But Very Distinct

Visual similarities are easily distinguished in the fitting routine; minor differences are significant





The chi-squared distribution is the distribution of a sum of the squares of *k* independent standard normal random variables

The chi-squared distribution is used in the common tests for goodness of fit of two criteria of qualitative data,

VUV ANALYTICS

Optical Differentiation of Isomers

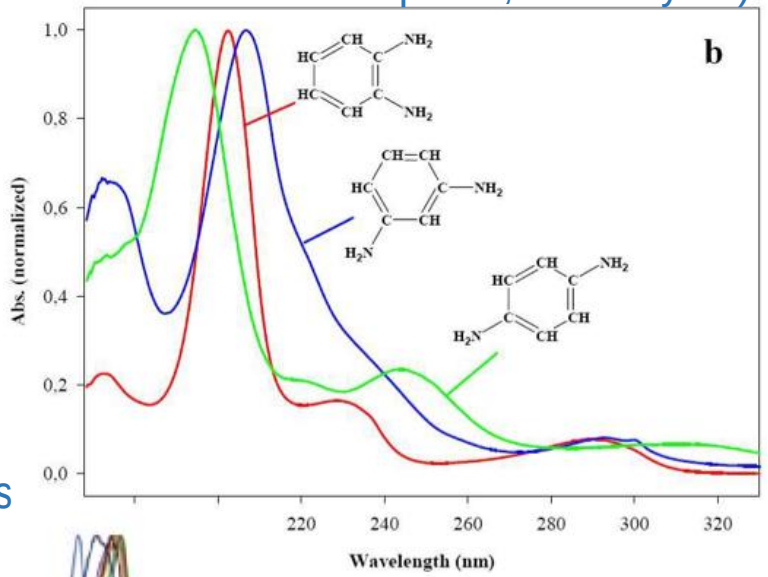
UV/Vis spectroscopy

Atom connectivity; overlap of molecular orbitals

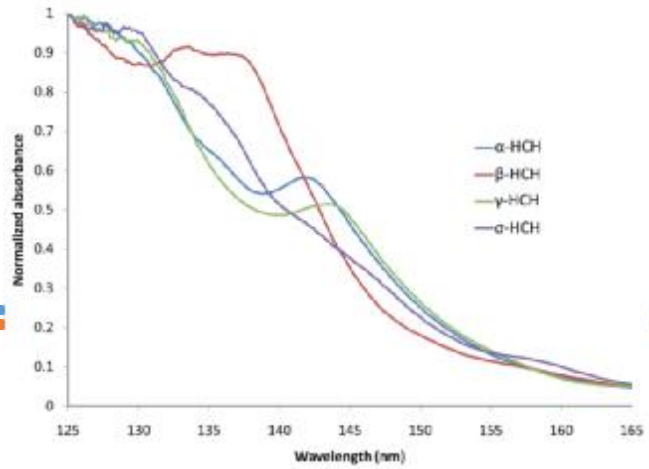
Electron transition between orbitals

Energy gap and probability of transition dependent on molecular structure

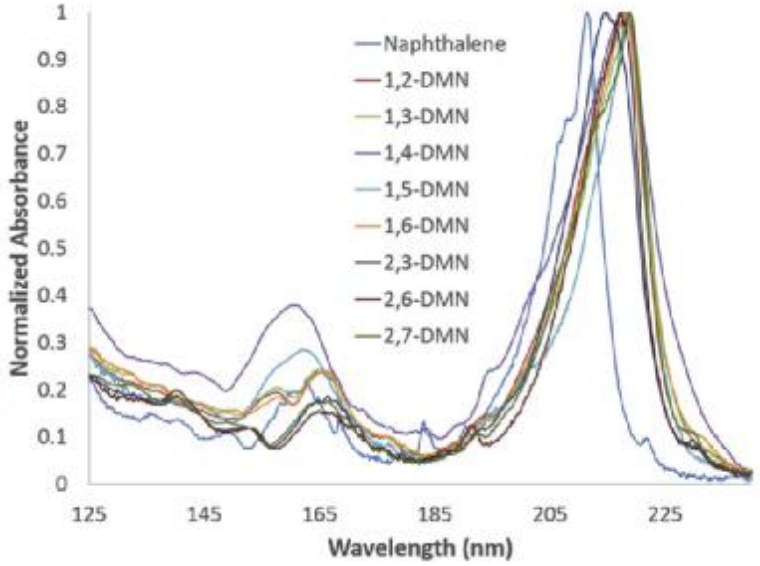
Diaminobenzene isomers (Handbook of UV Spectra, Chromalytica)



Hexachlorocyclohexane isomers



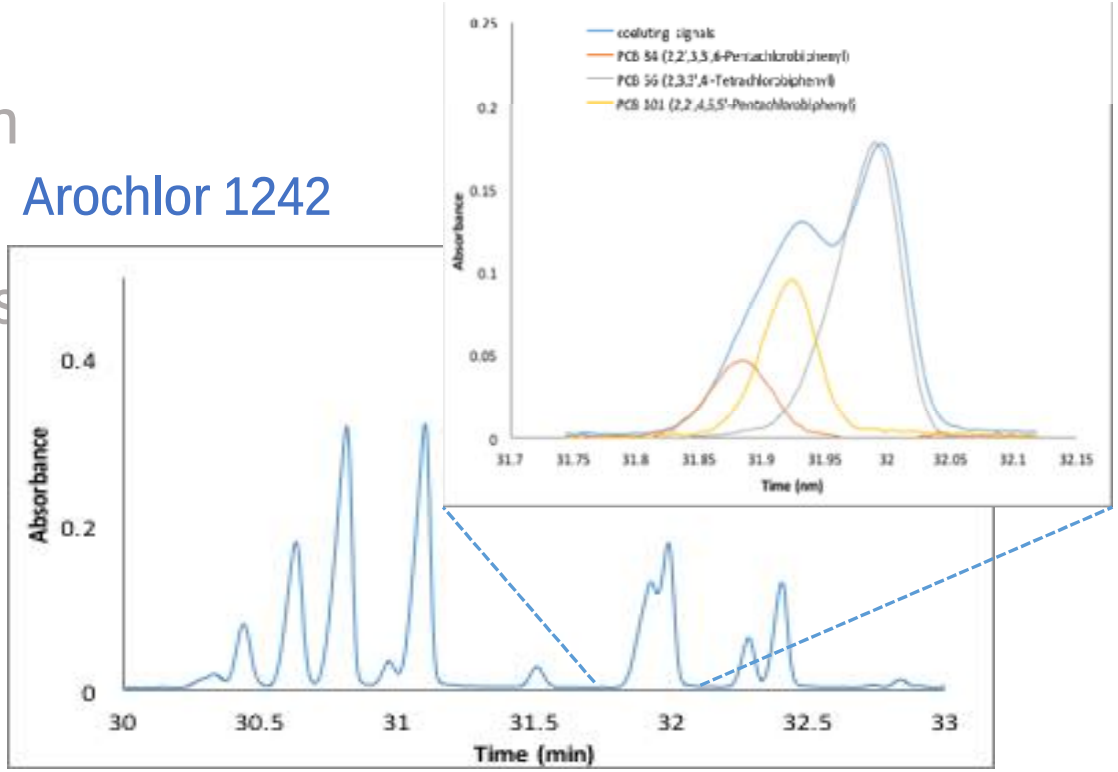
Dimethylnaphthalene isomers



Key Features of GC-VUV

- Universal and selective detection
- Unique, class similar spectra
- Optical differentiation of isomers
- (Spectral) Deconvolution of coeluting analytes
- Automated classification and speciation of mixtures
- Good quantitative performance

Arochlor 1242



Polychlorinated biphenyls in Aroclor mixtures

Qiu et al., *J. Chromatogr A* 2017, *1490*, 191-200.

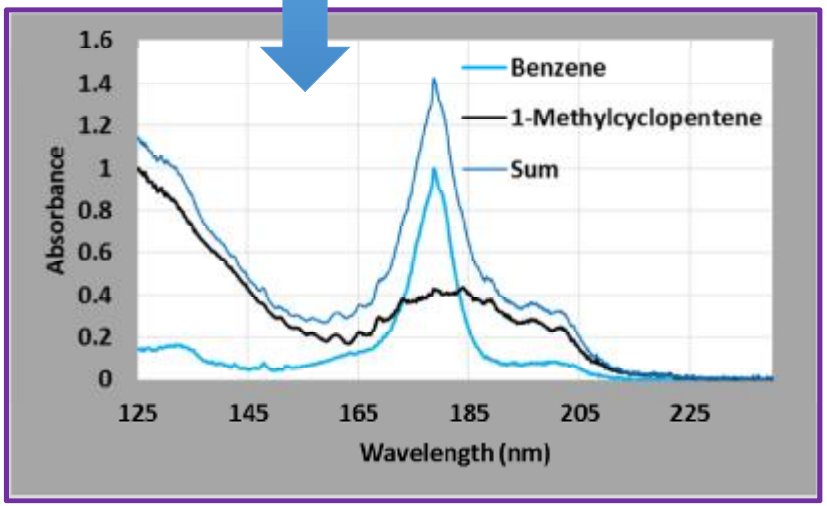
Deconvolution

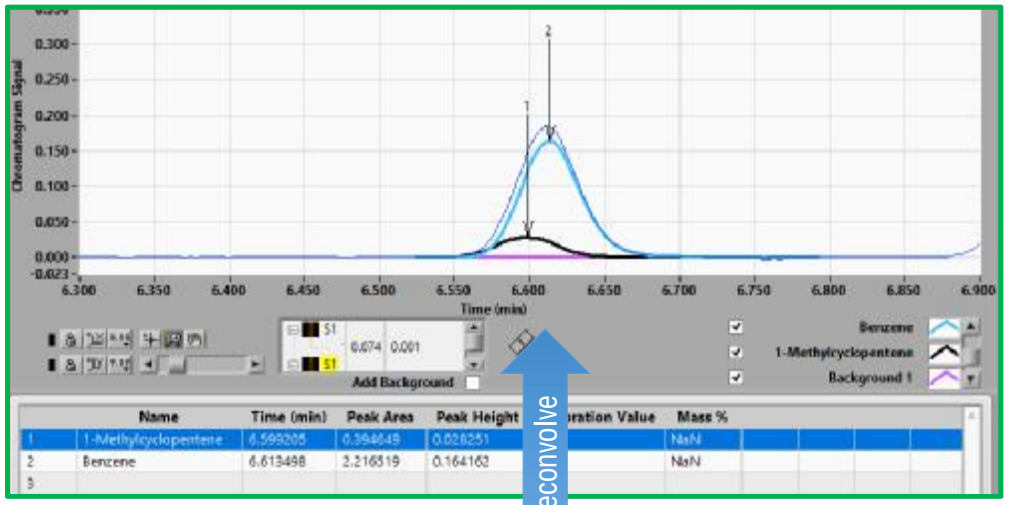
- Total absorption is proportional to the product of the concentration and the absorption cross section
- Co-elution is a sum of these products
- Linear regression allows for easy deconvolution of the compound concentrations; even for co-eluting compounds

Beer's Law: $A = \epsilon bC$

$A_{total} = A_1 + A_2 + \ldots A_n$

Additive





Deconvolve

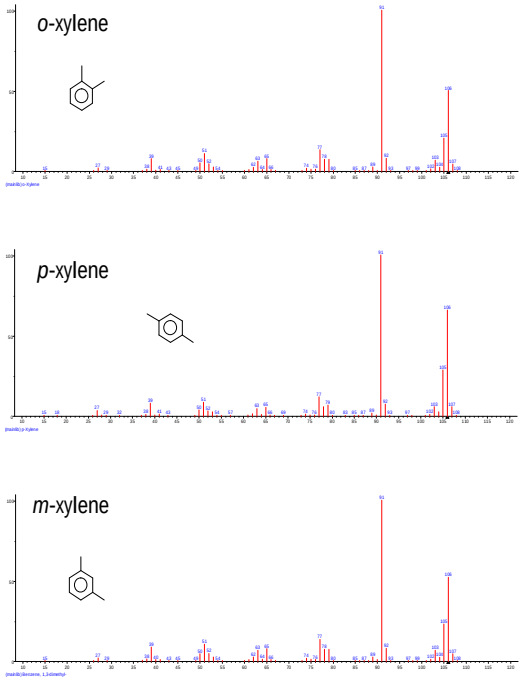
$A_{co\text{-}elution} = f_1A_1 + f_2A_2$

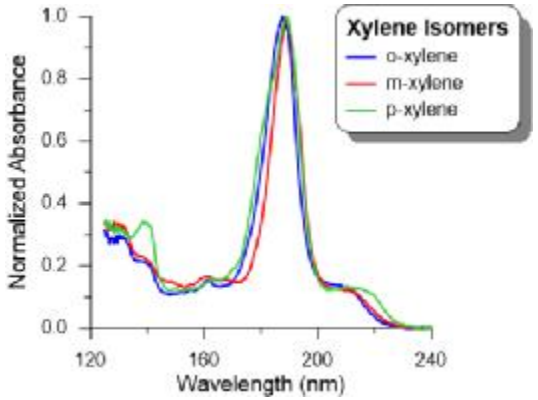
A_i = the absorbance of component i at a given λ

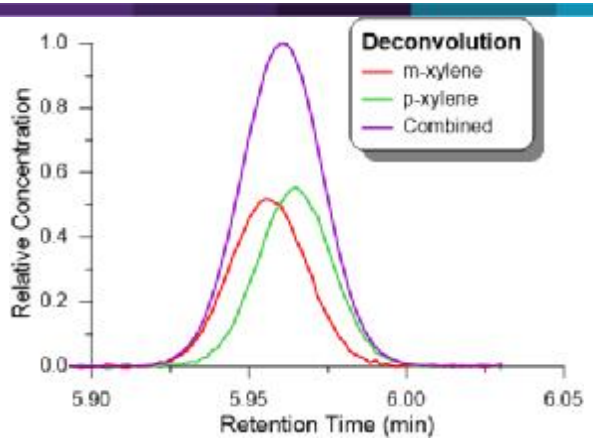
f_i = the fit coefficient of component i

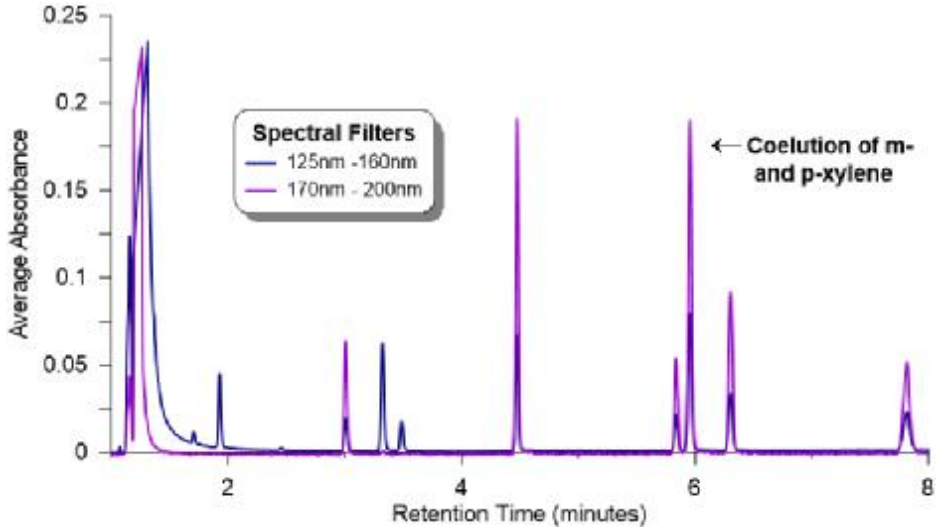
VUV ANALYTICS

Spectral Deconvolution of m&p Xylene







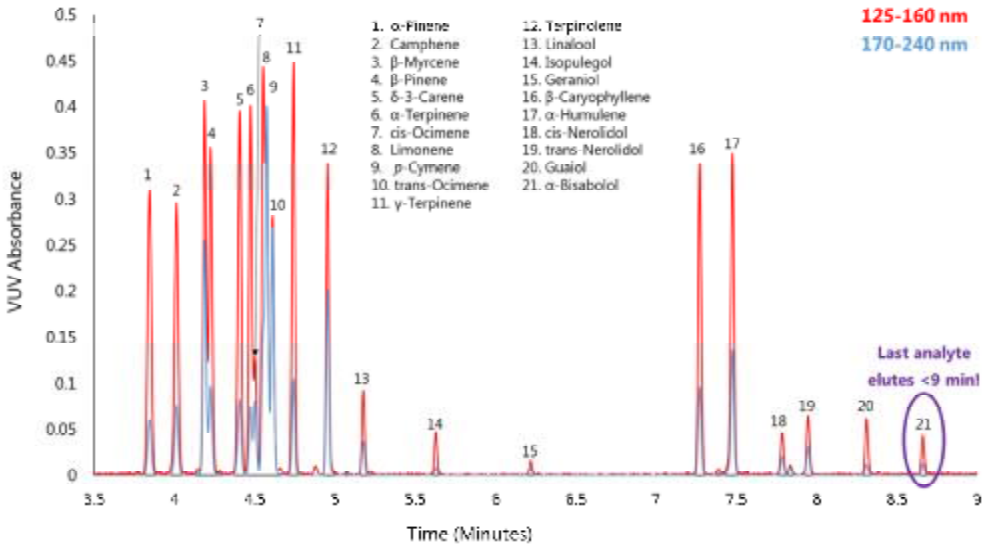


VUV ANALYTICS

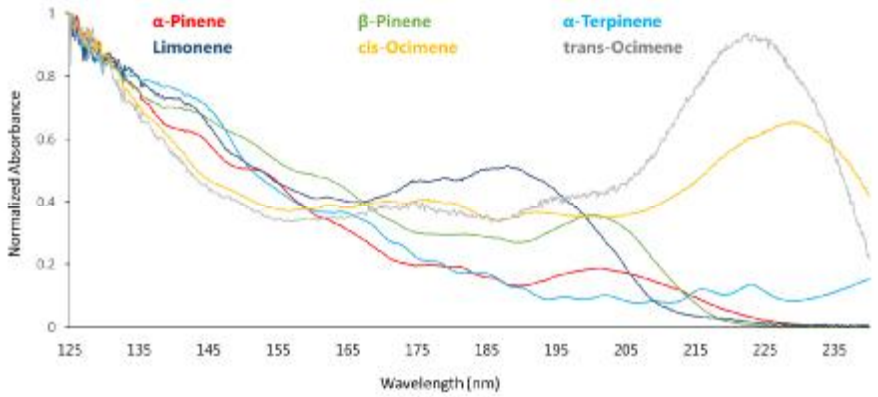
Fast GC-VUV Analysis of Terpene Isomers

Additional selectivity which makes chromatographic separation less stringent

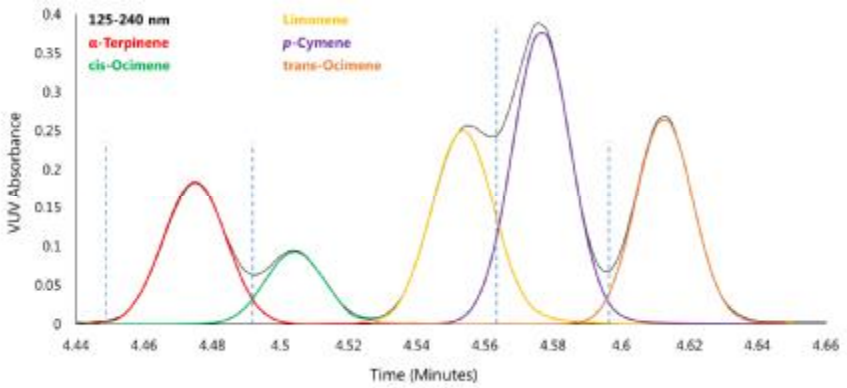
Fast GC-VUV Chromatogram of Terpenes



VUV Spectral Identification of Monoterpene Isomers



VUV Deconvolution of Co-Eluting Isomers



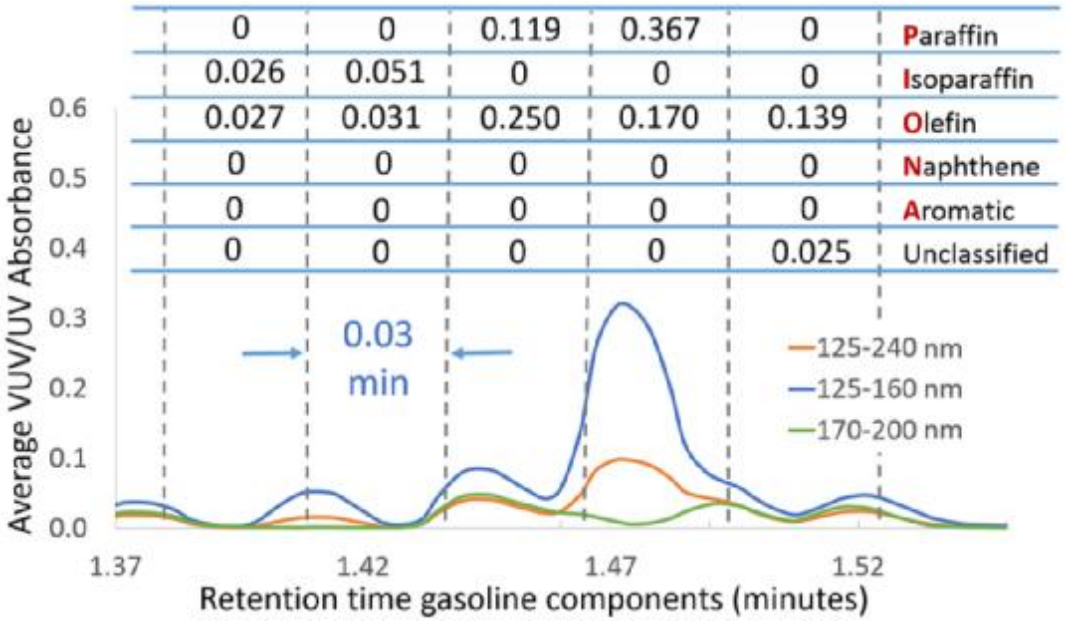
Summary:

- Terpenes have VUV spectra that are distinct
  - ø Includes structural isomers and co-eluting analytes
- VUV spectral identification of terpene isomers allows the chromatographic compression of GC runtimes
  - ø Can shorten GC runtimes by 2 – 3X or more
- Natural and forced co-elutions are deconvolved by VUV software
  - ø Eliminates inaccuracy inherent to dropping vertical integration lines to quantitate

Key Features of GC-VUV

- Universal and selective detection
- Unique, class similar spectra
- Optical differentiation of isomers
- Deconvolution of coeluting analytes
- Automated classification and speciation of mixtures (compositional analysis
- Good quantitative performance

Time Interval Deconvolution (TID)



PIONA analysis of finished gasoline (ASTM D8071)

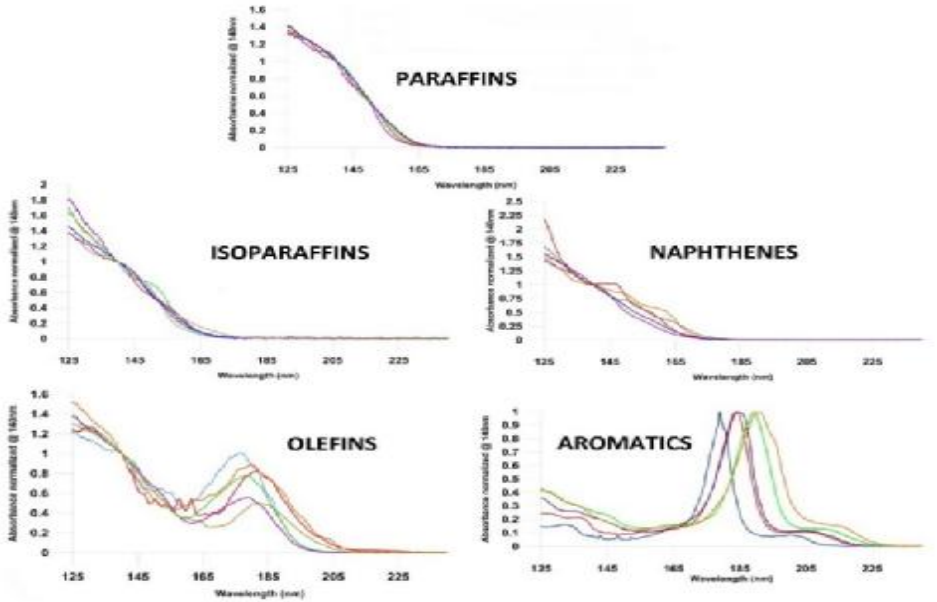
Walsh et al., *Anal. Chem.* 2016, *88*, 11130 – 11138.

PIONA Compound Characterization using VUV PIONA+

- Compositional Analysis of gasoline type samples

- Each PIONA compound class displays distinct spectral features
  - ø Enables straightforward compound class identification and quantitation

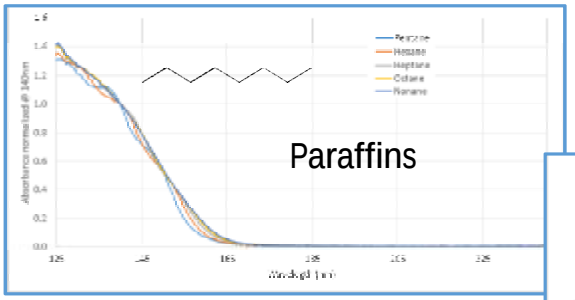
- PIONA compounds can be speciated through C6, and class identification >C6 using VUV PIONA^{+}
  - ø Flexibility to vary chromatographic conditions
  - ø Specific analytes such as individual oxygenates or aromatics belonging to the BTEX complex

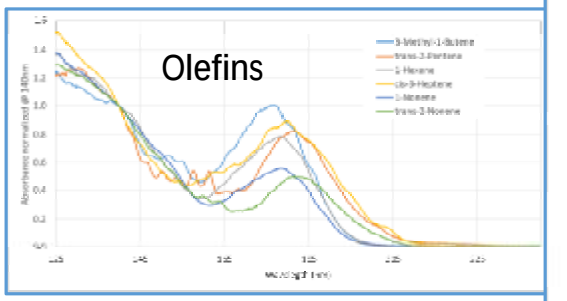


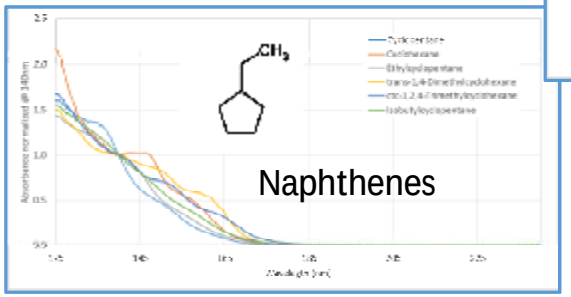
- ASTM Method D8071 provides information that historically required the use of several ASTM methods or more comprehensive methods.

  - ø A single-column GC-VUV separation method with a total runtime of 34 minutes.
  - ø ASTM approved for PIONA compound analysis in finished gasoline
  - ø No special setups, traps, pre-column tuning, or calibration requirements
  - ø Automated VUV PIONA+ analysis and reporting

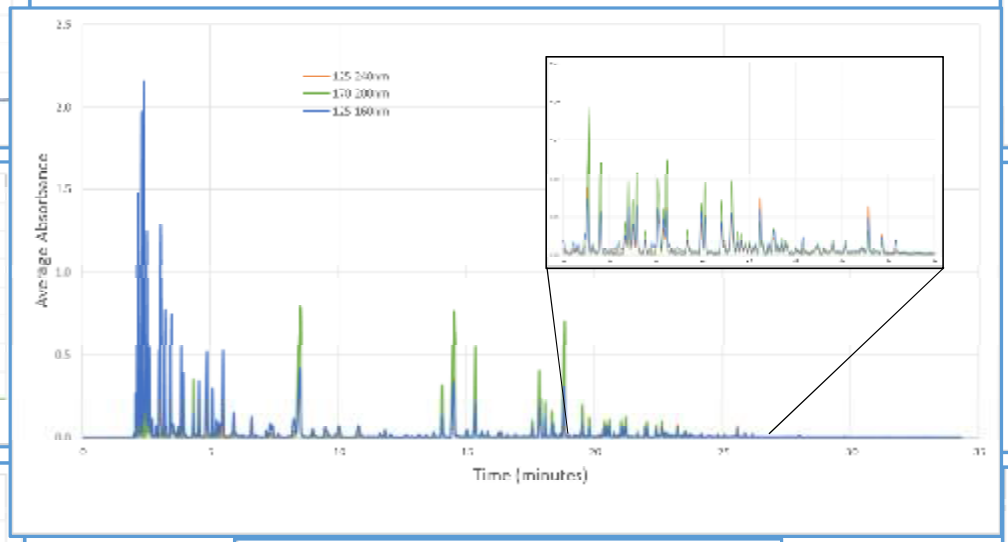
Group plus Compound Identification

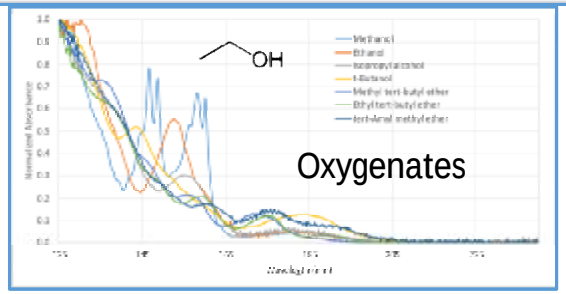


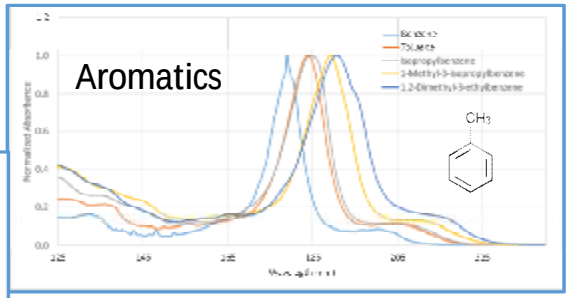


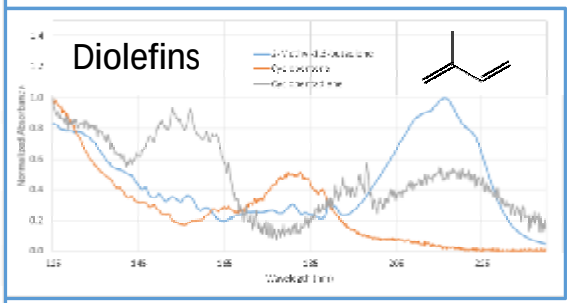


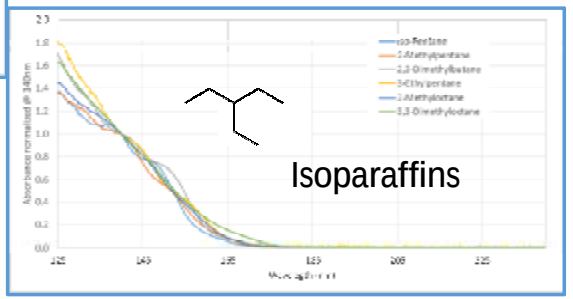
Typical Gasoline Sample

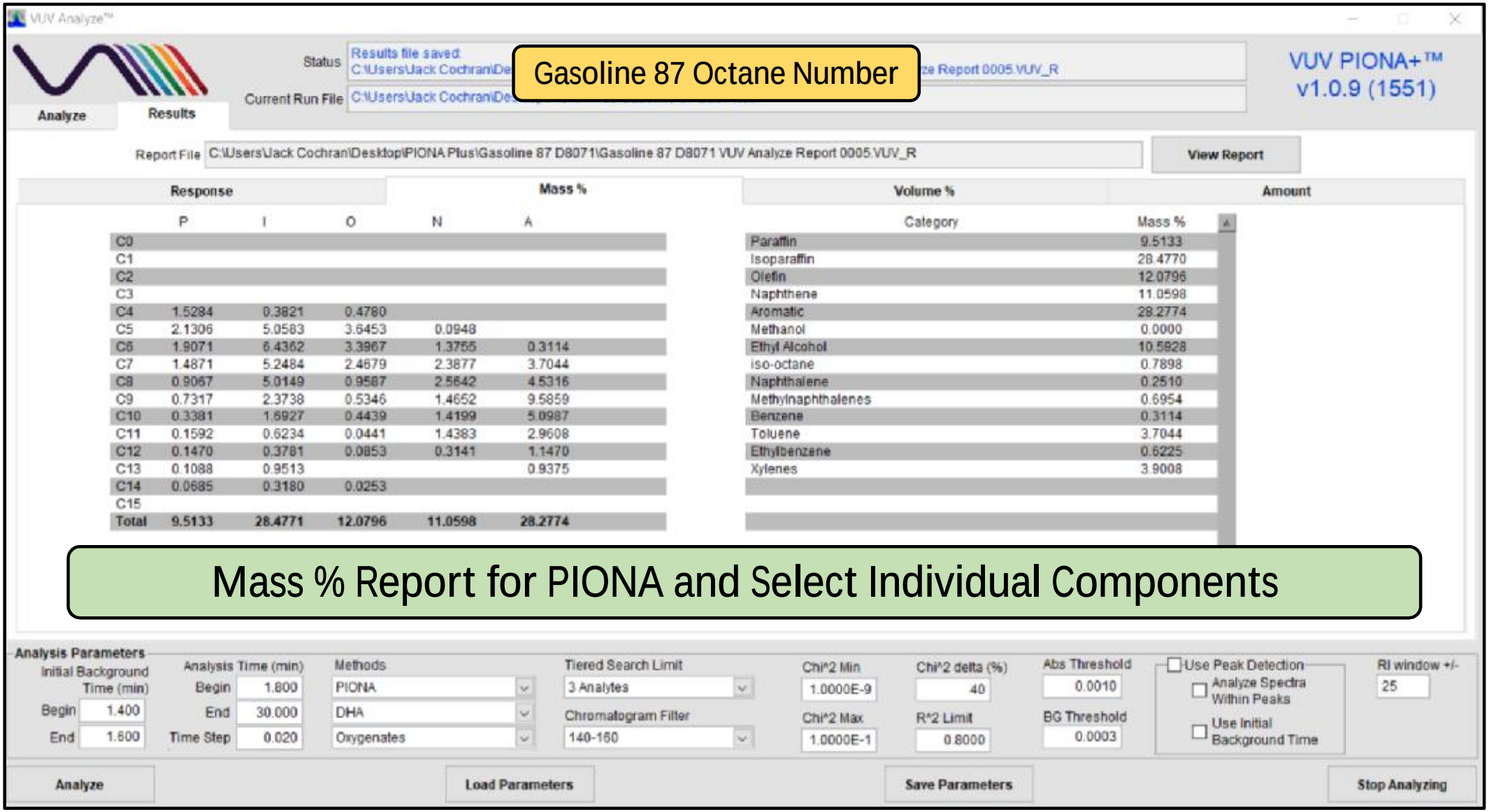











VUV Analyze™
Status
Results file saved
Current Run File
Gasoline 87 Octane Number
VUV PIONA+™
v1.0.9 (1551)
Analyze
Results
Report File
C:\Users\Jack Cochran\Desktop\PIONA Plus\Gasoline 87 D8071\Gasoline 87 D8071 VUV Analyze Report 0005.VUV_R
View Report
Response
Mass %
Volume %
Amount
P I O N A
C0
C1
C2
C3 1.5284 0.3821 0.4780
C4 2.1306 5.0583 3.6453 0.0948
C5 1.9071 6.4362 3.3967 1.3755 0.3114
C6 1.4871 5.2484 2.4679 2.3877 3.7044
C7 0.9067 5.0149 0.9587 2.5642 4.5316
C8 0.7317 2.3738 0.5346 1.4652 9.5859
C9 0.3381 1.6927 0.4439 1.4199 5.0987
C10 0.1592 0.6234 0.0441 1.4383 2.9608
C11 0.1470 0.3781 0.0853 0.3141 1.1470
C12 0.1088 0.9513 0.9375
C13 0.0685 0.3180 0.0253
C14
C15
Total 9.5133 28.4771 12.0796 11.0598 28.2774
Category Mass %
Paraffin 9.5133
Isoparaffin 28.4770
Olefin 12.0796
Naphthene 11.0598
Aromatic 28.2774
Methanol 0.0000
Ethyl Alcohol 10.5928
iso-octane 0.7898
Naphthalene 0.2510
Methylnaphthalenes 0.6954
Benzene 0.3114
Toluene 3.7044
Ethylbenzene 0.6225
Xylenes 3.9008
Mass % Report for PIONA and Select Individual Components
Analysis Parameters
Initial Background Time (min)
Begin 1.400
End 1.600
Analysis Time (min)
Begin 1.800
End 30.000
Time Step 0.020
Methods
PIONA
DHA
Oxygenates
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

Key Features of GC-VUV

- Universal and selective detection
- Unique, class similar spectra
- Complementarity to MS
- Deconvolution of coeluting analytes
- Automated classification and speciation of mixtures
- Good quantitative performance

Instrumental Detection Limits

Paraffin IDLs averaged 41 pg on column

PAH IDLs averaged 28 pg on column

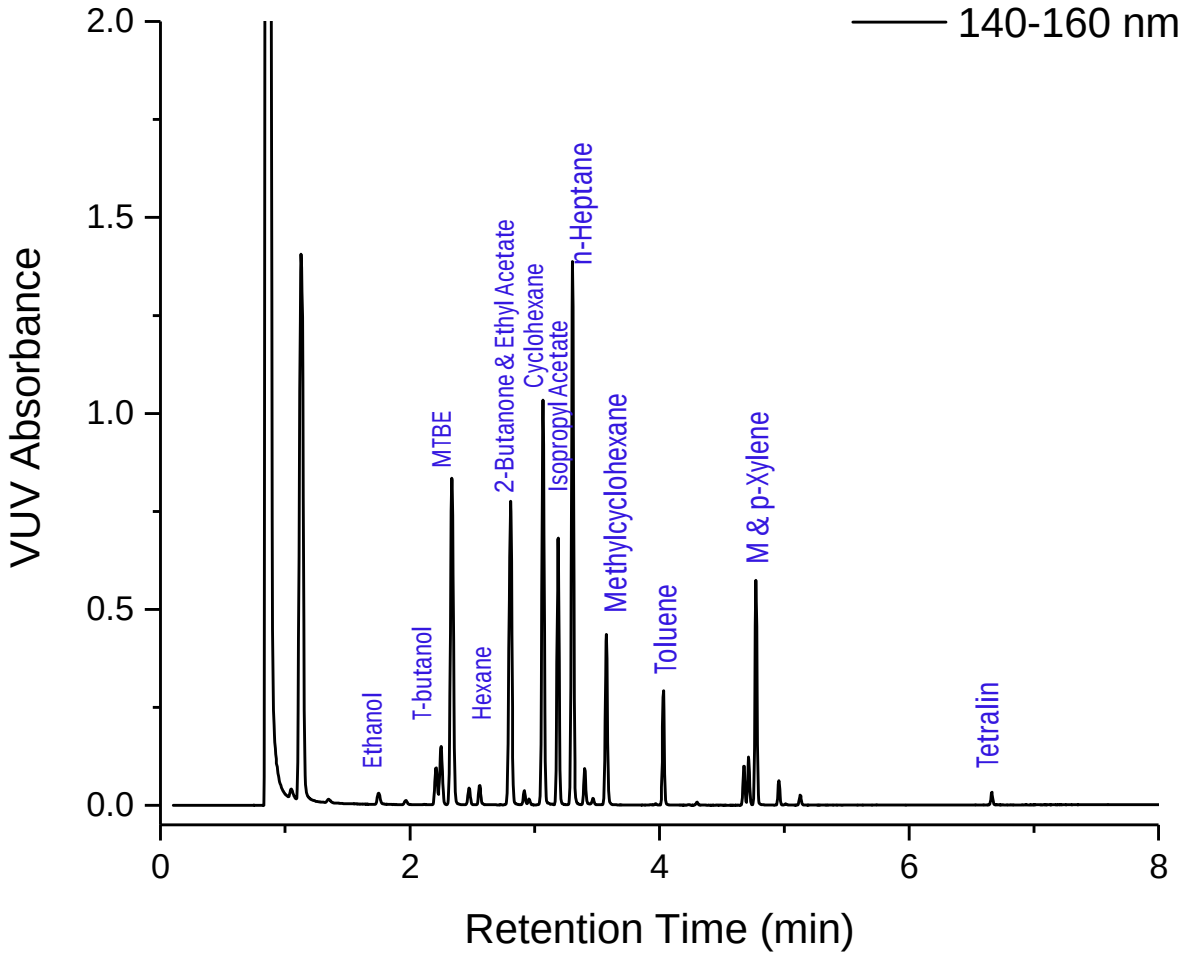
Terpene IDLs averaged 28 pg on column

FAME IDLs averaged 34 pg on column

Fragrance allergen [A], [B], and [C] IDLs averaged 35, 44, and 36 pg on column

Schug et al., *Anal. Chem*. 2014, *86*, 8329-8335.

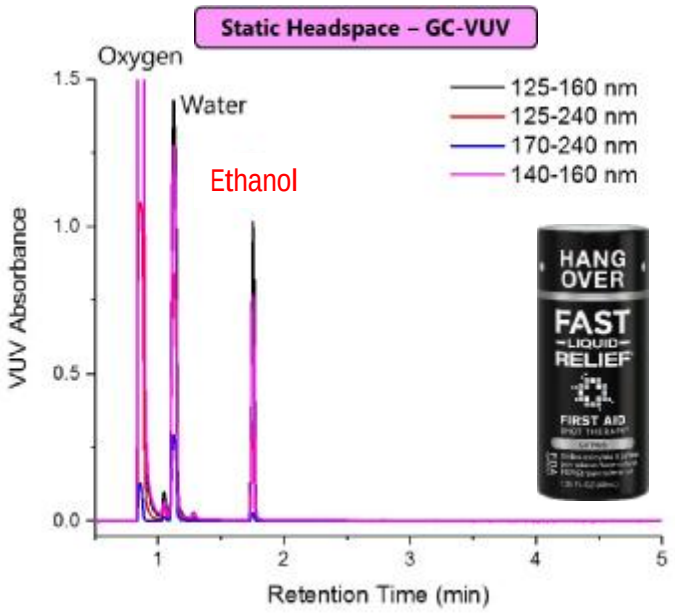
Combined Class 2 & 3 Solvents

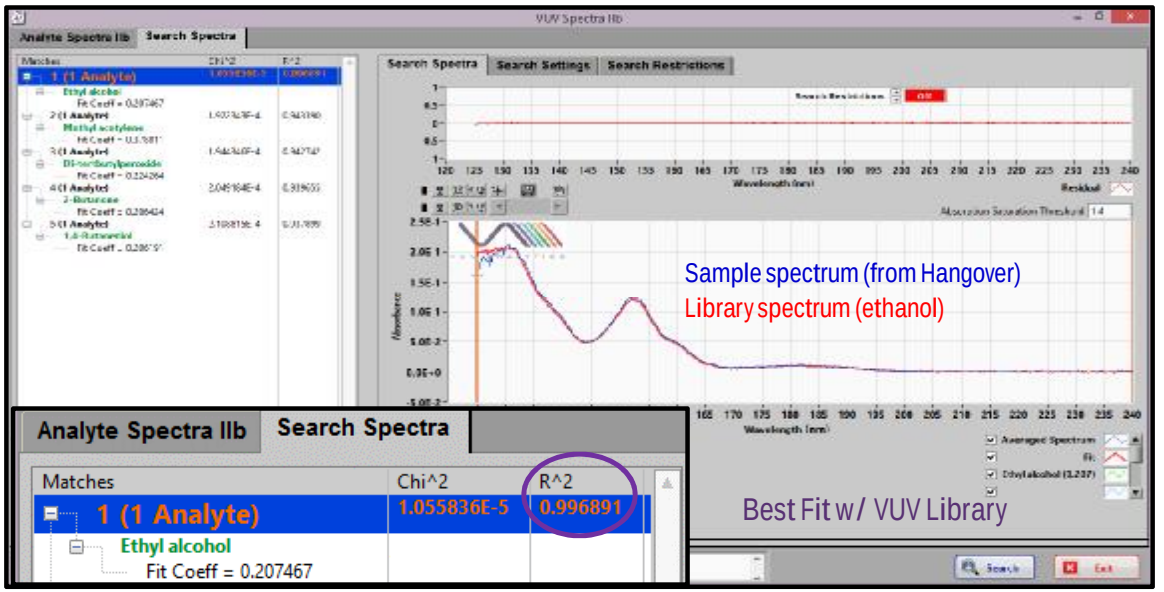


Class 2&3 Residual Solvents
200 mg Infant Acetaminophen
2 mL Water
0.25X USP Limit (ppm) Spike

VUV ANALYTICS

Analyzing Untargeted Unknowns by GC-VUV: Hangover Pain Relief



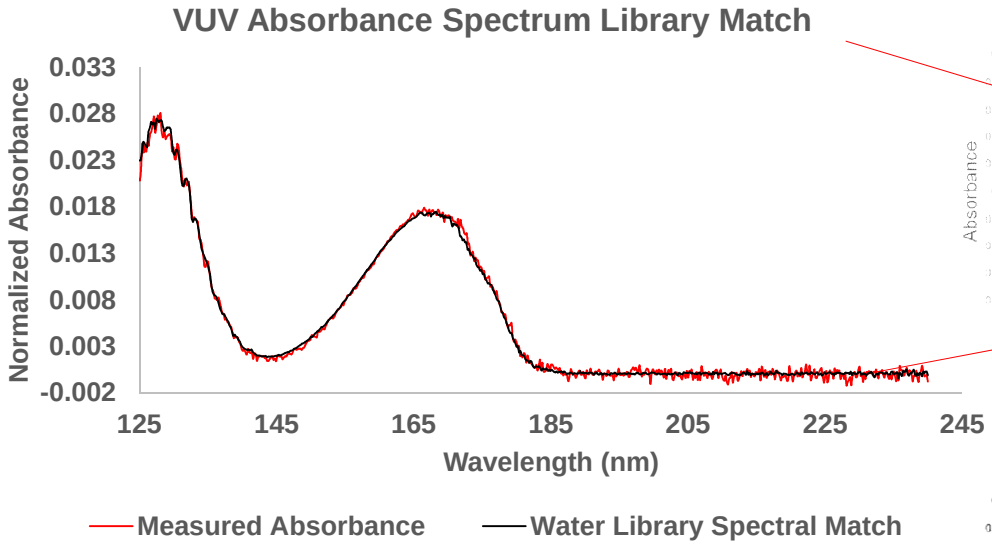


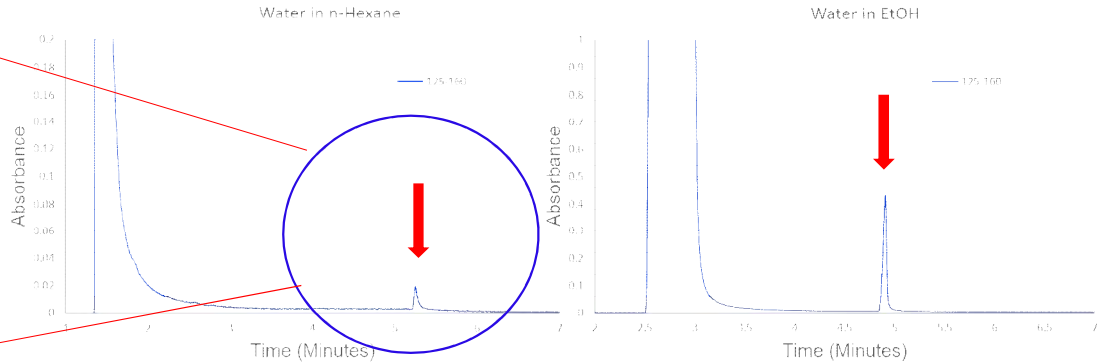
Summary:

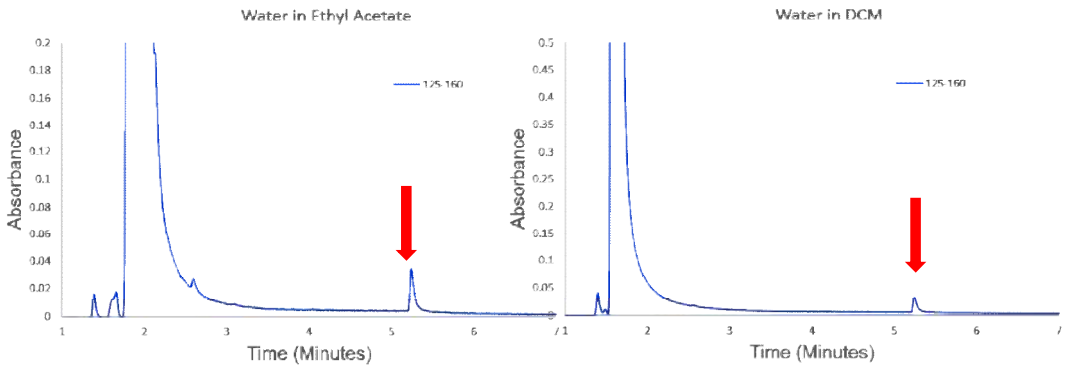
- Applied GC-VUV residual solvents method to over-the-counter hangover medicine
- Detected an unexpected compound in the sample injected through static headspace
- Identified the unknown analyte as ethanol using VUV spectral library matching

VUV ANALYTICS

Water Quantitation with GC-VUV





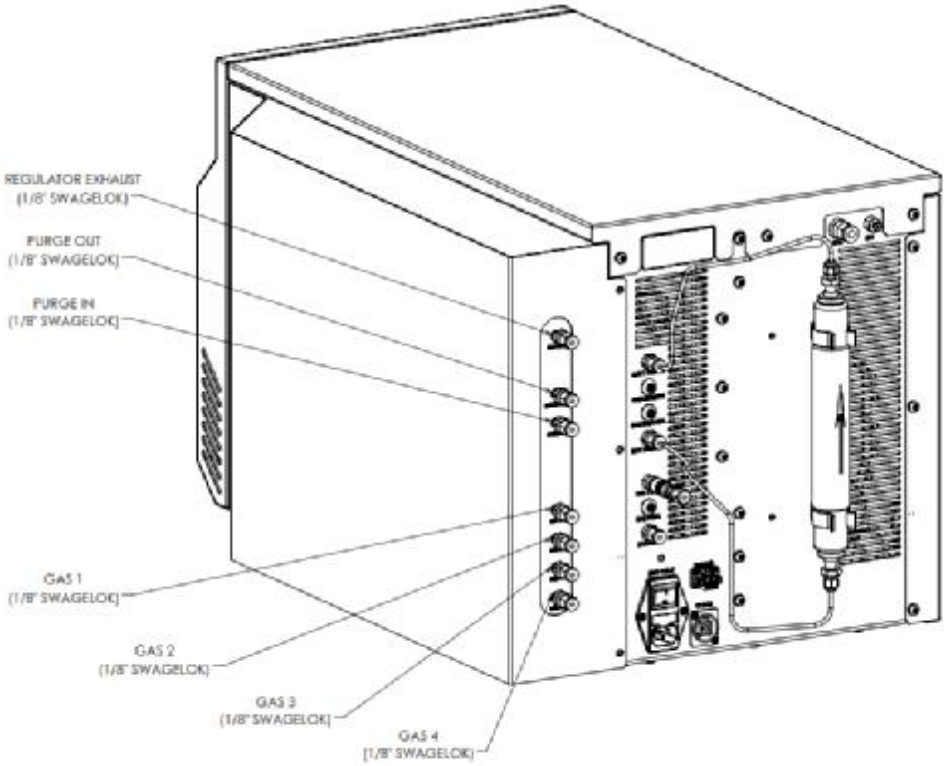


Advantages Compared to Karl Fischer:

- Fast and reliable
- No expensive/toxic reagents
- Definitive Quantitation
- Not affected by interferences and side reactions that can occur using existing KFT methods

VUV ANALYTICS

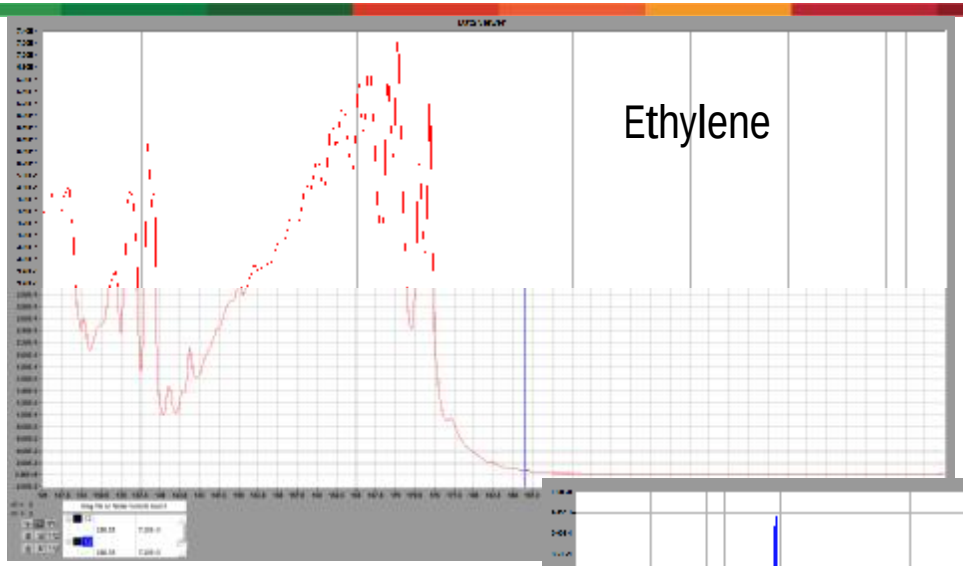
Introducing the SVGA-100

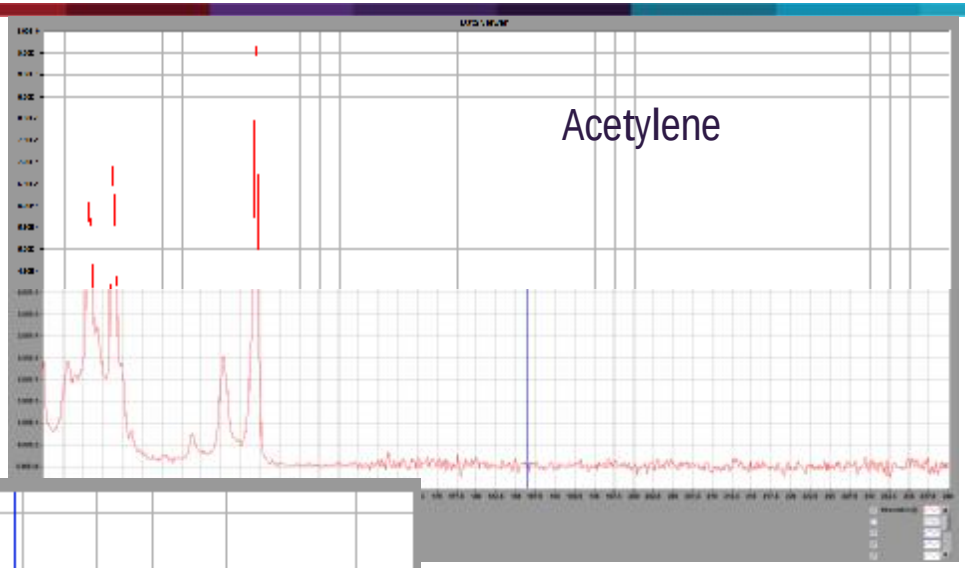


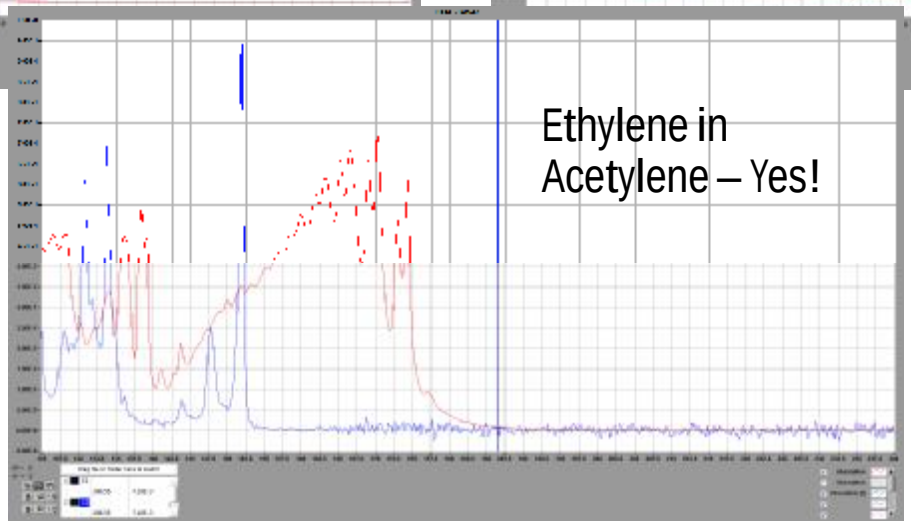
Streaming Gas Analysis Instrument

VUV ANALYTICS

Ethylene / Acetylene Analysis



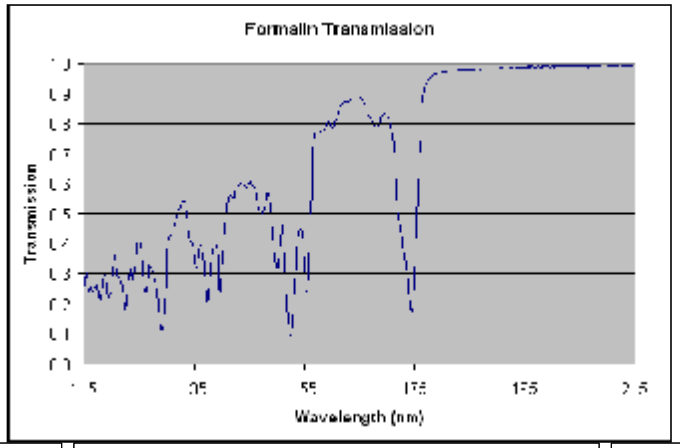


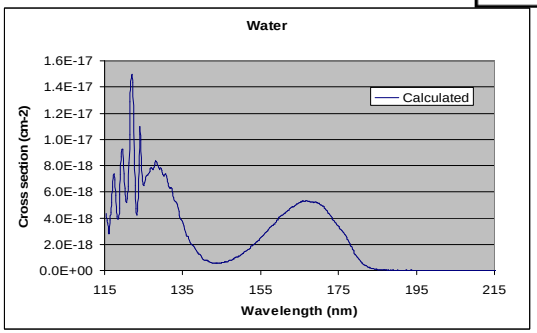


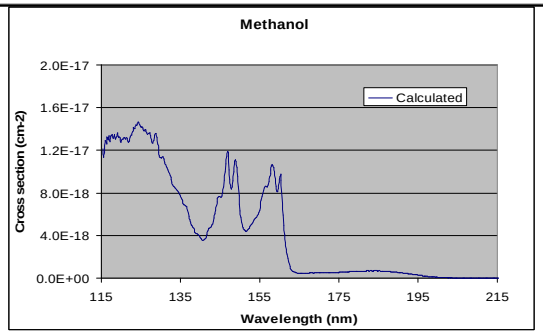
VUV ANALYTICS

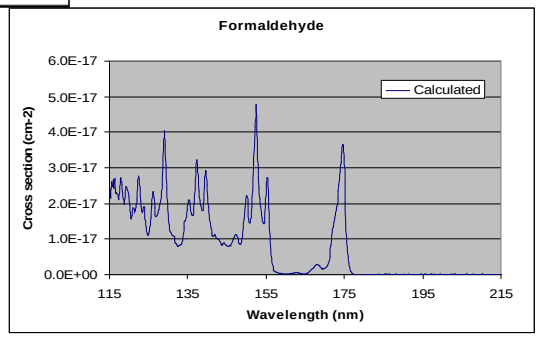
Formalin Headspace – No Separation Case

- Formalin solution headspace was sampled continuously
- Absorption cross sections for water, methanol, and formaldehyde was applied to total absorption





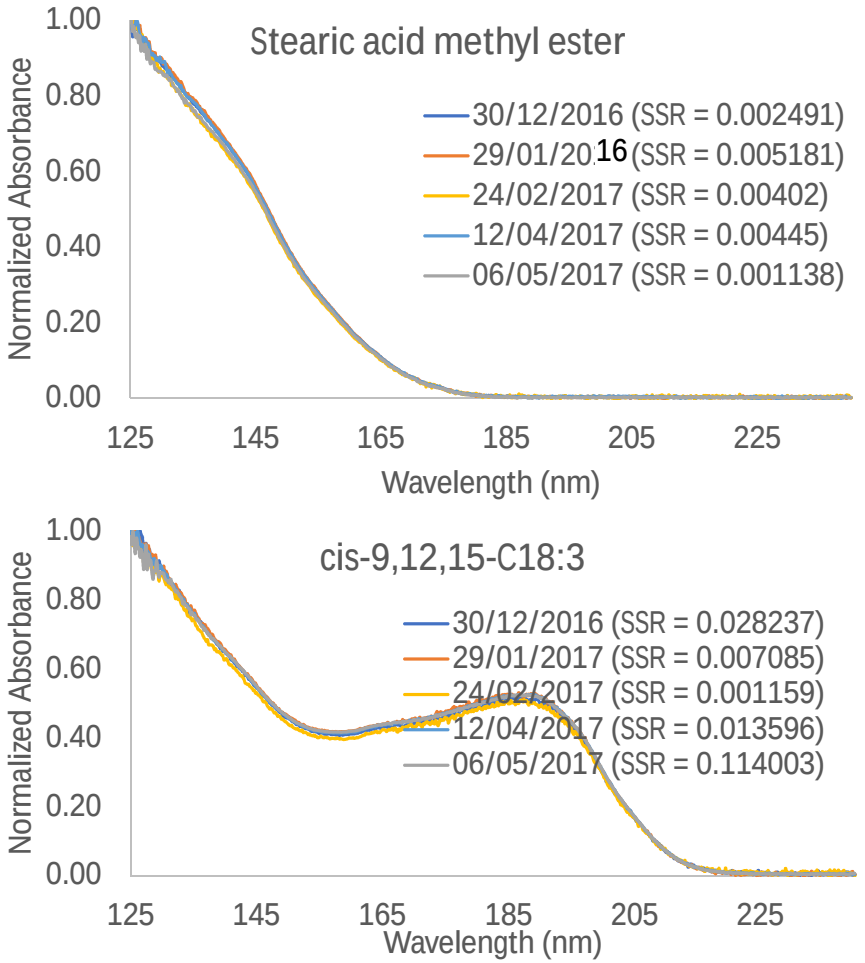




VUV ANALYTICS

Additional Thoughts

- No vacuum
- Robustness
- Reproducibility of spectra
- Fast GC
  - Spectral vs. chrom resolution

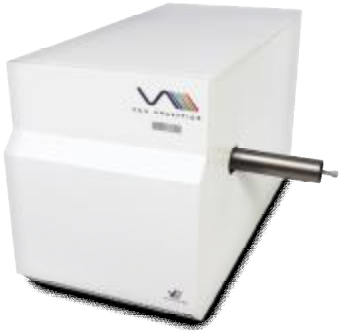


Key Features of GC-VUV

- Universal and selective detection
- Unique, class similar spectra
- Optical differentiation of isomers
- Deconvolution of coeluting analytes
- Automated classification and speciation of mixtures
- Good quantitative performance

What's Next?

- GC-VUV/MS: parallel detection
- VUV is complementary to MS



Thank you for your attention!

VUV ANALYTICS

Science in a new light

www.vuvanalytics.com

korba@amedis.cz

AMEDIS