We don’t have anything against mass spectrometry.
We just think it’s time for a **worthy alternative.**

GC-VUV, využití absorpční UV spektrometrie ve vakuové oblasti spektra ve spojení s plynovou chromatografií

František Laštovička, AMEDIS, spol.s r.o.

VITATOX 2021, 4.10.2021

All you need is...
AMEDIS

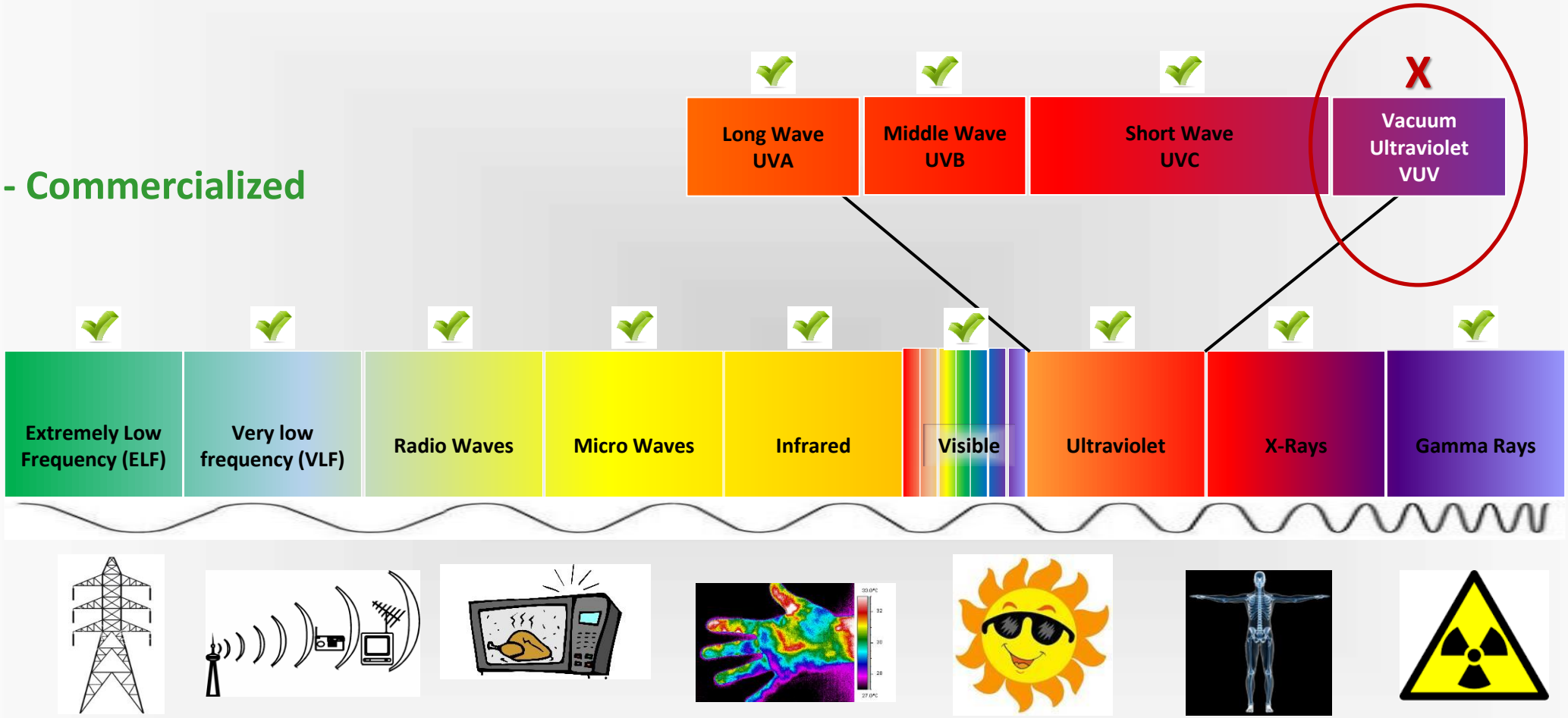
VUV ANALYTICS

VUV Detection Overview

VUV ANALYTICS

VUV = Vacuum Ultraviolet 10 –200 nm (120 – 240 – 430 nm)

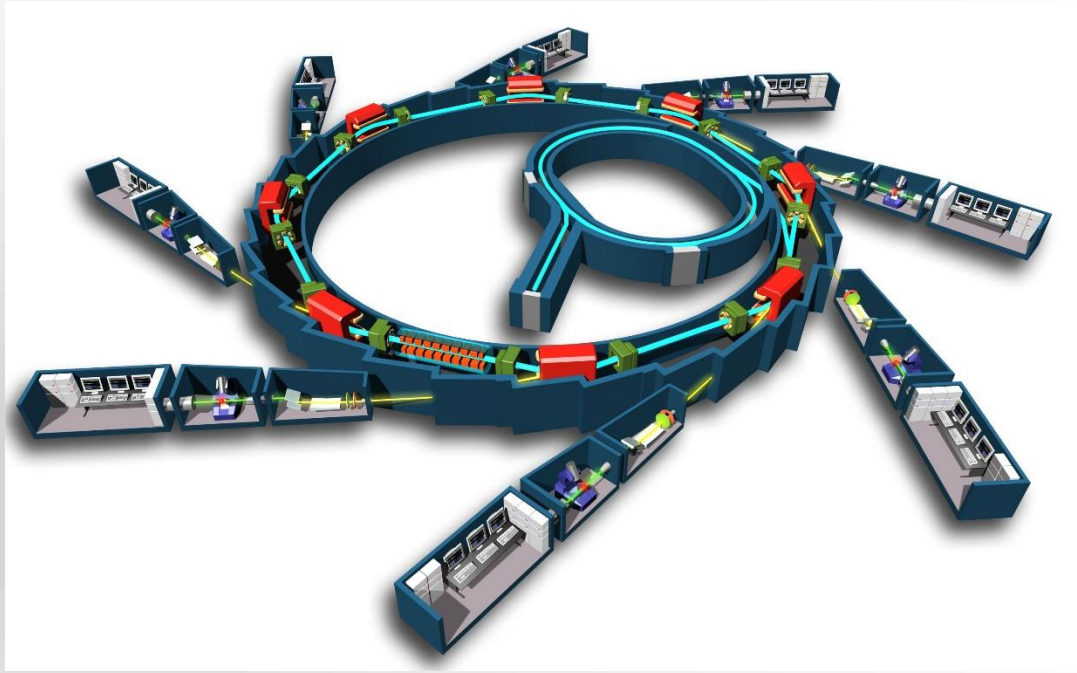
✓ - Commercialized



The Electromagnetic Spectrum

VUV ANALYTICS

First VUV Measurements: Synchrotron



BROOKHAVEN NATIONAL LABORATORY

SOLEIL SYNCHROTRON

- **National Synchrotron Light Source (NSLS)** at Brookhaven National Laboratory in Upton, New York
- Used to conduct fundamental experiments in Chemistry and Physics
- UHV Chambers, incredibly bright sources
- The National Synchrotron Light Source II (NSLS II) cost $912,000,000 just to build alone

VUV ANALYTICS

Recent Market Trend

- **Increased data content**
  - More selective analytical power / detection
  - Simplify background matrix
  - More robust data
  - Provide more accurate compound identification
  - Improve quantitation and repeatability
  - Lower detection levels

Introducing the VGA-100 / VGA-101

Another powerful tool in the toolkit!

The world's first Vacuum Ultraviolet Absorption gas chromatography detector

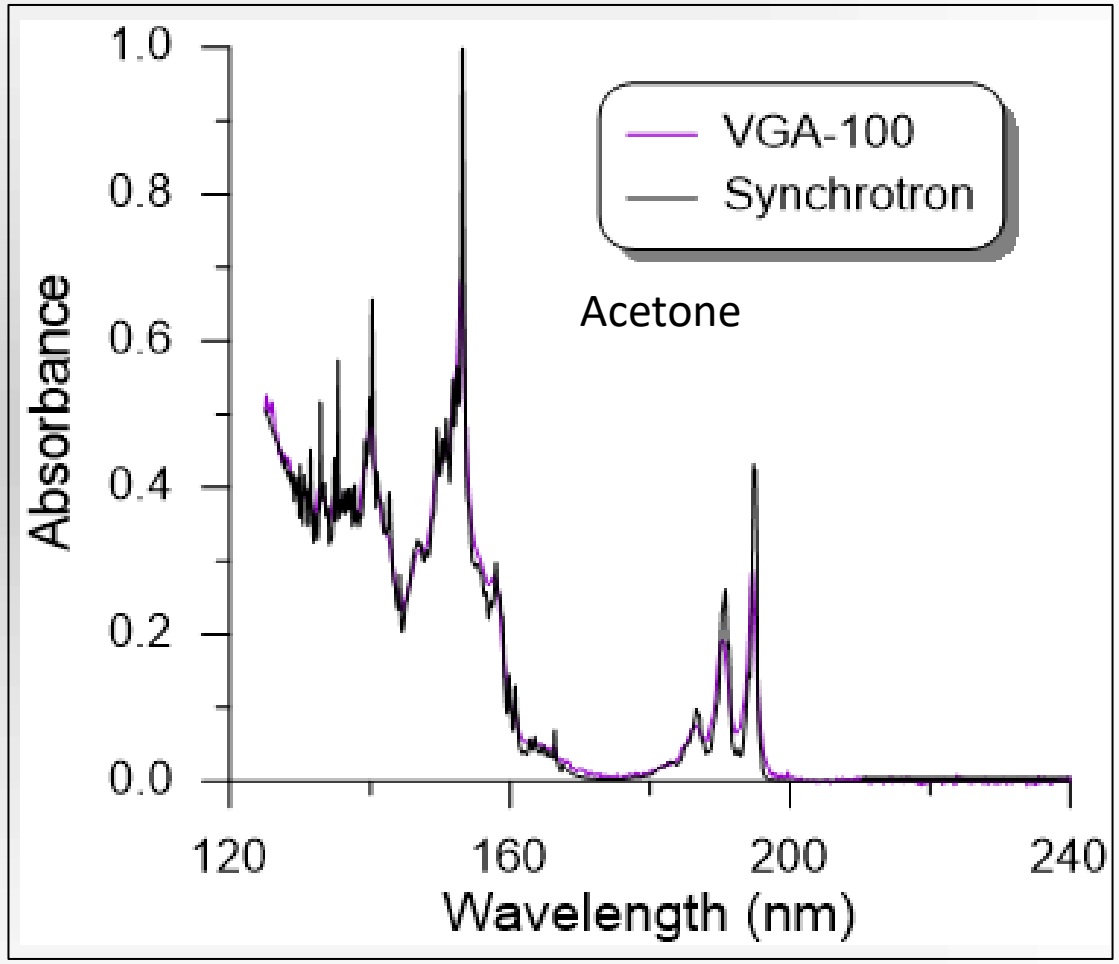
VUV ANALYTICS

The World's First VUV Absorption Detectors: VGA-100 / VGA-101

- VUV Analytics has made vacuum ultraviolet (VUV) absorption available to the general scientific community
  - VUV absorption (VGA-100: 120-240nm ; VGA-101: 120 – 430 nm) enables powerful detection capabilities and a new unique orthogonal separation
- Benefits of the VUV detector include:
  - Universal detection with Powerful selectivity
    - Strong absorption of all gas phase molecules with exception of hydrogen, helium, nitrogen and argon
    - Unambiguous compound identification (exception: large aliphatic hydrocarbons)
    - Ability to deconvolve co-eluting analytes
    - Reduce matrix contributions with spectral filters
    - Clear and easy isomer differentiation
  - Excellent sensitivity
    - Low picograms,
    - Spectral filters increase analyte sensitivity in targeted wavelength regions
  - Non-destructive analysis
    - No ionization, analyze intact molecules
  - Excellent temporal resolution
    - Up to 100Hz Sampling
    - Dynamic Make-up gas control
  - Predictable linear response / No frequent calibration required
    - Beer's law: 1st principle detection reduces calibration burdens: robust and uniform response factors
  - Reliable & Easy to use
    - ➢ No routine maintenance necessary, no vacuum pumps, Ozone cleans
    - Long Life Lamp

VUV ANALYTICS

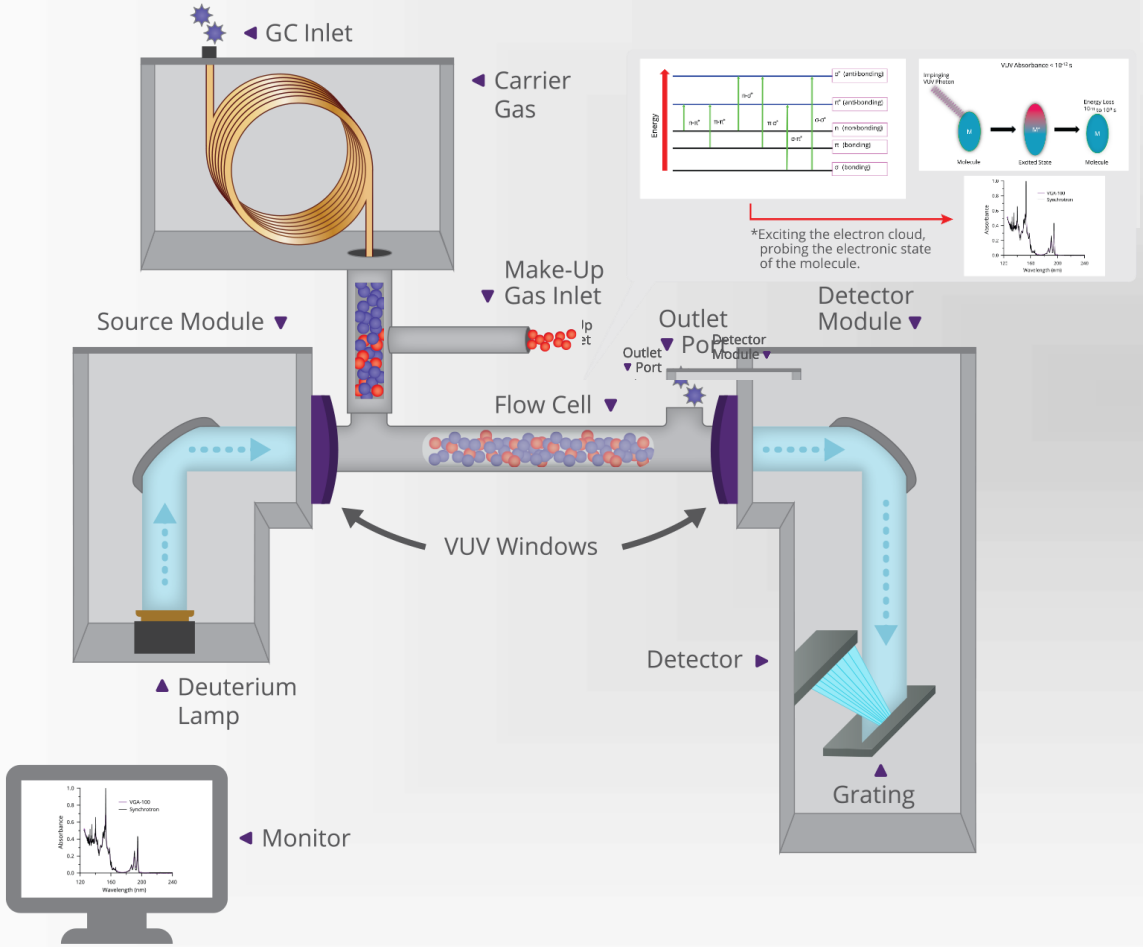
GC-Vacuum Ultraviolet Absorbance Spectroscopy (GC-VUV)



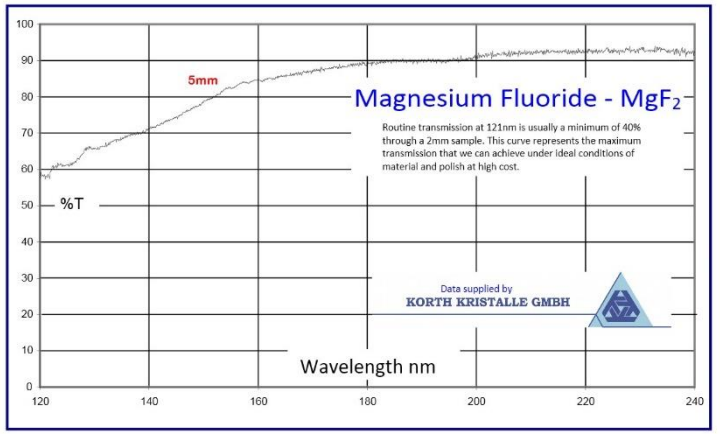
Brookhaven on your benchtop: VUV Spectra *without* a Beamline

VUV ANALYTICS

Vacuum Ultraviolet Absorbance Spectrophotometer

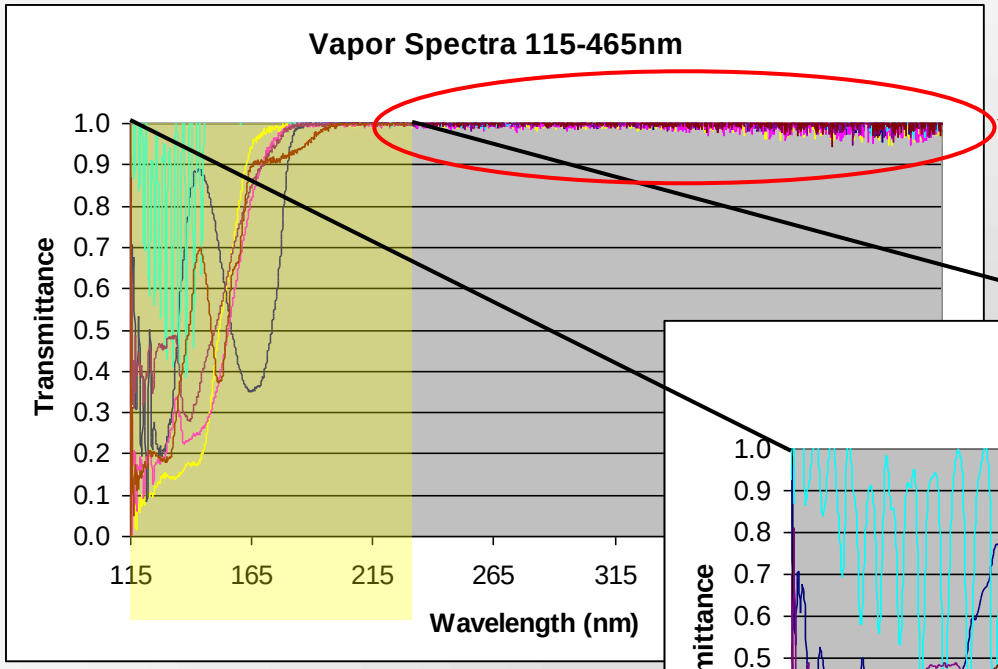


- Material Selection: MgF2 windows to transmit VUV radiation, Ultraclean Environment
- D_2 Source
- Non-Vacuum environment, Inert makeup gas (N_2 , He, Ar) used to ensure constant flow in the flow cell
- Patented Optical Design and Environment
- Optical Mirrors, grating, and backthinned CCD
- Transfer line and cell heated up to 300°C or 430°C (VGA-101)
- Flow cell dimensions 10cm x 0.1cm – 78 ul (VGA-100) or 10cm x 0.05cm – 39 ul (VGA-101)
- Easily interfaced with any GC via a heated transfer line
- Self cleaning Ozon source
- Self diagnostics
- Factory installed and aligned

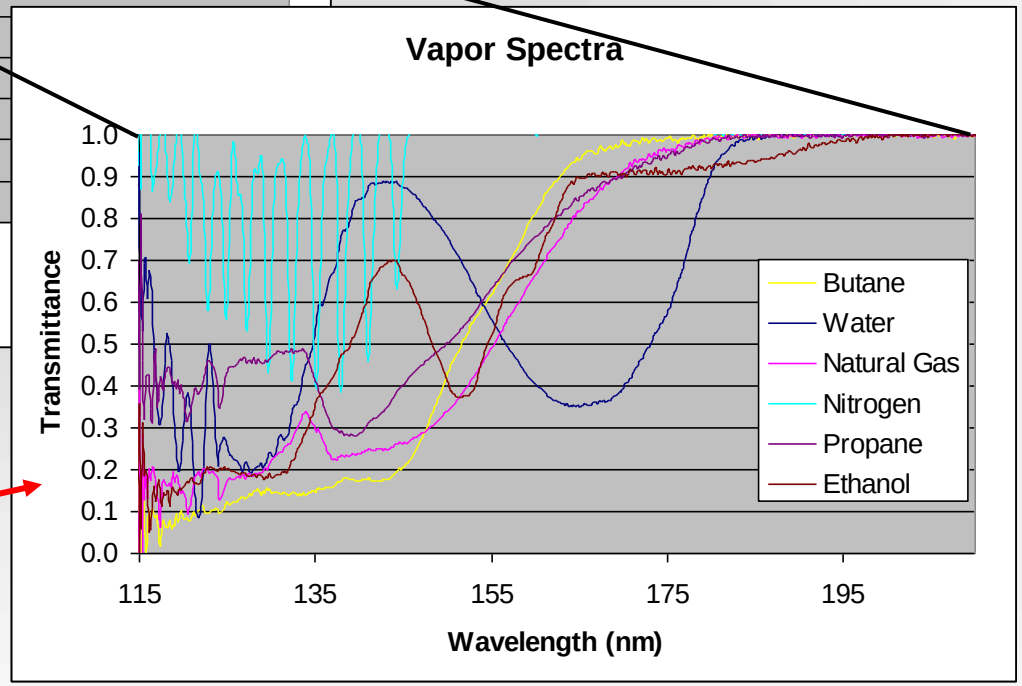


VUV ANALYTICS

VUV Gas Phase Spectra



Most gas phase compounds have little or no absorption in the visible or UV region

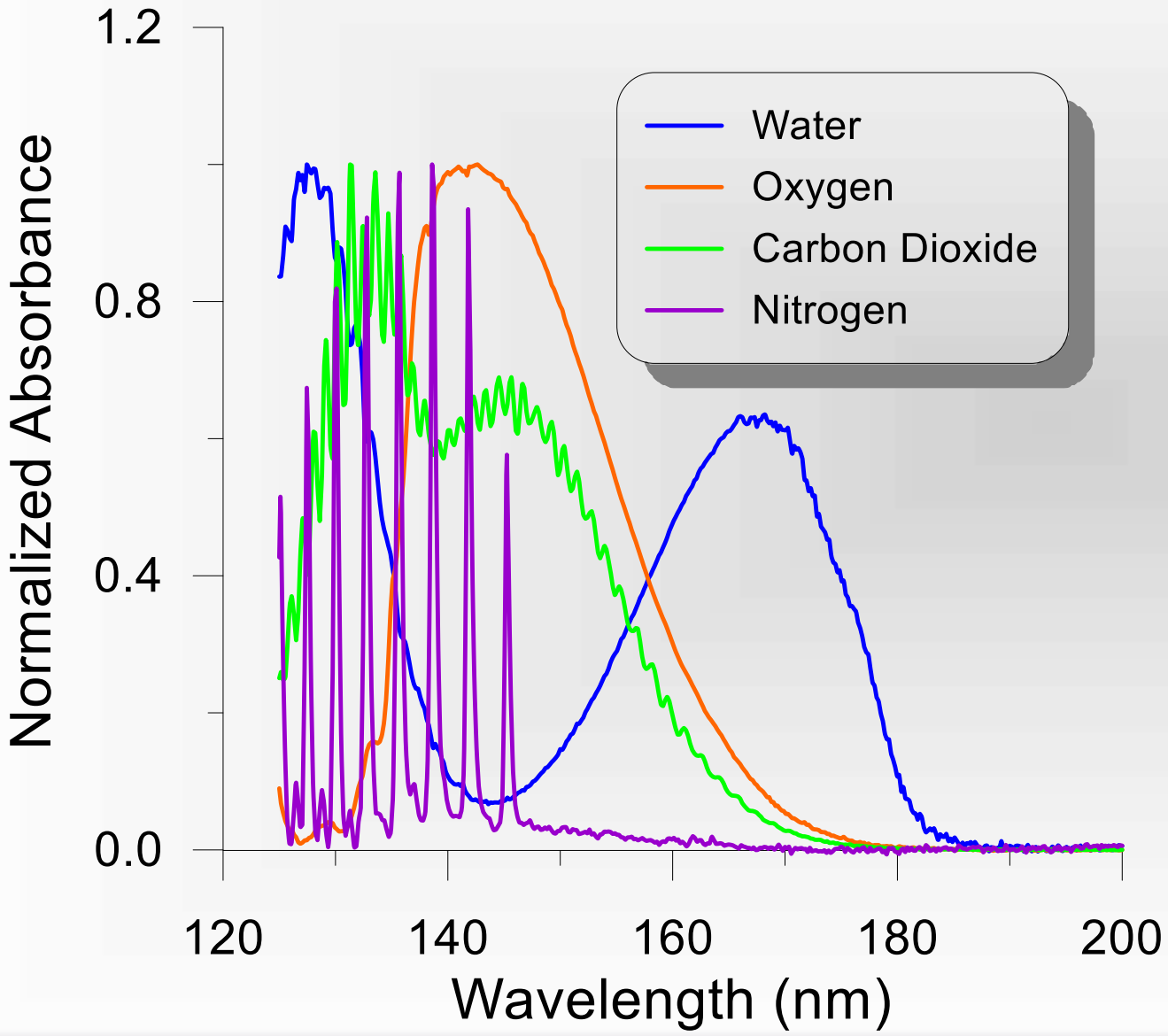


Everything absorbs in the Vacuum Ultraviolet region

Often hundreds of times stronger than in IR absorption

VUV ANALYTICS

VUV – All compounds absorb strongly

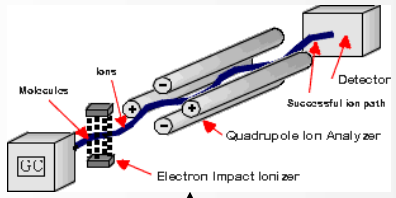


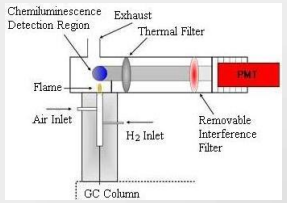
*"The excitation **energies associated with** electrons forming **most single bonds are** sufficiently high that absorption occurs in the so-called **vacuum ultraviolet** region (λ<185nm), where components in the atmosphere also absorb strongly. **Because of experimental difficulties associated with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

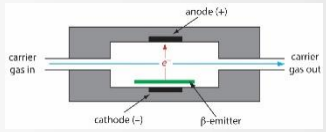
- Principals of Instrumental Analysis, by Douglas Skoog, Sixth Edition, 2006

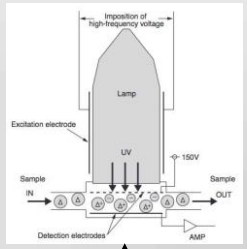
Schug et al., *Anal. Chem*. **2014**, *86*, 8329-8335

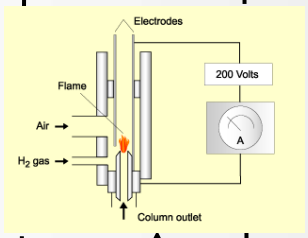
The First New GC Detector Technology in ~30 Years!

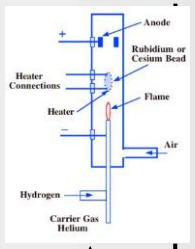


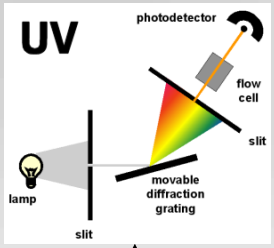


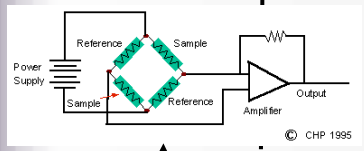


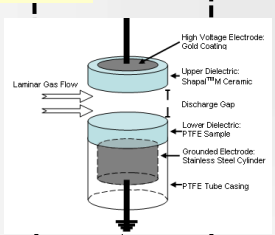


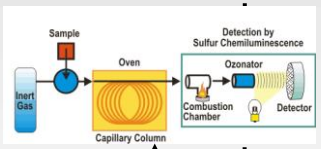












TCD 1950 | MS 1952 | FID 1958 | ECD 1959 | BID 1960 | NPD 1961 | FPD 1962 | PID 1976 | SCD 1982 | UV 1983 | VUV 2014

VUV ANALYTICS

Product Overview

VGA-100 Detector

VGA-101 Detector with enhanced features

SVGA-100 Analyzer

2014 Gulf Coast Conference
VGA-100
"Best New Analytical Instrument"

Best New Analytical Instrument
VGA-100
GCC
New Product Showcase Winner

The Analytical Scientist
VGA-100
“Top 5 Innovation Award"

the Analytical Scientist
TASLAs 2014
Top 5

R&D-100 Award
VGA-100
“Analytical / Test Category Winner"

2015 R&D 100 WINNER

2016 ISA Analysis Symposium
SVGA-100
"Innovative Product of the Year"

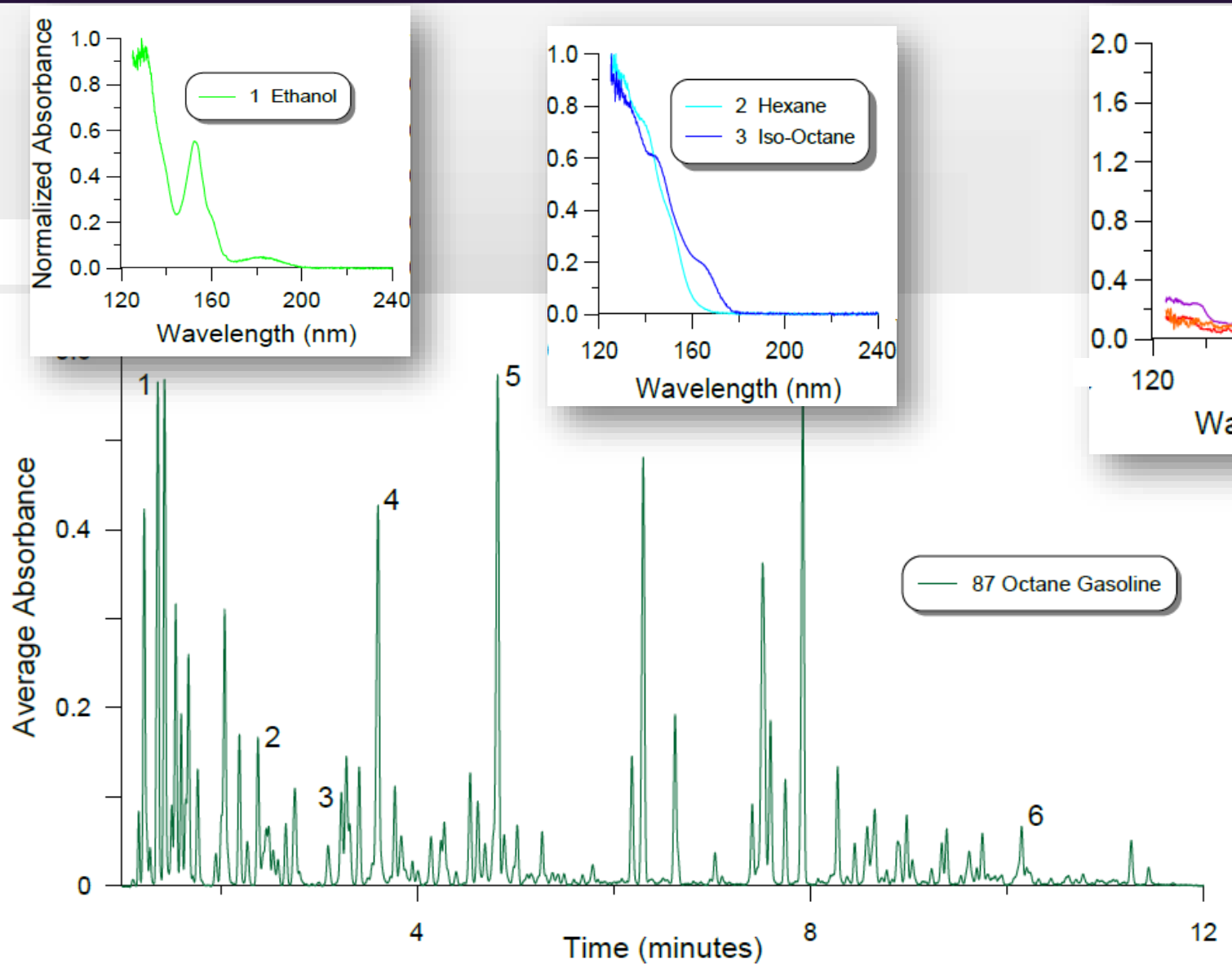
Innovative Product of the Year Award
SVGA-100
ISA Analysis Symposium2016
24–28 April 2016
Galveston Convention Center
Galveston, Texas USA

Compound Identification and Compound Deconvolution

VUV ANALYTICS

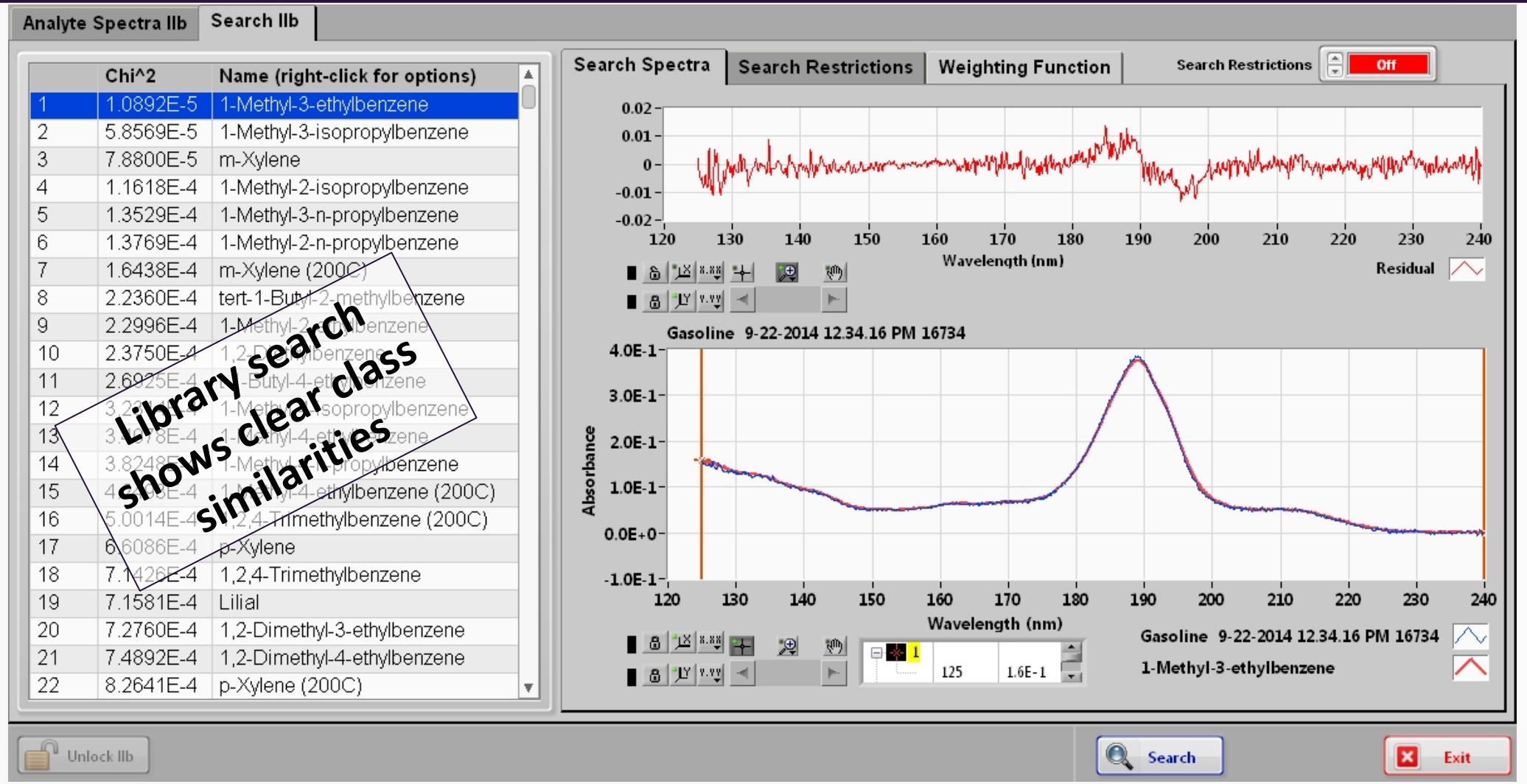
Compound Specific Absorption Spectra

- All chromatogram peaks represent unique compound absorption
- Compound classes show like absorption responses



VUV ANALYTICS

Library search and Unambiguous Compound Identification



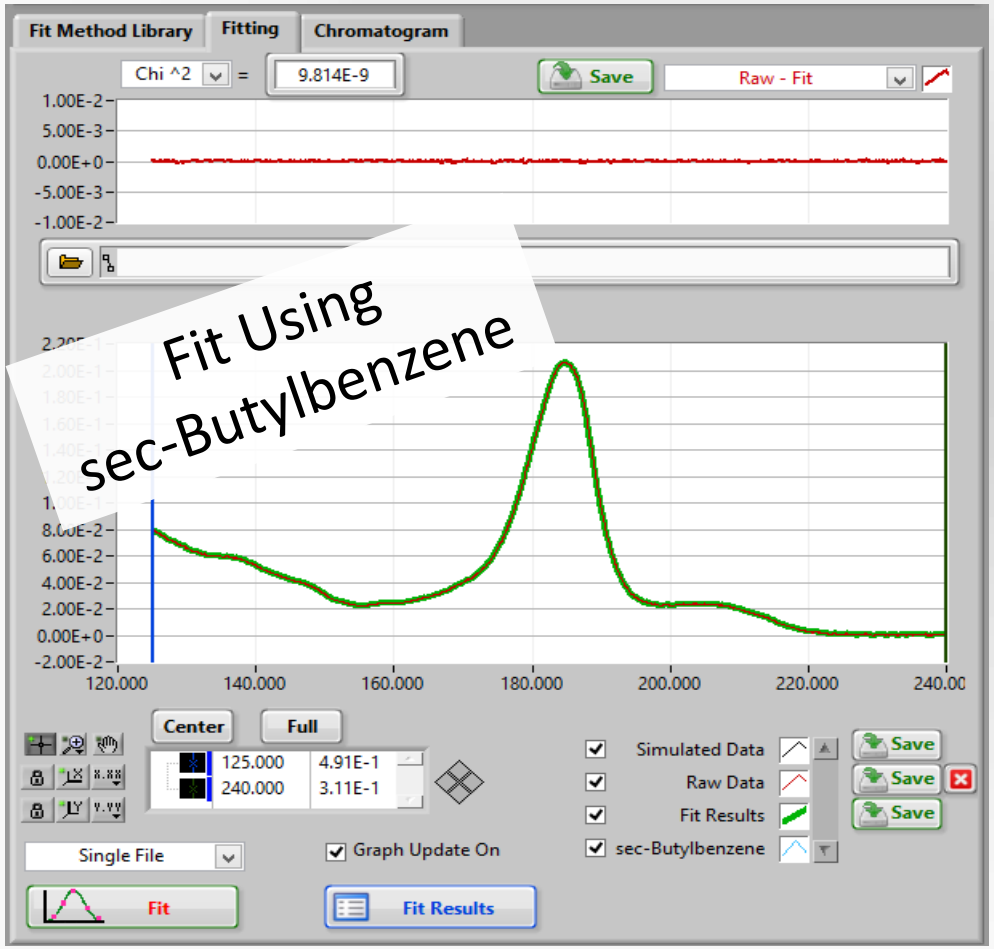
Spectra are very robust;

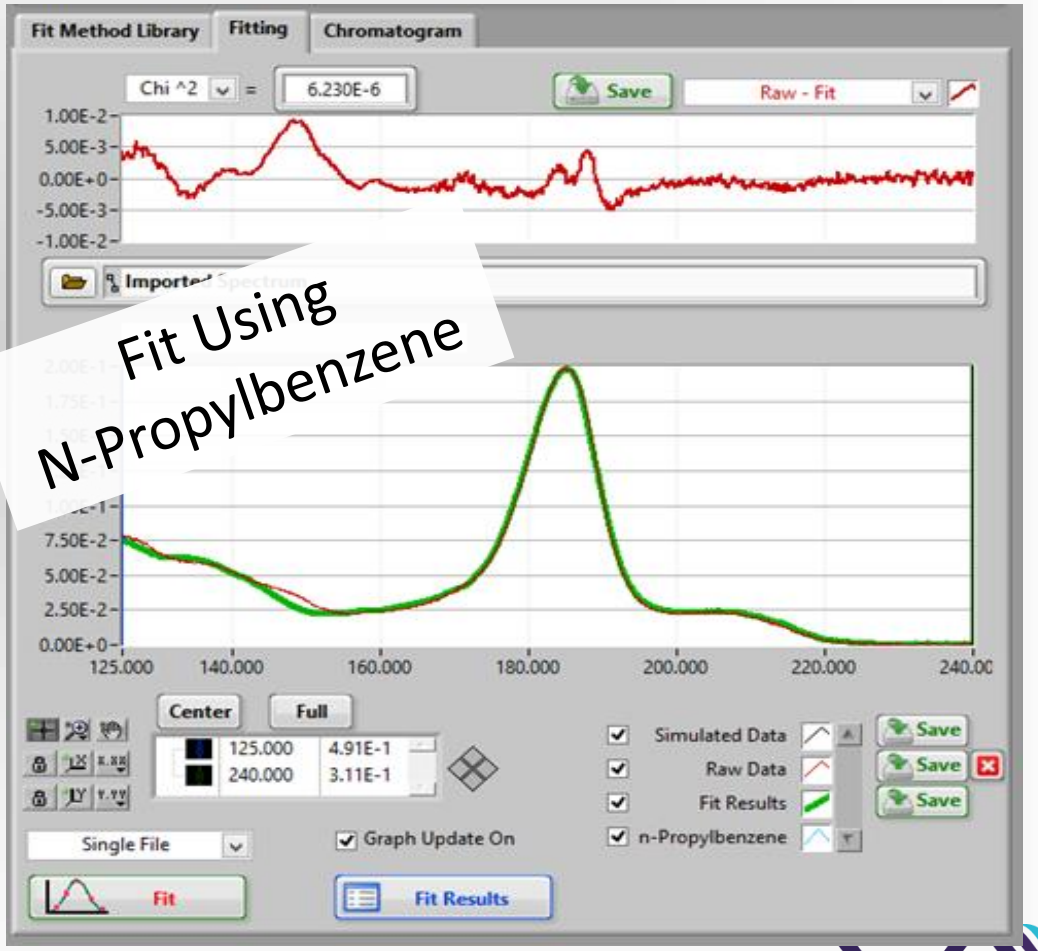
No ghost components in the library match list

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

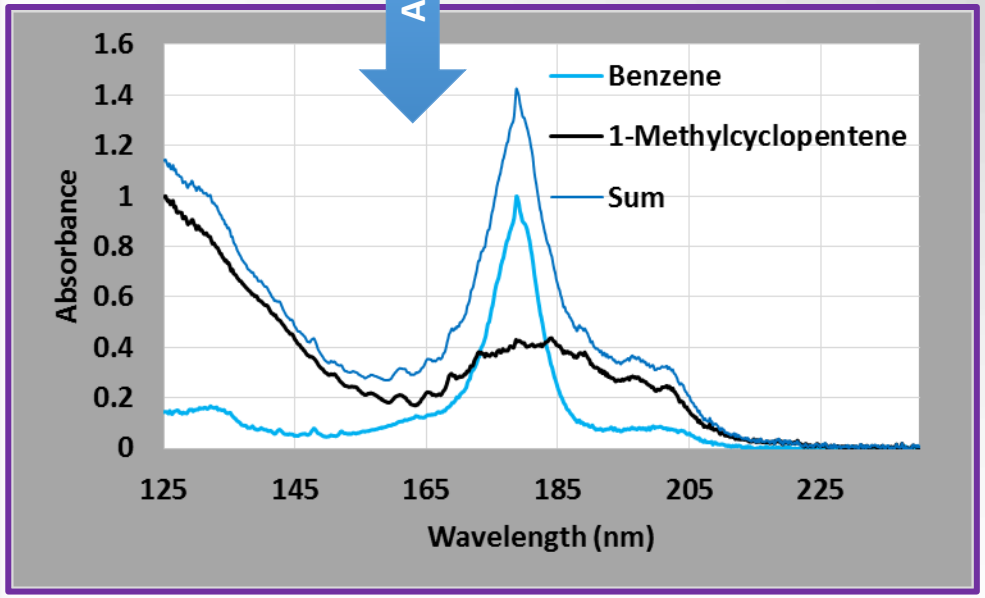
Deconvolution

- 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

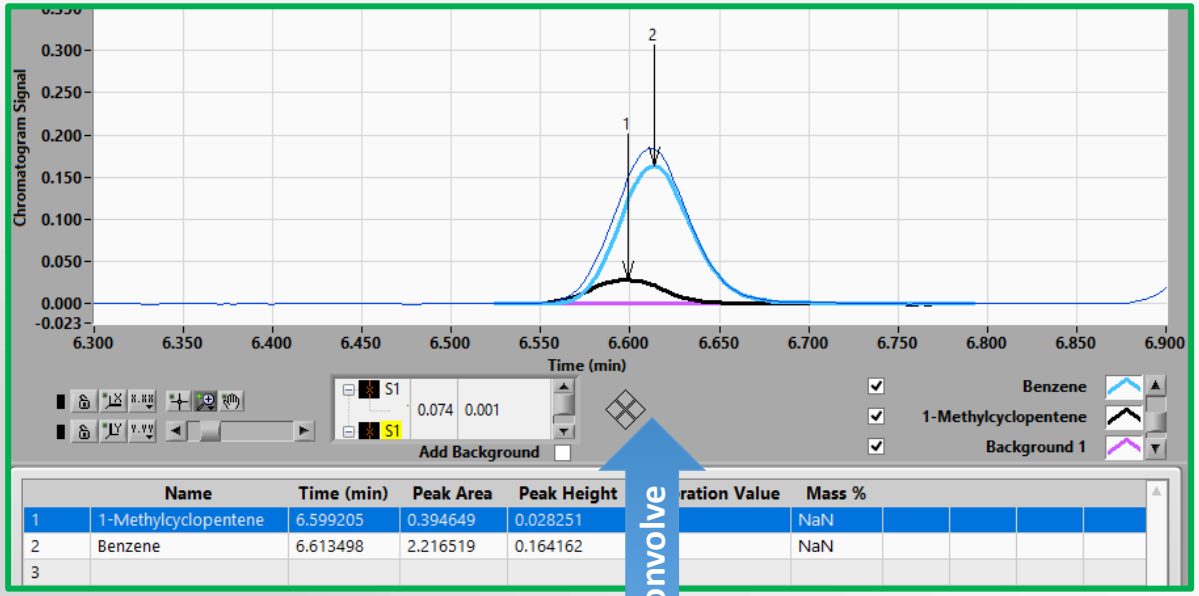
Beer's Law: $A = \epsilon bC$

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

Additive



Deconvolve



	Name	Time (min)	Peak Area	Peak Height	Mass %
1	1-Methylcyclopentene	6.599205	0.394649	0.028251	NaN
2	Benzene	6.613498	2.216519	0.164162	NaN
3					

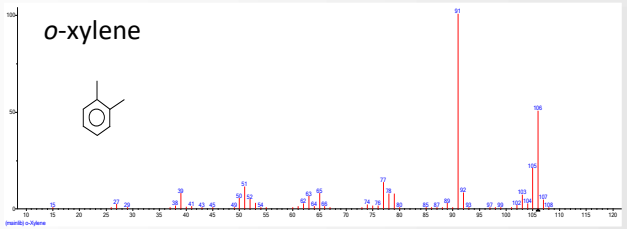
$A_{co\text{-}elution} = f_1A_1 + f_2A_2$

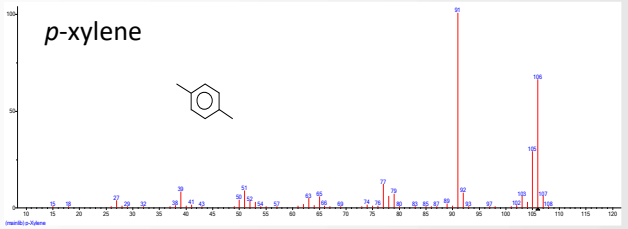
A_i = the absorbance of component i at a given λ

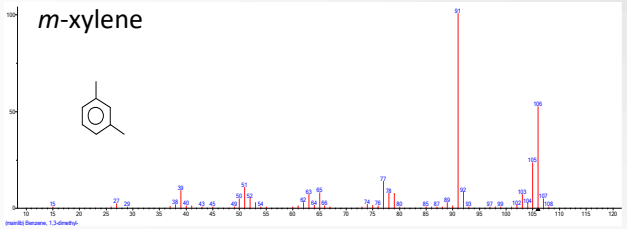
f_i = the fit coefficient of component i

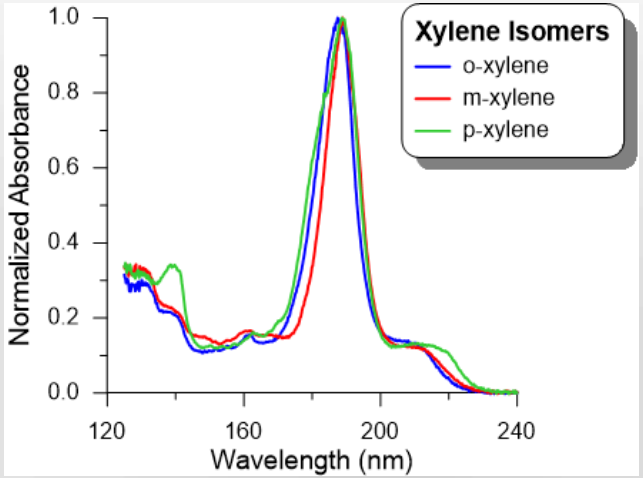
VUV ANALYTICS

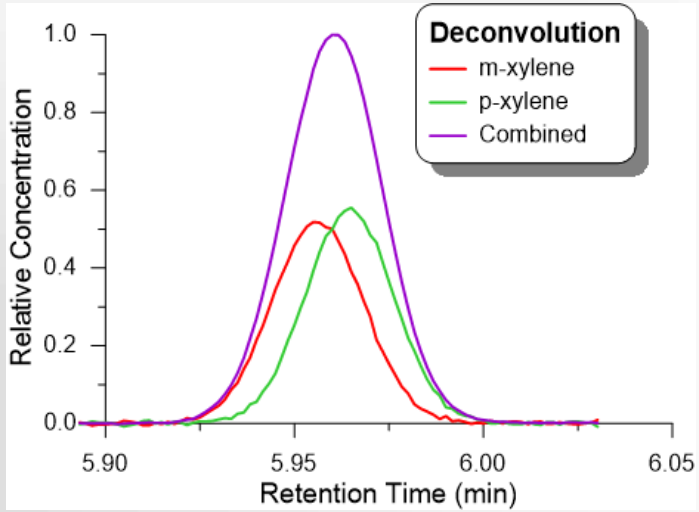
Spectral Deconvolution of m&p Xylene

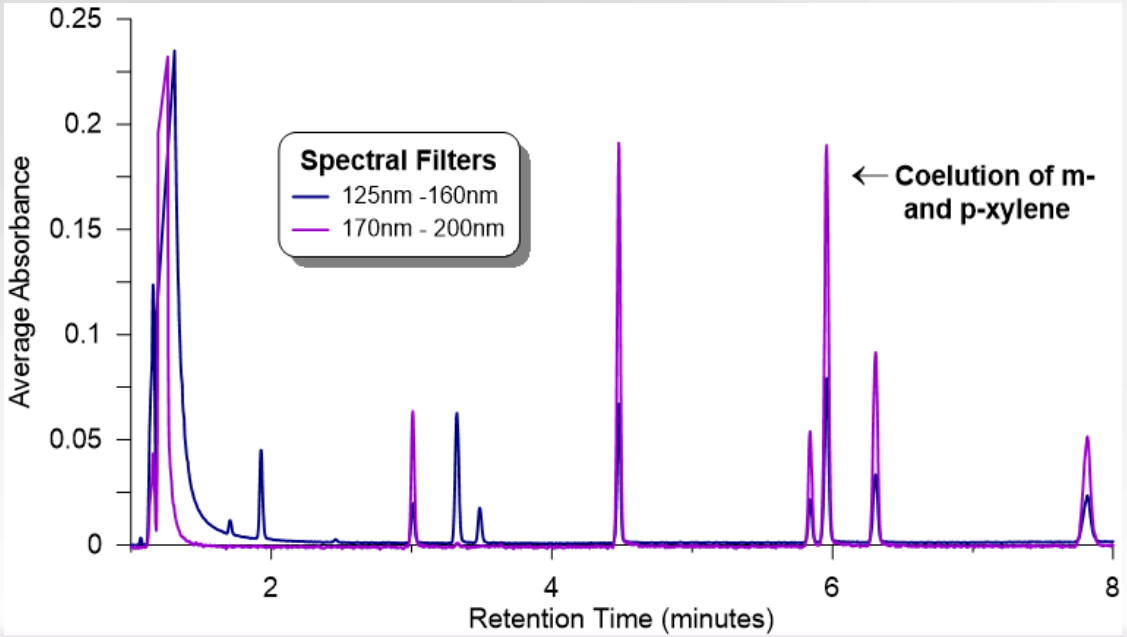










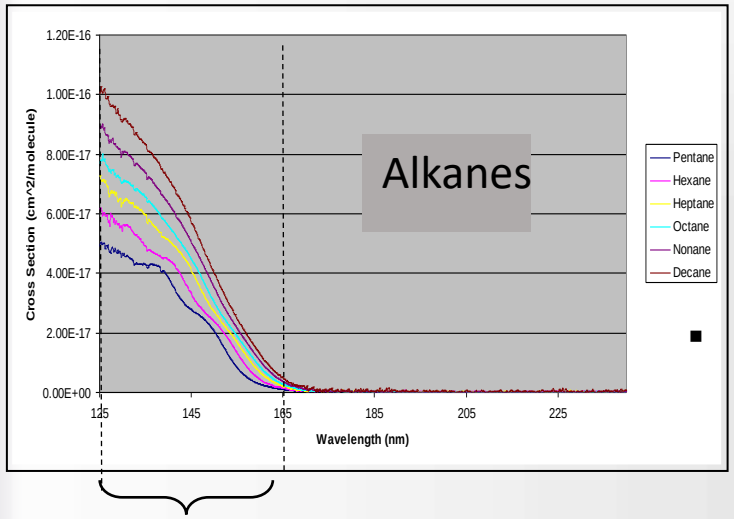


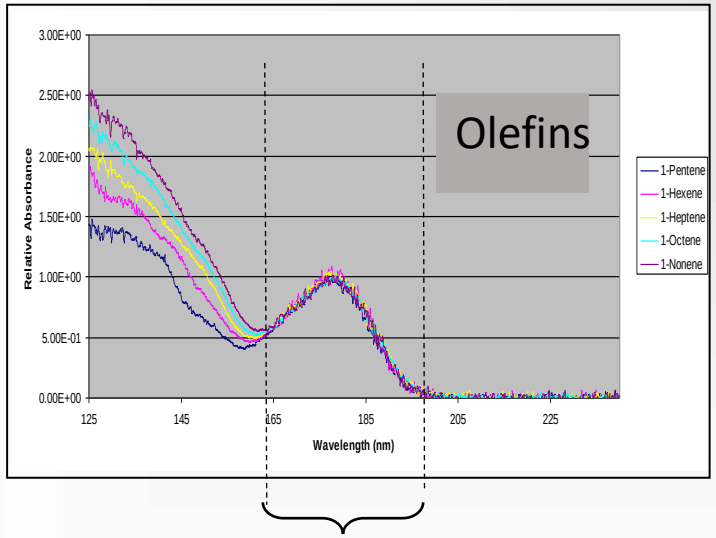
VUV ANALYTICS

Class Analysis
(Use of Spectral Filters)

VUV ANALYTICS

Spectral Filters – “Class Discrimination”

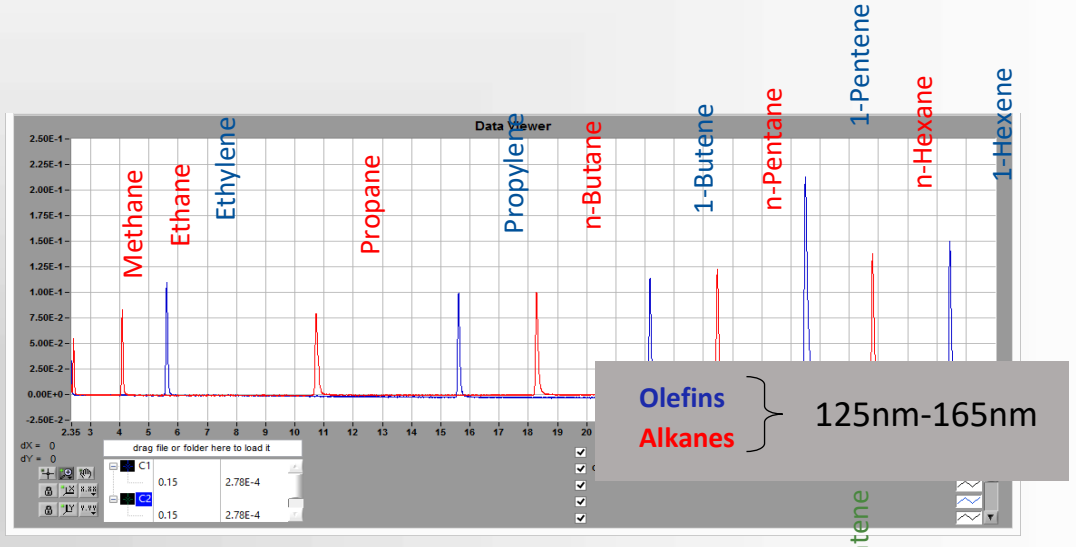


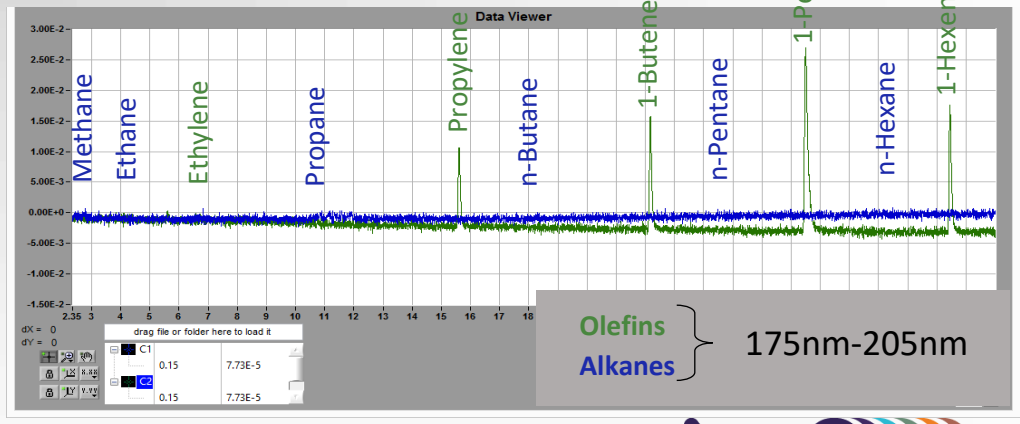


Spectral filters are useful because some compounds absorb more strongly than others in certain regions of the VUV spectrum

- Saturated aliphatic compounds absorb strongest in the 125-160 nm region
- Aromatics and other unsaturated compounds have characteristic λ_{Max} values in the 170-200 nm region

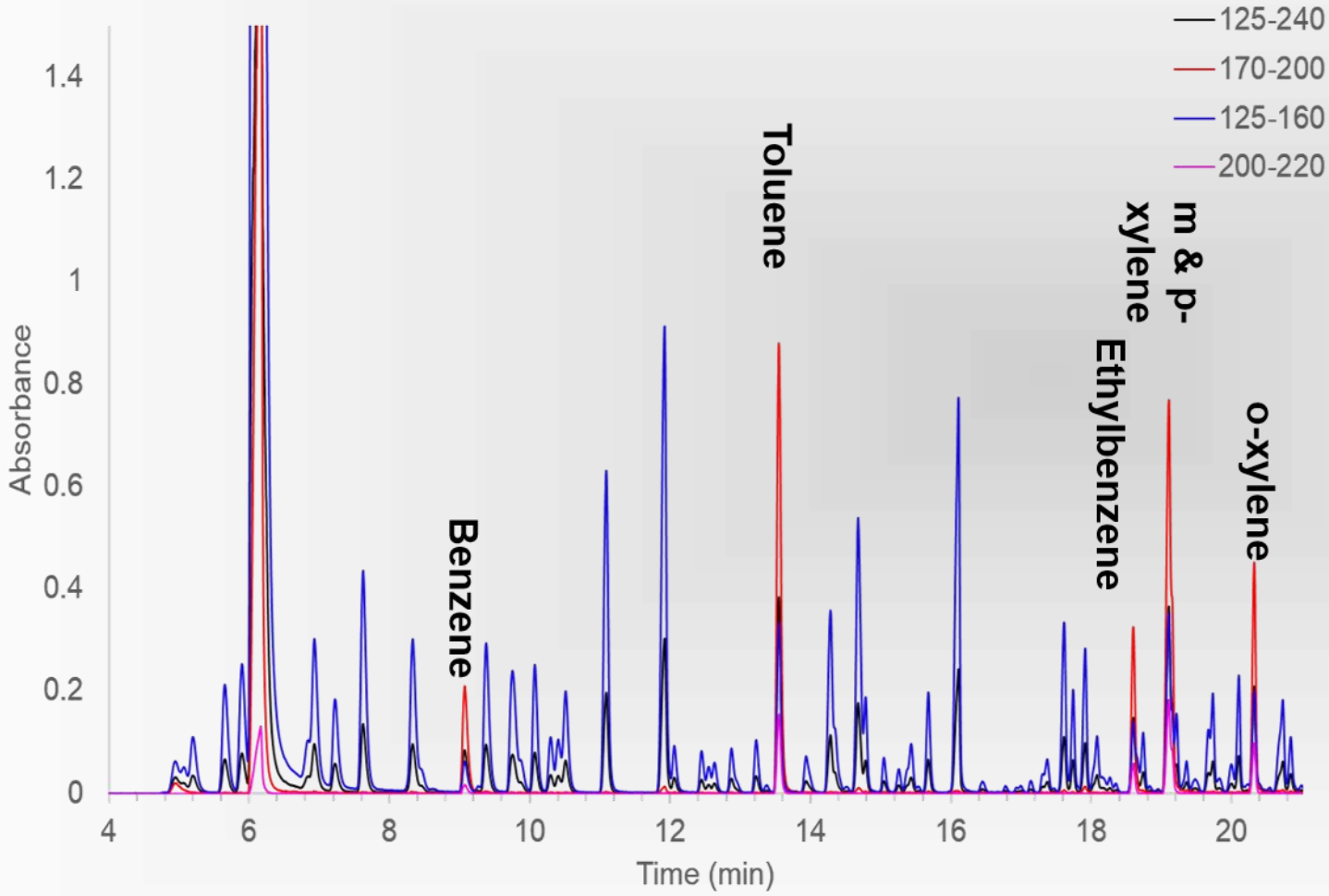
Overlay of Alkane and Olefin Standards



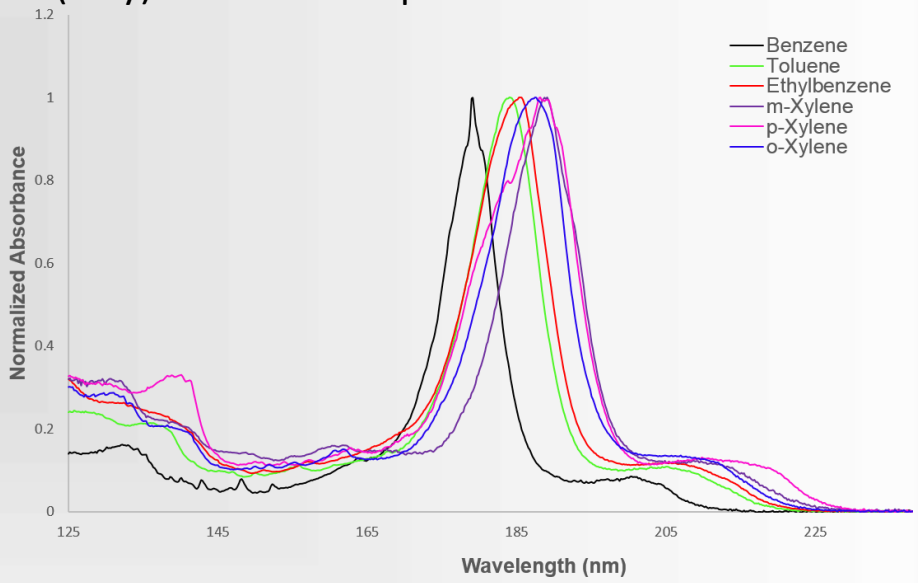


VUV ANALYTICS

Peak ID and VUV Absorbance Spectra



Full spectral data
Aromatic components
Aliphatic components
(Poly) aromatic components



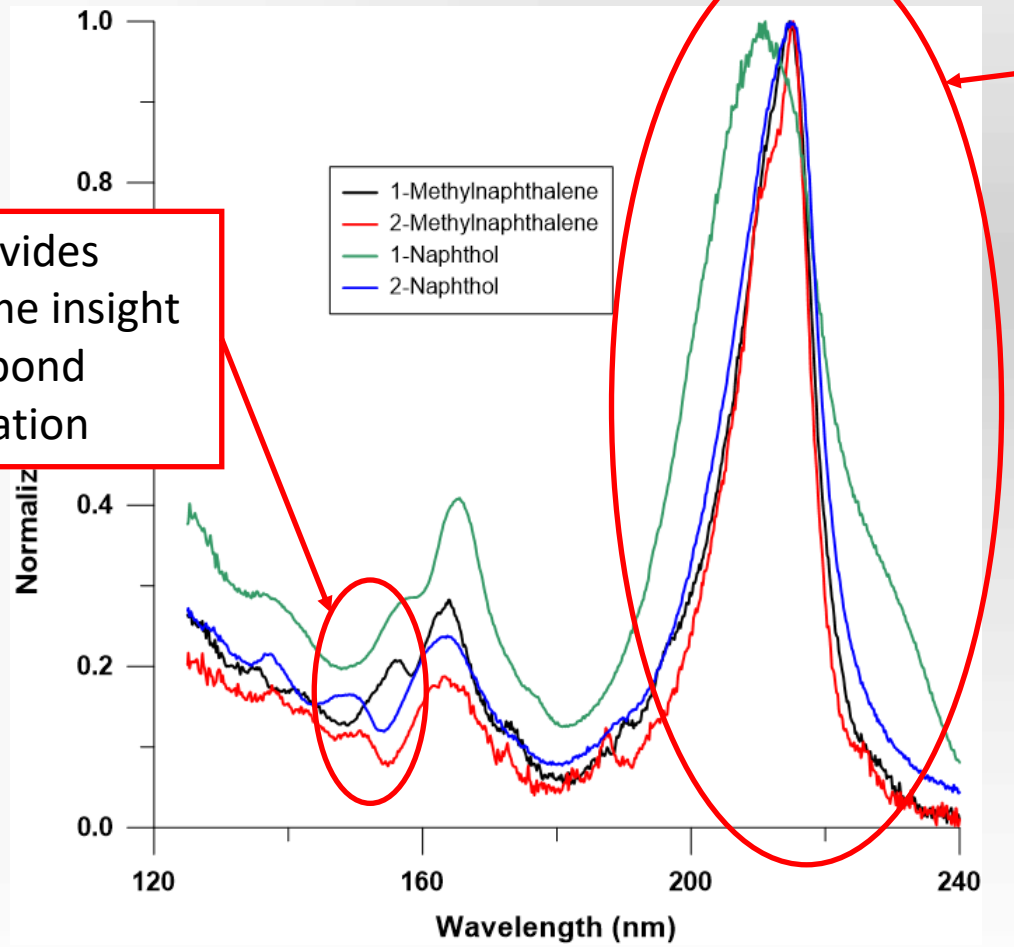
VUV ANALYTICS

Isomer Identification

VUV ANALYTICS

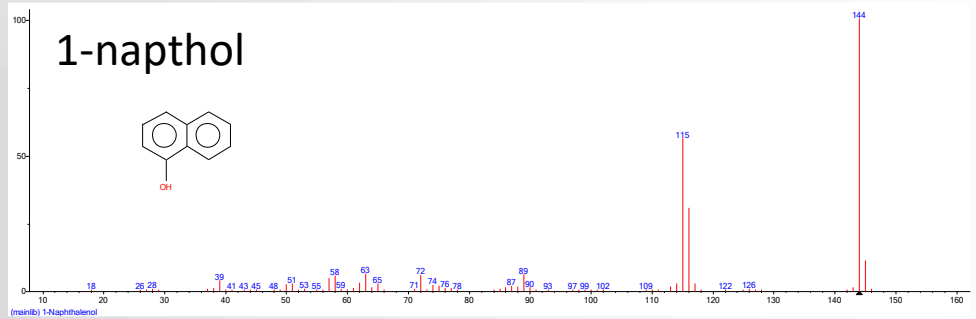
Isomer Identification

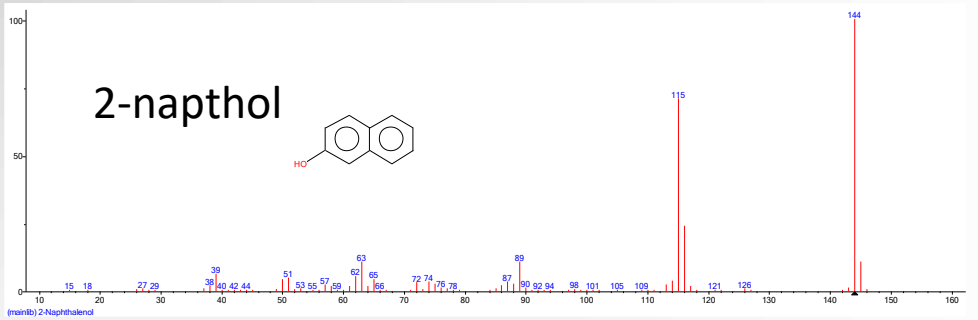
Many isomers have unique absorption spectra



Shows common class

Provides some insight to bond location



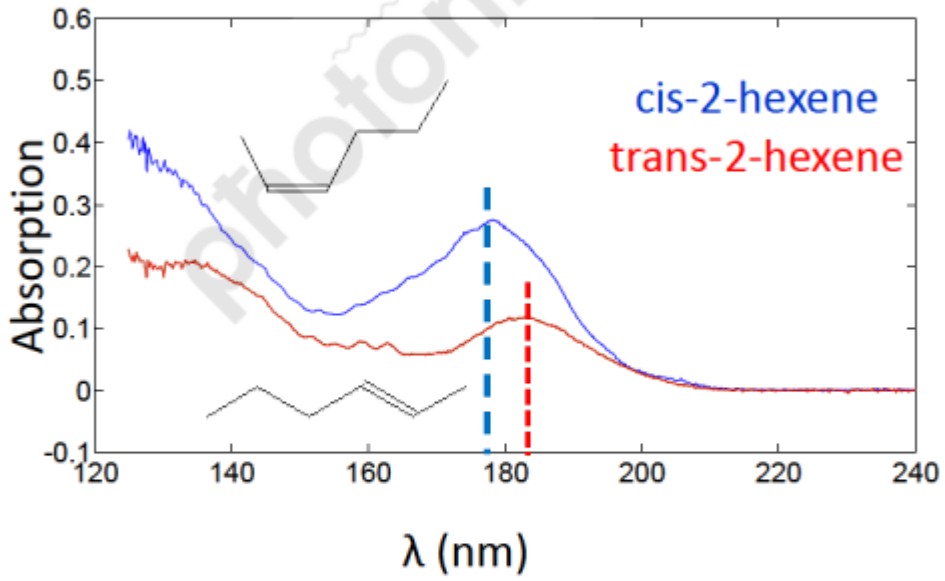


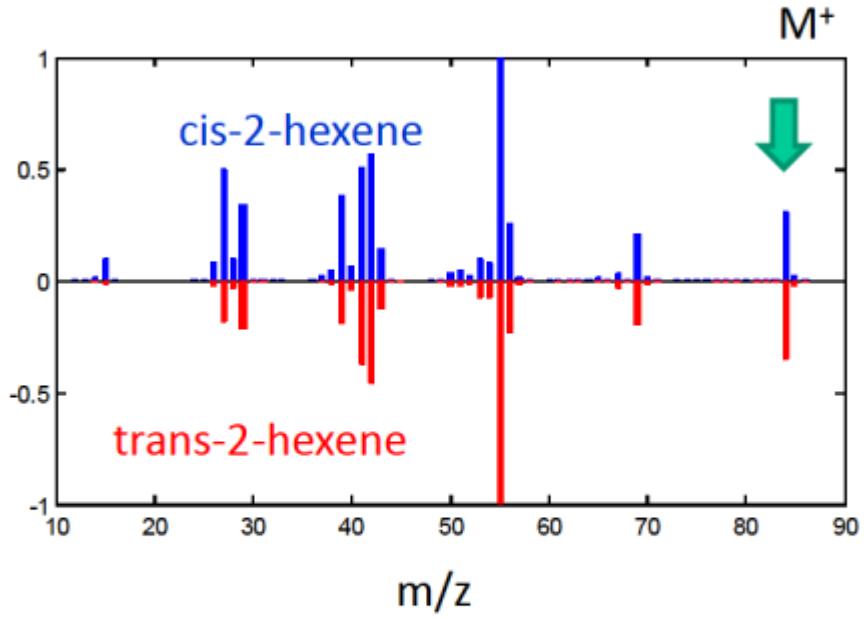
Chiral compounds (i.e. optical isomers) are the exception

VUV ANALYTICS

Spectral differences Cis-/Trans-

cis/trans isomers:





VUV Spectra show clear shift of maxima and differences in shape

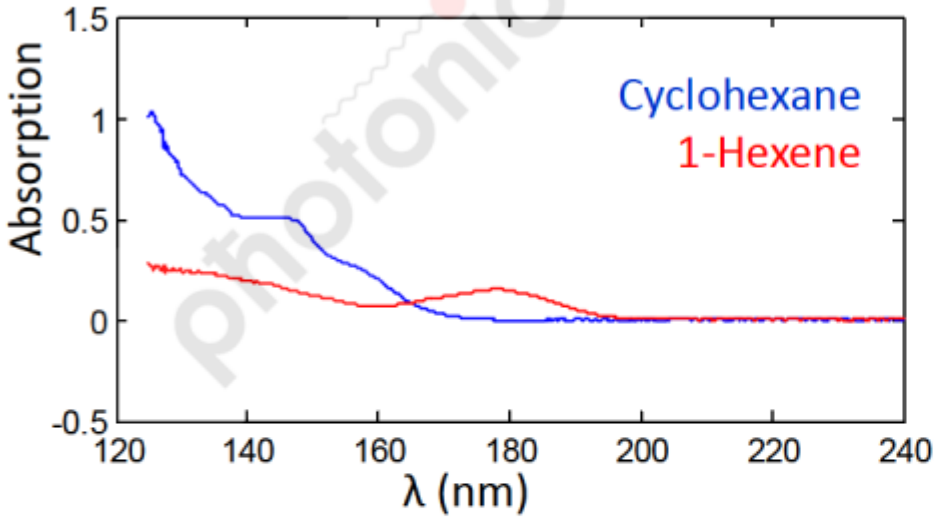
- 70eV EI Spectra does not provide selective Information
- soft Ionization would also not provide additional information

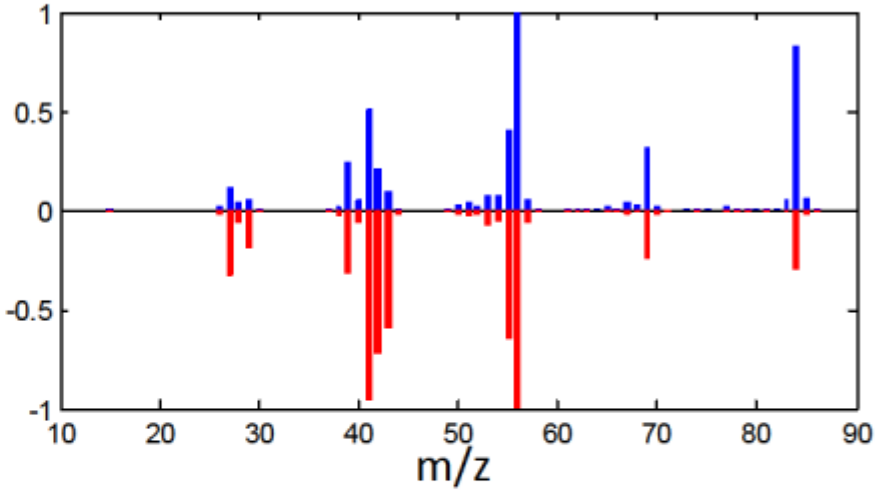
VUV ANALYTICS

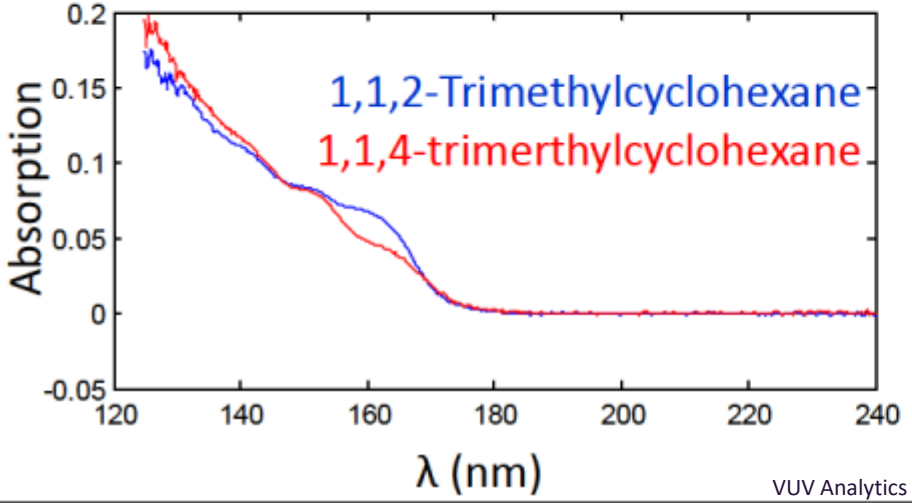
Spectral differences

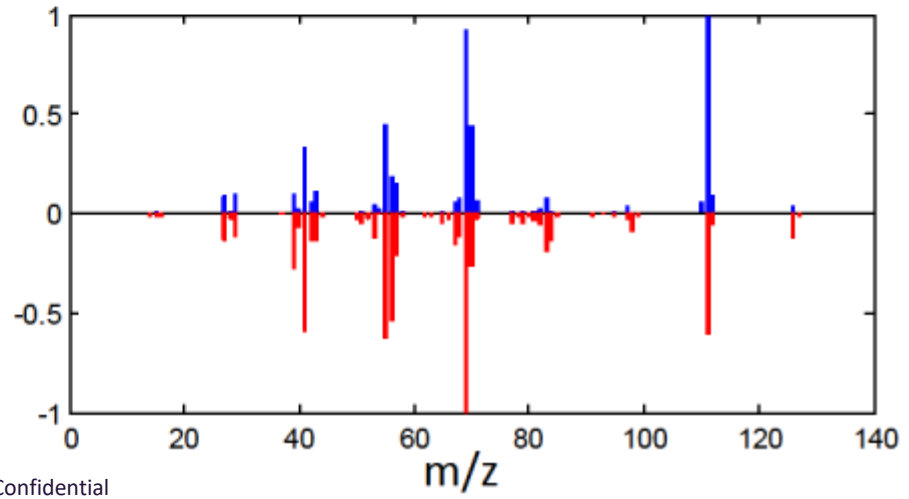
Constitutional isomers

Common separation and identification problem for (GCx)GC-MS (e.g. petro chemistry)





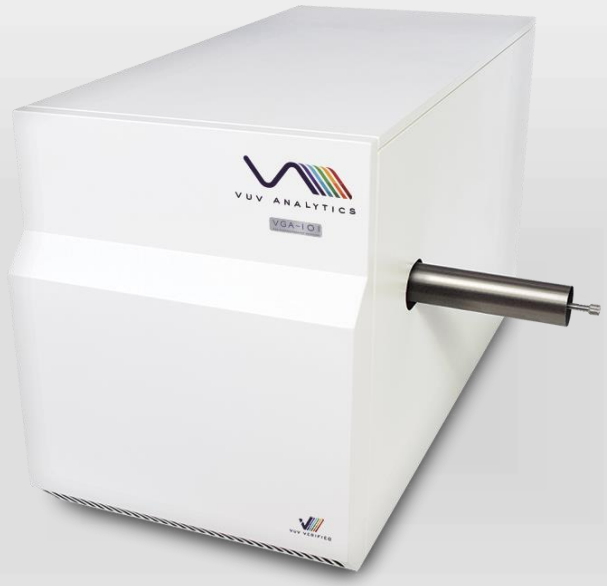




VUV Analytics Confidential

Application for this Universal Detector

Environmental



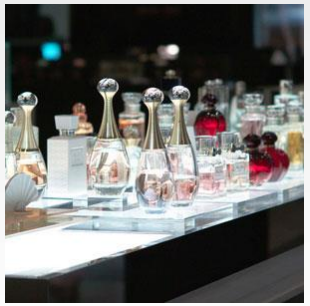
Specialty Gas

Oil & Gas

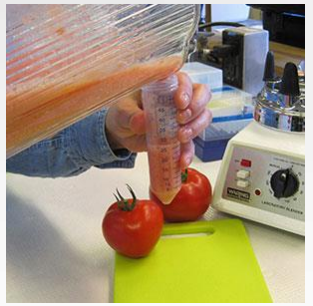
Agrochemical

Forensics

Fragrances & Flavors



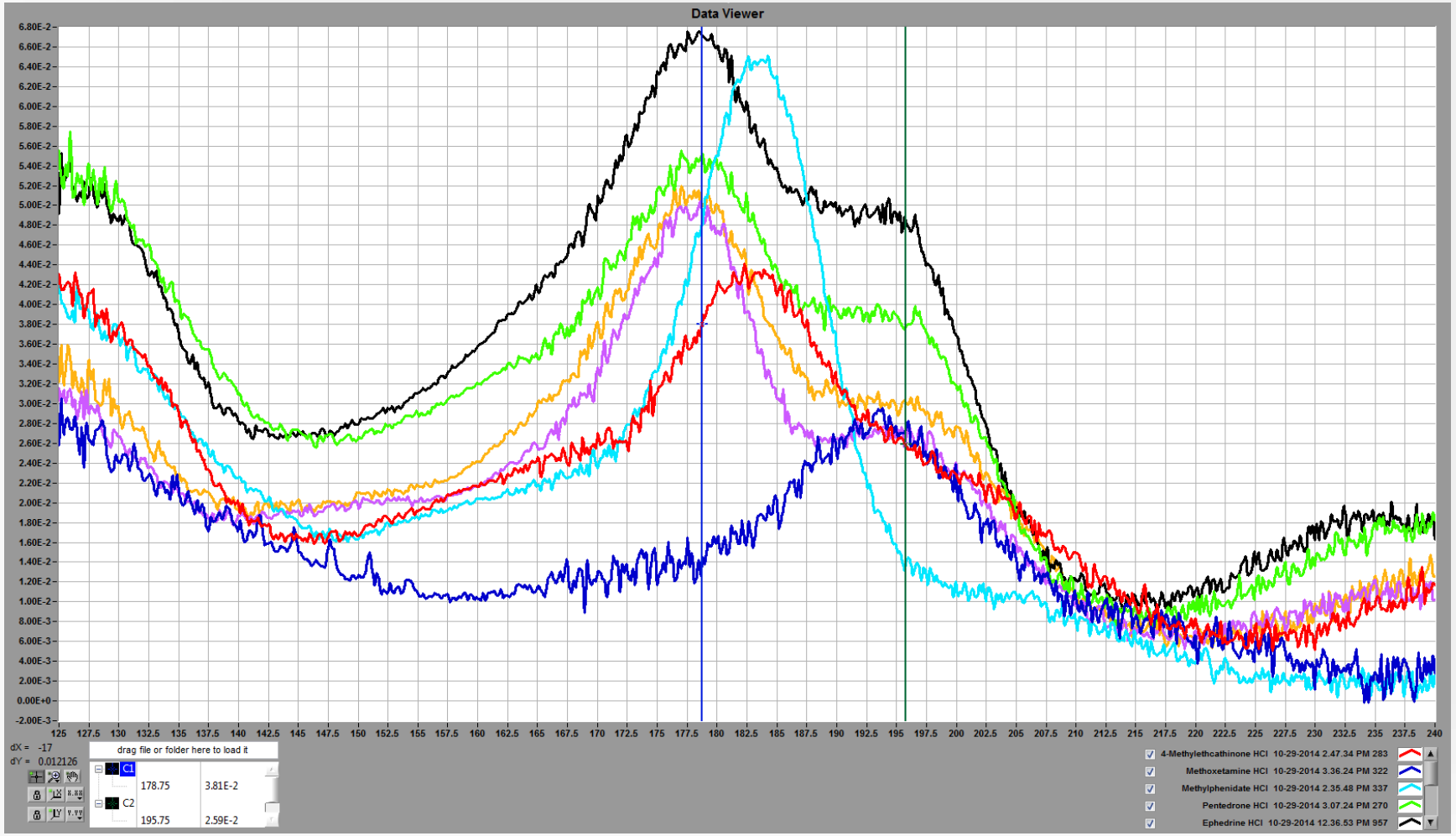
Petrochemical



Food & Beverage Safety

VUV ANALYTICS

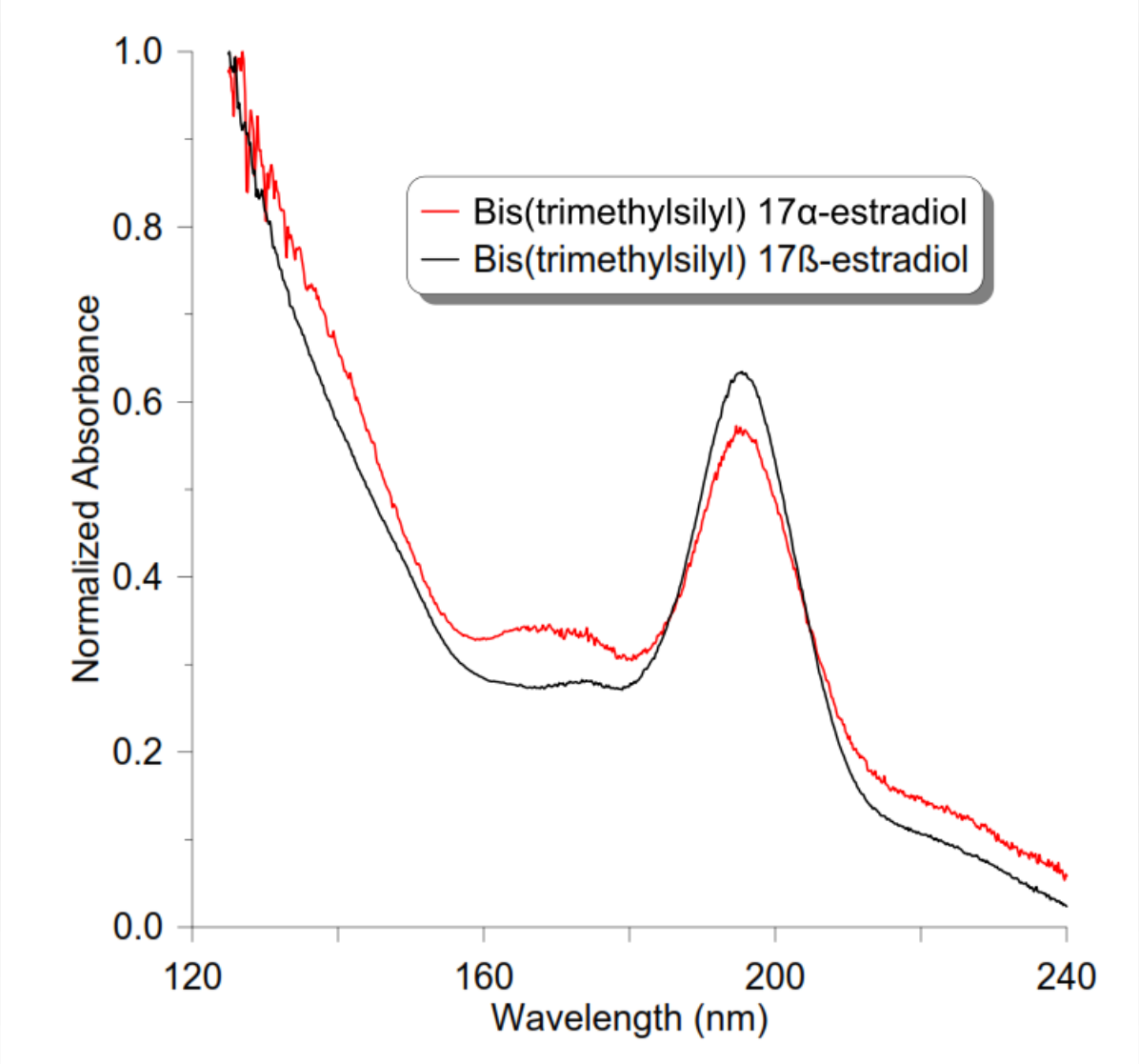
Drug Compounds



--- 4-Methylethcathinone HCL
--- Methoxetamine HCL
--- Methylphenidate HCL
--- Pentedrone HCL
--- Ephedrine HCL

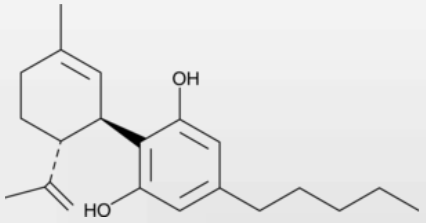
VUV ANALYTICS

Estradiols

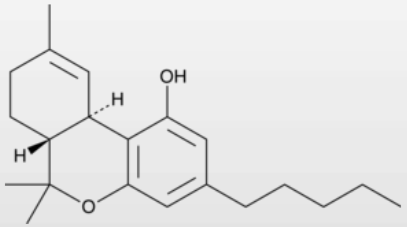


VUV ANALYTICS

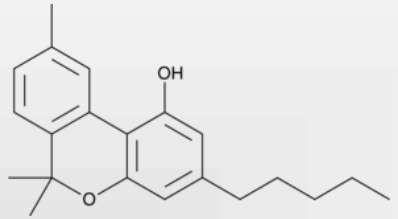
Cannabinoid Standard Analysis: Comparison of Spectra



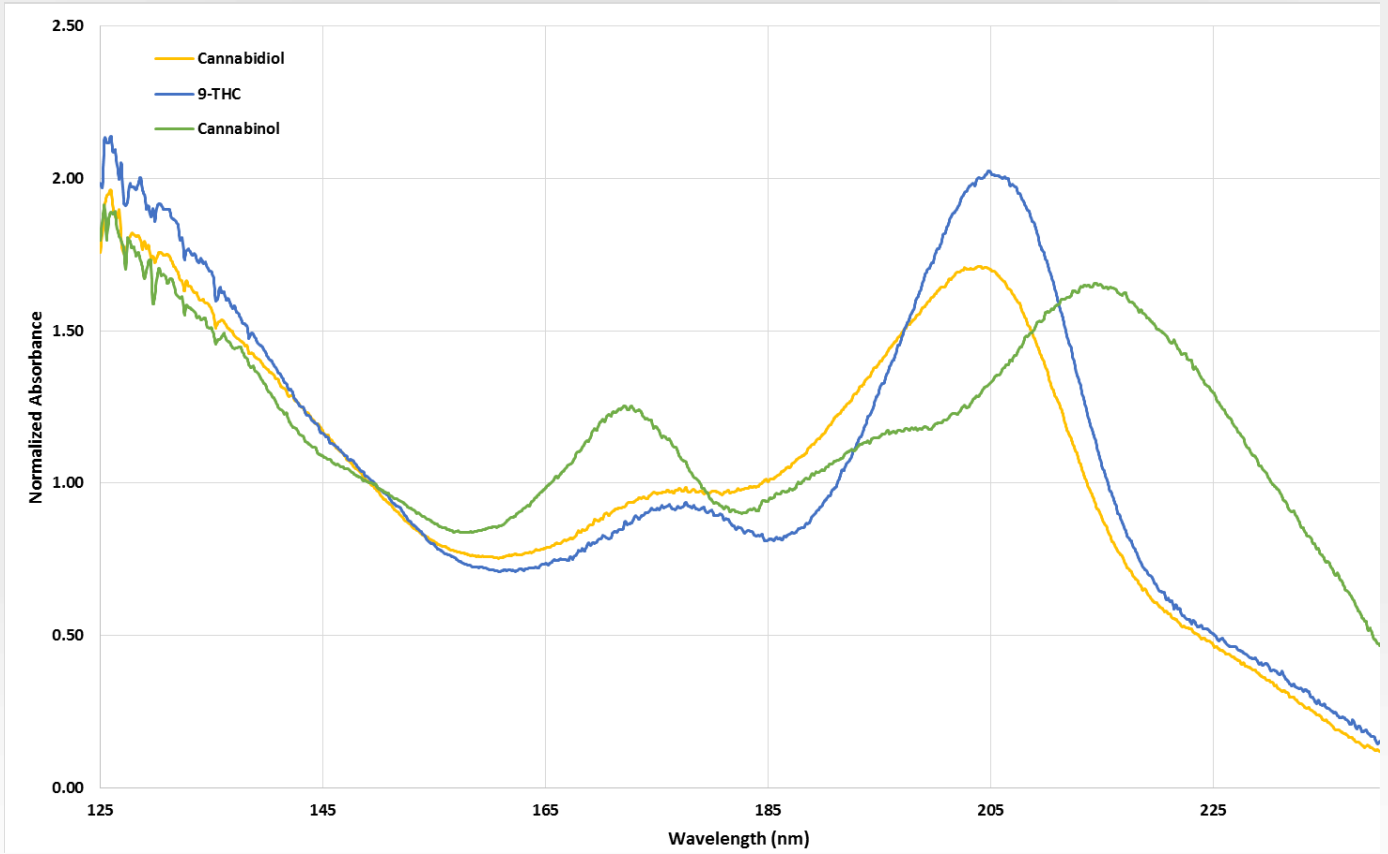
Cannabidiol



Δ^9-THC

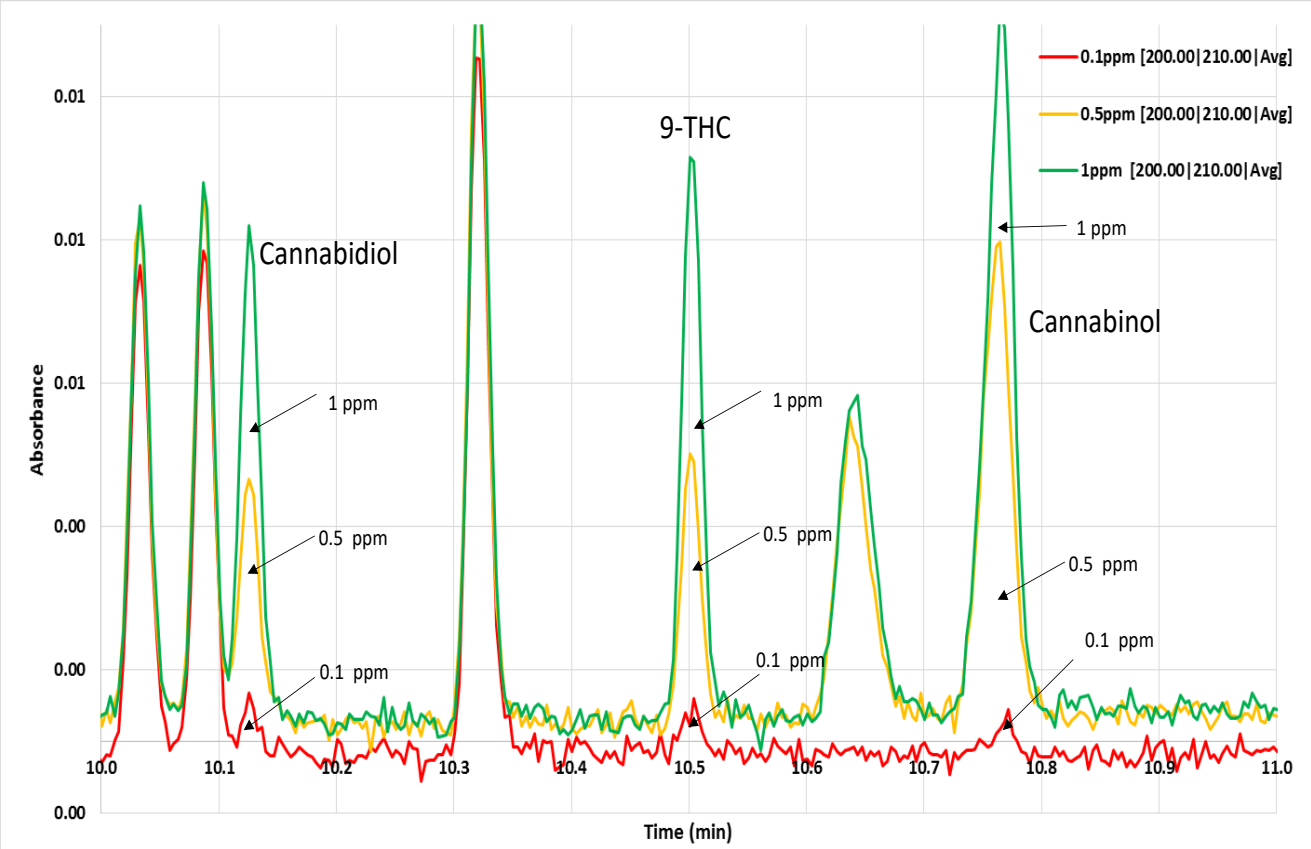


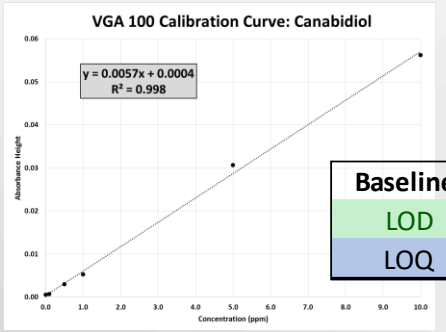
Cannabinol



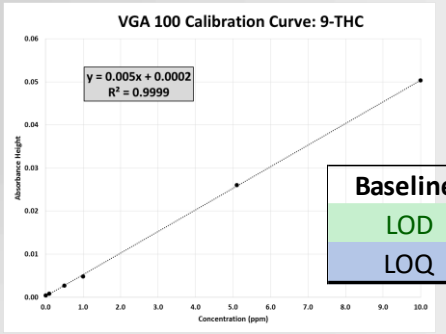
VUV ANALYTICS

Cannabinoid Standard Analysis: Chromatographic and Quantitative Comparison

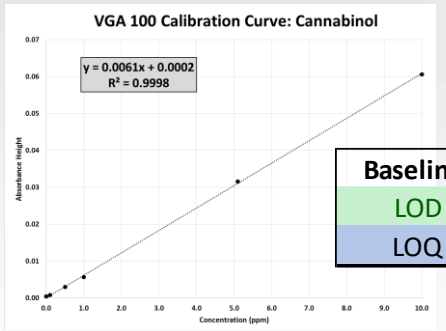




Baseline	ppm	ppb	Min ppb	Max ppb
LOD	0.0967	96.7	94.6	98.9
LOQ	0.3224	322.4	315.3	329.8



Baseline	ppm	ppb	Min ppb	Max ppb
LOD	0.0806	80.6	80.2	81.1
LOQ	0.2688	268.8	267.3	270.3

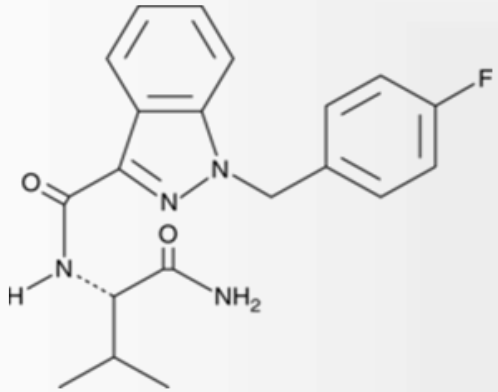


Baseline	ppm	ppb	Min ppb	Max ppb
LOD	0.0522	52.2	51.8	52.6
LOQ	0.1739	173.9	172.7	175.2

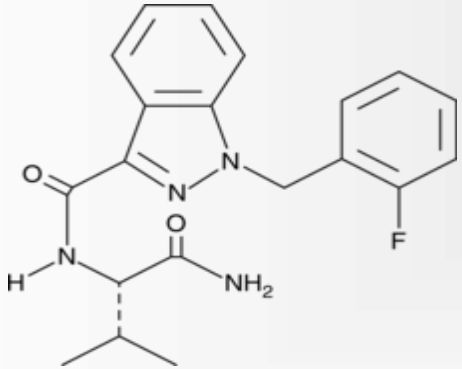
*Data acquired by VGA-100 detector

VUV ANALYTICS

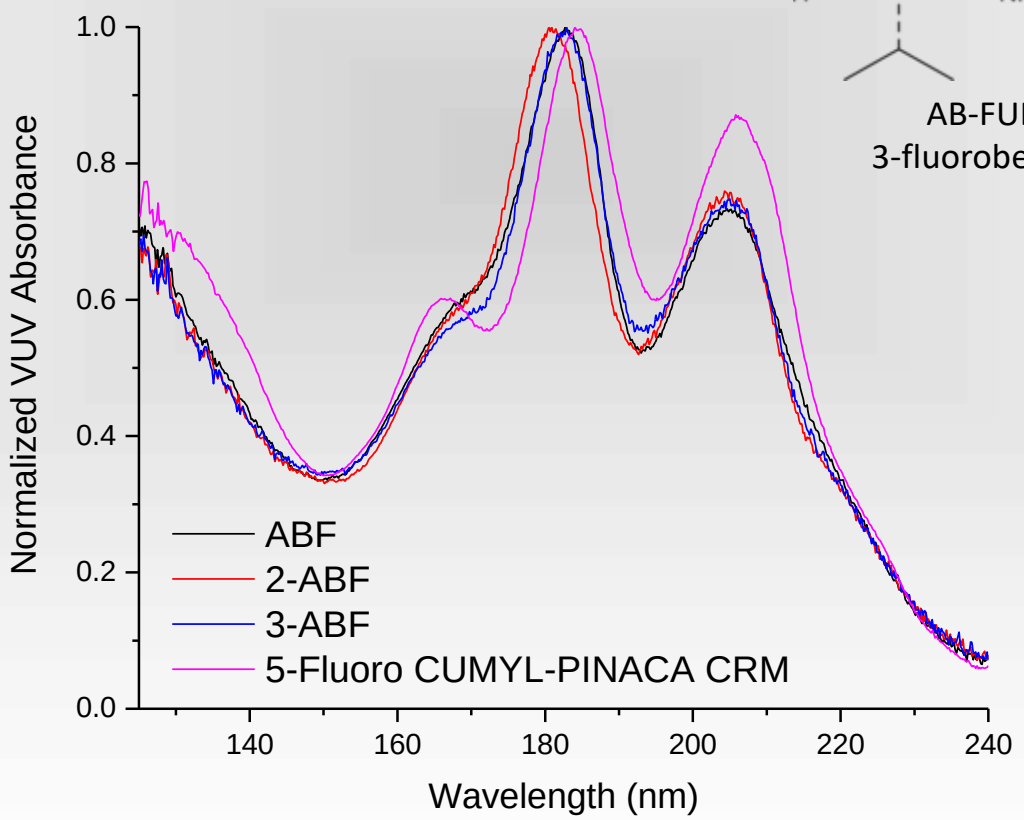
Synthetic Cannabinoid Analysis: Indazole Carboxamide Compound Class

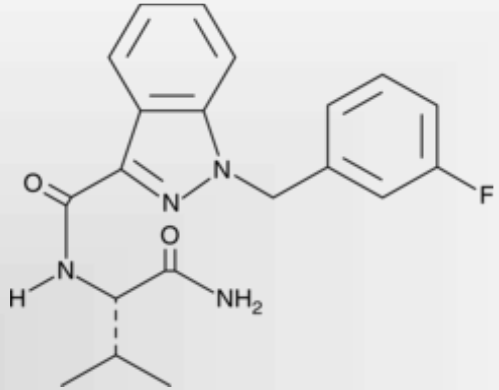


AB-FUBINACA

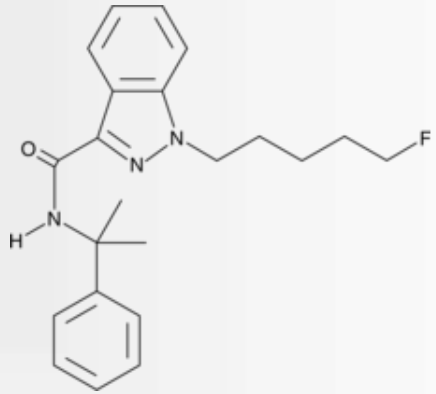


AB-FUBINACA
2-fluorobenzyl isomer





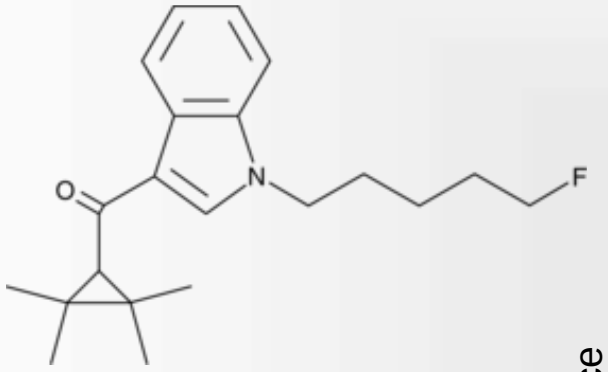
AB-FUBINACA
3-fluorobenzyl isomer



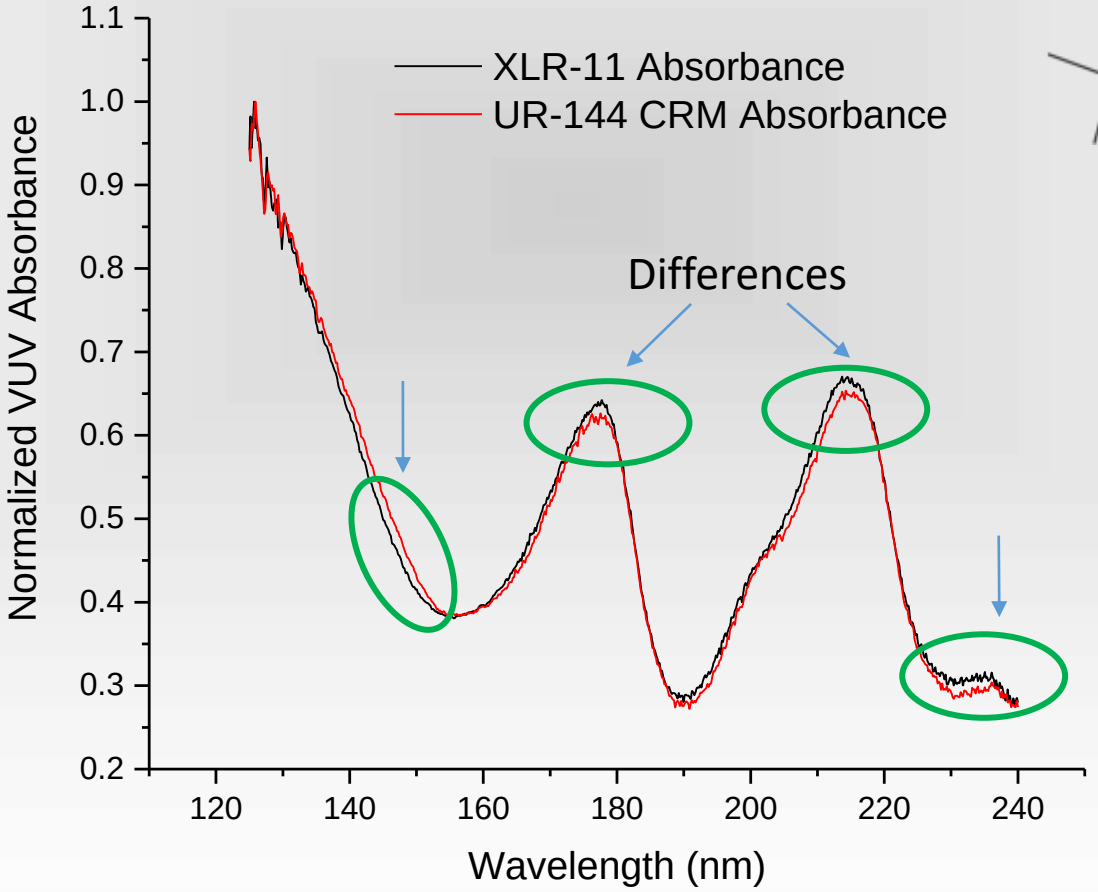
5-fluoro CUMYL-PINACA (CRM)

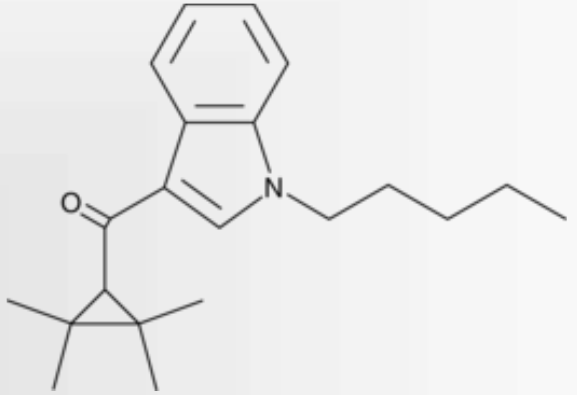
VUV ANALYTICS

Synthetic Cannabinoid Analysis: Cyclopropyl Compound Class



XLR-11

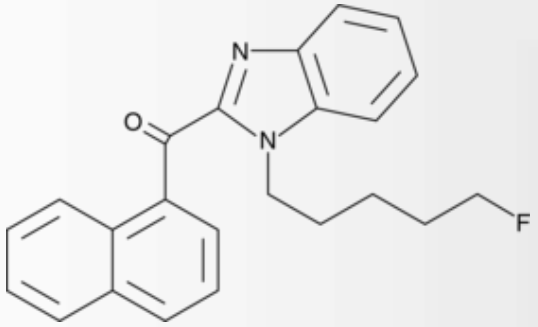




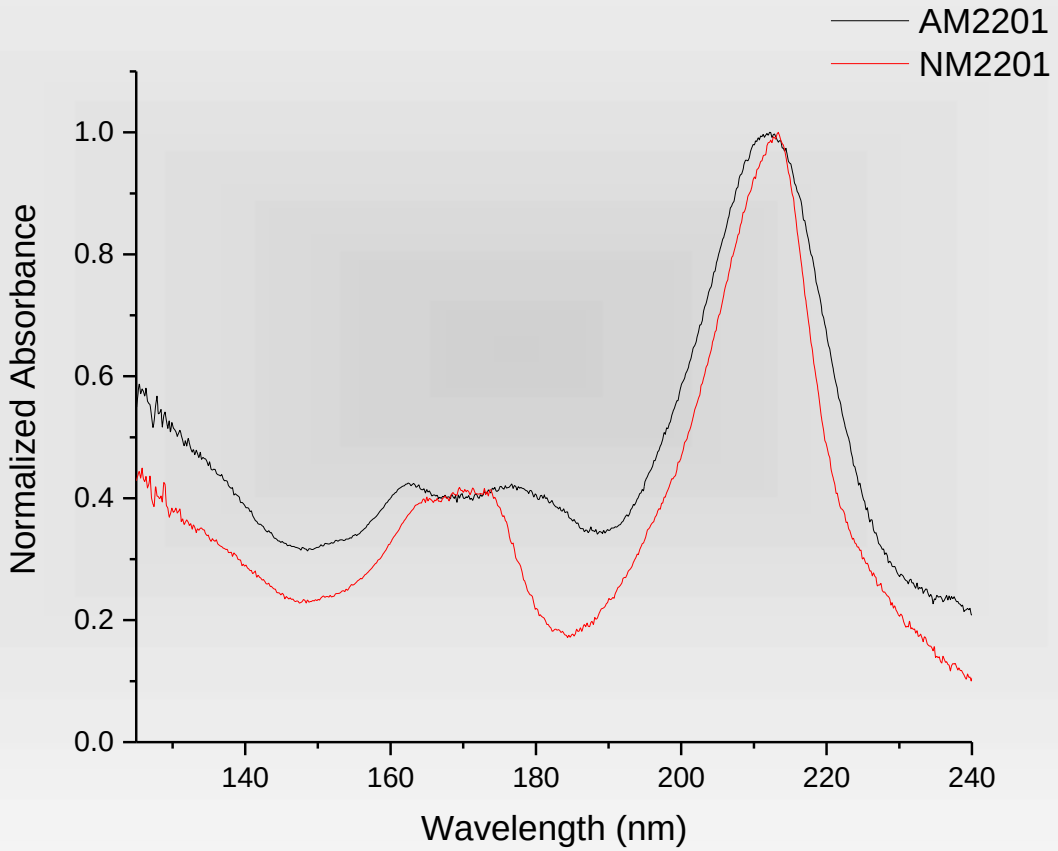
UR-144

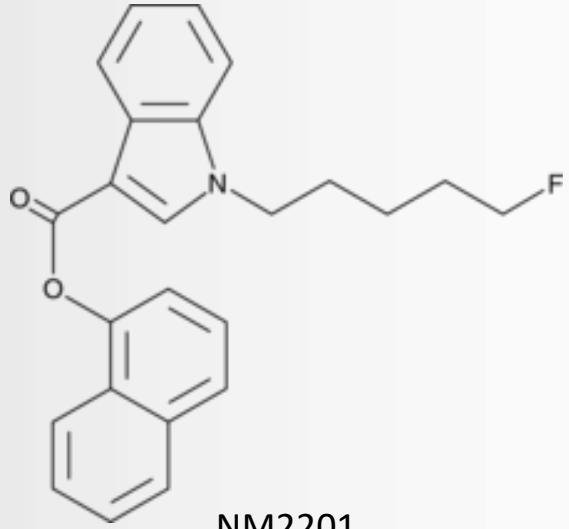
VUV ANALYTICS

Synthetic Cannabinoid Analysis: Naphthoylindole Compound Class



AM2201 benzimidazole analog

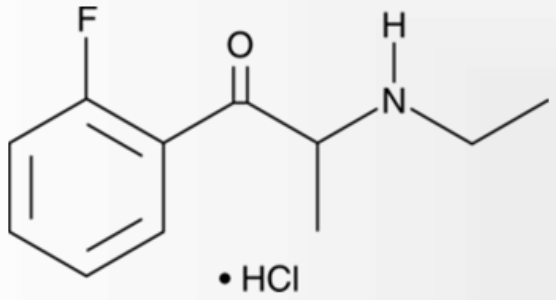




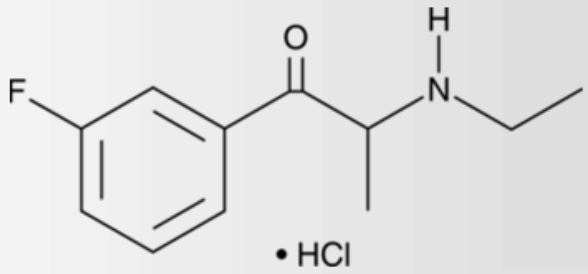
NM2201

VUV ANALYTICS

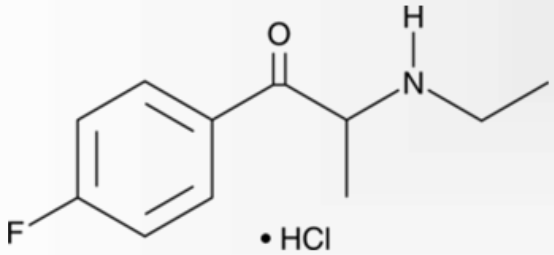
Stimulant Analysis:
Cathinone Compound Class



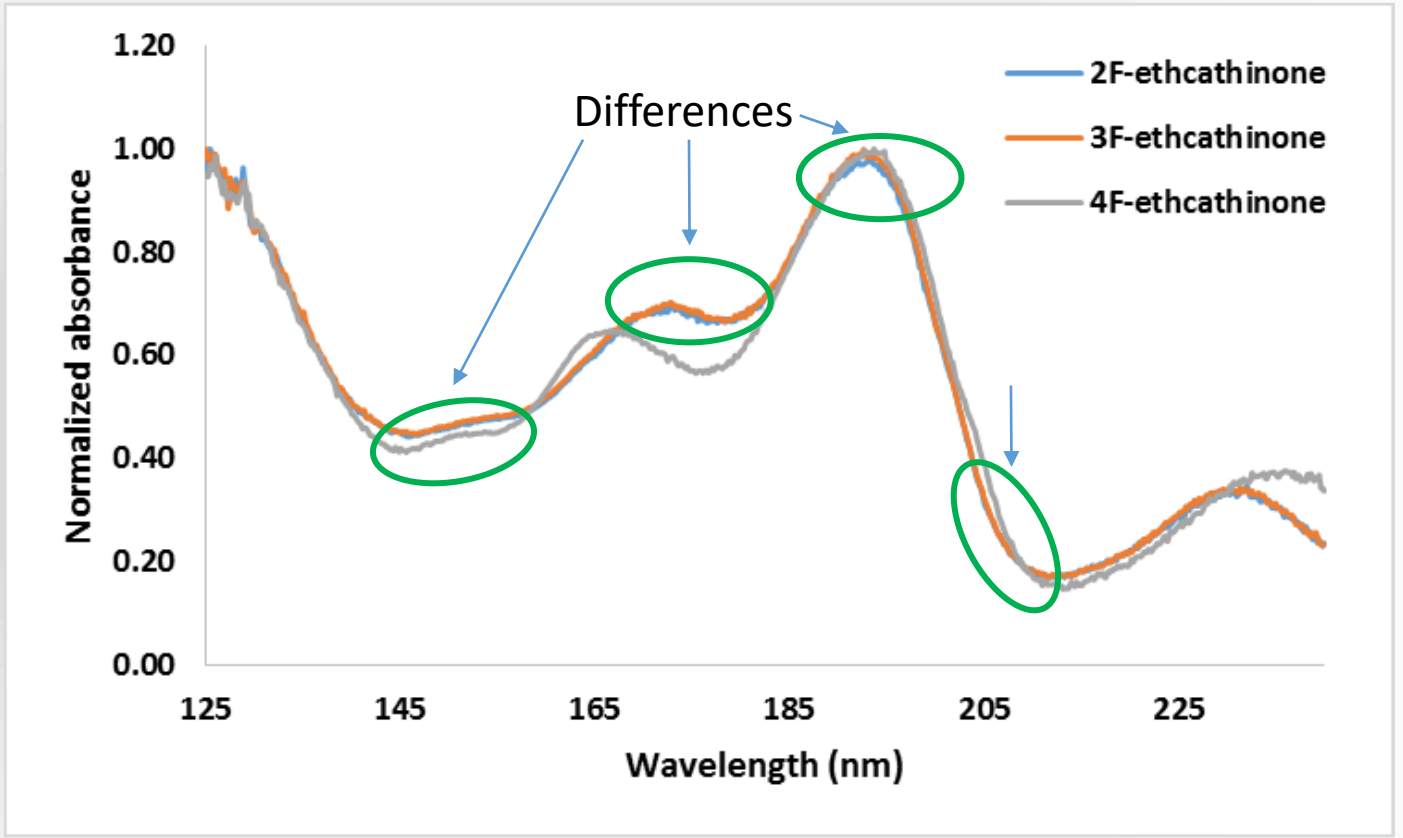
2F-ethcathinone



3F-ethcathinone



4F-ethcathinone



VUV ANALYTICS

LC-MS/MS SCIEX Triple Quad™ and QTRAP® systems

3500 Series

4500 Series

5500+ Series

6500+ & SelexION

7500 Series

Pushing the limits

Exion LC

microLC

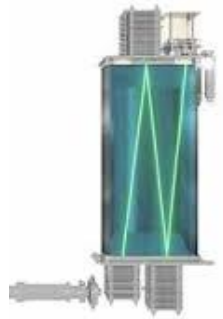
nanoLC

UHPLC, MicroLC and NanoLC systems

6600⁺ & SelexION

X500 Series

SCIEX TripleTOF® and X500 Series



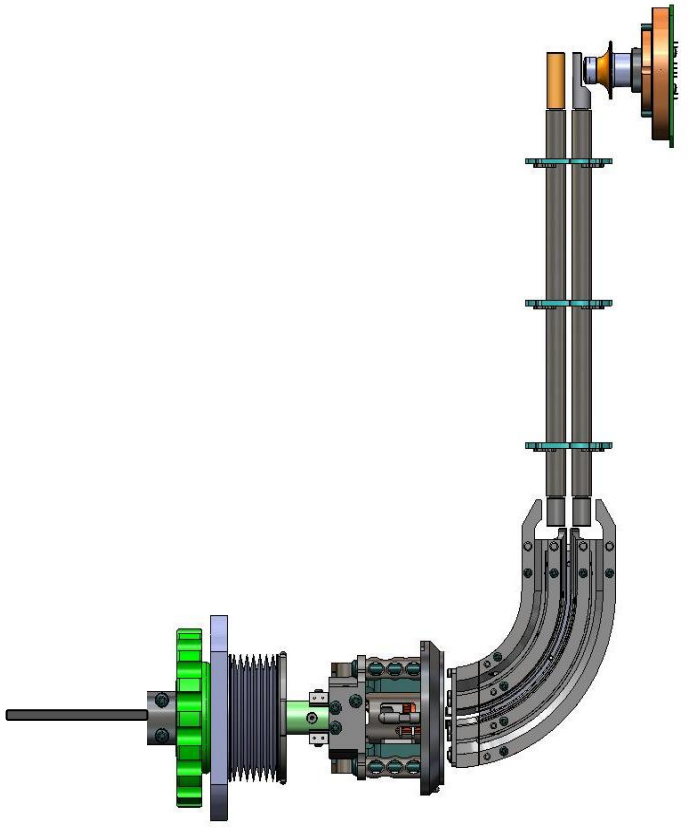
AMEDIS

authorized distributor of SCIEX

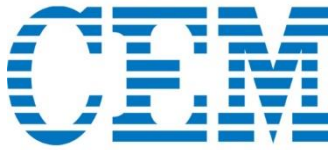
GC-MS SCION Instruments systems

GC-MS 436-GC Series

GC-MS 456-GC Series



All you need is ...



AMEDIS