Photoionization Workshop Summary

"Photoionization (APPI/PI): Applications, Developments and Discussions"

65th ASMS Conference on Mass Spectrometry and Allied Topics, Indianapolis, IN
Monday, June 5th, 5:45 – 7:00 pm, Room 239

Organized by: Eleanor Riches and Ralf Zimmermann

We opened with a brief overview in the photoionization field and then we introduced our four discussion leaders:

- **Eric Reiner** (**Environmental Chemistry**, APPI-MS, Environment Canada, Canada) "ATMOSPHERIC PRESSURE PHOTO- IONIZATION FOR GC-MS? Putting POPs in the Spotlight"
- **Priscila Lalli** (**Petroleomics**, APPI-IMS-MS, Florida State University, USA) "Structural Determination of Polycyclic Aromatic Hydrocarbons by Ion Mobility Mass Spectrometry"
- **Thomas Bierkandt** (**Combustion Chemistry**, Synchrotron SPI-MS, Univ. Duisburg, Germany) "Isomer-resolved Species Identification and Quantification by Synchrotron-based Photoionization Mass Spectrometry"
- **Andreas Walte** (**Thermal Process Analysis**, REMPI/SPI-MS, Photonion GmbH, Germany, "Vacuum Photoionization Mass Spectrometry - *An approach for online analysis of complex mixtures*)"

All speakers did an excellent job, explaining fundamentals and applications of APPI and PI. The workshop demonstrated a continued strong interest in this field as it attracted again a large audience (about 60-70 people), about the same as last year. We were very pleased with the allocation of Monday as the day of the APPI/PI workshop.
Again the start was slightly delayed due to attendees still collecting refreshments at 5:45. We suggest placing the refreshments in the back of the workshop rooms.
Each of the discussion leaders kept to their 10 min allotment of time, which allowed enough time for discussions.

Selected Questions and Answers

Q1: What is the source of humidity variation?

A1: Could be leakage in nitrogen generator

Q2: What is the difference between APCI and APPI regarding humidity effects?

A2: Adduct formation due to water is smaller with APPI

Q3: What are the advantages of APPI?

A3: Easier to analyse complex mixtures, e.g. house dust has thousands of compounds, therefore GCxGC APPI-MS helps a lot.

Q4: Have you used dopants in order to improve sensitivity, especially for compounds with low cross sections?

Photoionization (APPI/PI): Applications, Developments and Discussions

Monday, June 5th, 5:45-7:00 pm
Room 239 (Indianapolis Convention Center)

Organized by Eleanor Riches and Ralf Zimmermann

Discussion Leaders (Presentation max. 10 min each)

- **Eric Reiner**
  (**Environmental Chemistry**, APPI-MS, Environment Canada, Canada)
- **Priscila Lalli**
  (**Petroleomics**, APPI-IMS-MS, Florida State University, USA)
- **Thomas Bierkandt**
  (**Combustion Chemistry**, Synchrotron SPI-MS, Univ. Duisburg, Germany)
- **Andreas Walte**
  (**Thermal Process Analysis**, REMPI/SPI-MS, Photonion GmbH, Germany)

Photoionization (APPI/PI): Applications, Developments and Discussions

- APPI and PI Ionizes a wide range of compounds (polars to non-polars)
  - Wide bandwidth ionizer
- APPI features lower susceptibility to ion suppression than ESI or APCI, PI is ion suppression free
  - Simpler clean-ups mean ease and better recoveries
  - Use with faster chromatography and even flow injection analysis
- Large linear dynamic range
  - Great for quantitative analysis

Can APPI and PI be mainstream technologies or are they best suited for niche applications?

Photoionization (APPI): Important Niche Application for Explosives and Narcotics Trace Detection

Morpho Detection

IT4DX IMS

MS ETD

Implant Sciences

QS-B220 IMS

1st Detect

Bruker

DE-tector IMS

Why not APCI

Discharge sources in air create atmospheric NO_3^- ions that interfere with NO_3^- nitrate ions from nitrate explosives

Photoionization (APPI): Ion Source for LC-MS or direct infusion MS – Niche application?

- Most MS vendors offer a commercially available APPI ionization source – wide availability to all MS users
- Operates at atmospheric pressure so is fully compatible with liquid (or gas) flow introduction at high flow rates
- Has been utilized in diverse fields of analysis:
  - Petroleomics
  - Pharmaceutical
  - Food
  - Environmental
  - Some limited work related to biological samples

Photoionization (APPI): Ion Source for LC-MS or direct infusion MS – Niche application?

- Most MS vendors offer a commercially available APPI ionization source – wide availability to all MS users

Sciex

Thermo

Bruker

Shimadzu

Waters

Agilent

MasCom

Photoionization (PI): Applications for specific niche purposes

- Many PI-MS applications for on-line detection (Laser- or Lamp-PI) or as detector for gas chromatography or thermal analysis
- Vacuum ionization: No susceptibility to ion suppression but lower sensitivity than EI (PI cross sections, VUV-photon generation)
- High selectivity (no/little fragmentation)
- Mainly niche, but systems are becoming commercially available

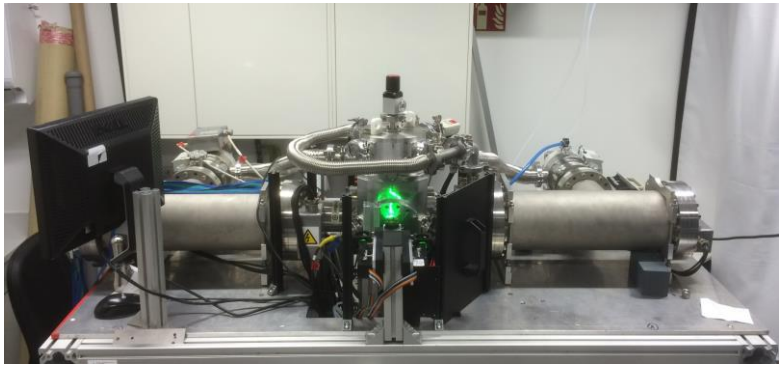
Jeol
(GC-PIMS)

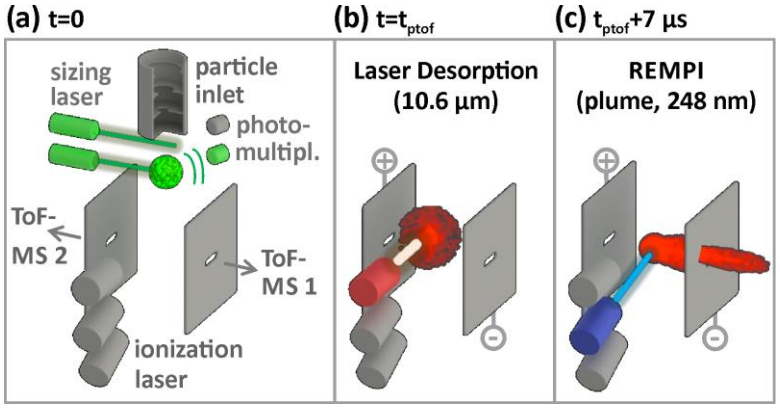
Hexin
(on-line)

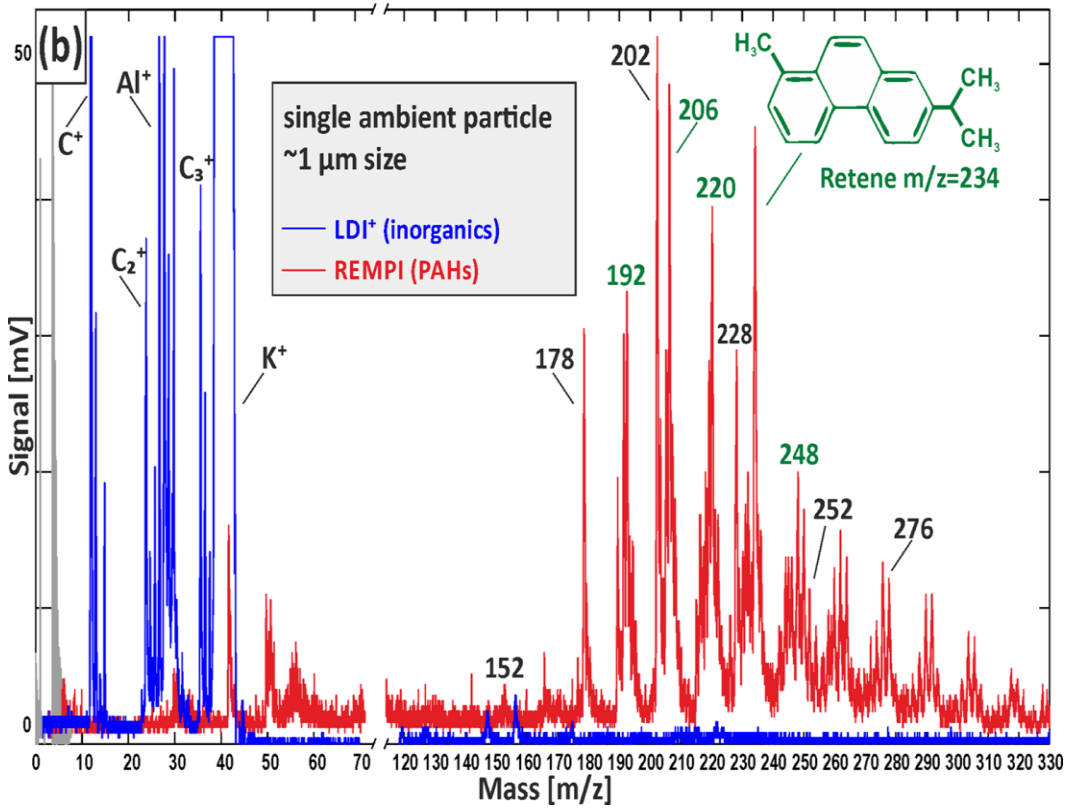
Photonion
(TG-PIMS, on-line, GC-PIMS)

Photoionization (PI): Applications for specific niche purposes

- **Example: On-line Polycyclic aromatic Hydrocarbon detection on Single Aerosol Particles (Zimmermann et al., TOD pm 4.10)**







ATMOSPHERIC PRESSURE PHOTO- IONIZATION FOR GC-MS? Putting POPs in the Spotlight

PUTTING POPS IN THE SPOTLIGHT

Robert A. Di Lorenzo* , Vladislav Lobodin†, Sladjana Besevic‡, Karl J. Jobst‡, Eric J. Reiner‡,

* - Department of Physiology and Experimental Medicine, Hospital for Sick Children, Toronto, Ontario, Canada
† - National High Field Magnetic Laboratory, Florida State University, Tallahassee, Florida, USA
‡ - Laboratory Services Branch, Ontario Ministry of the Environment and Climate Change, Toronto, Ontario, Canada

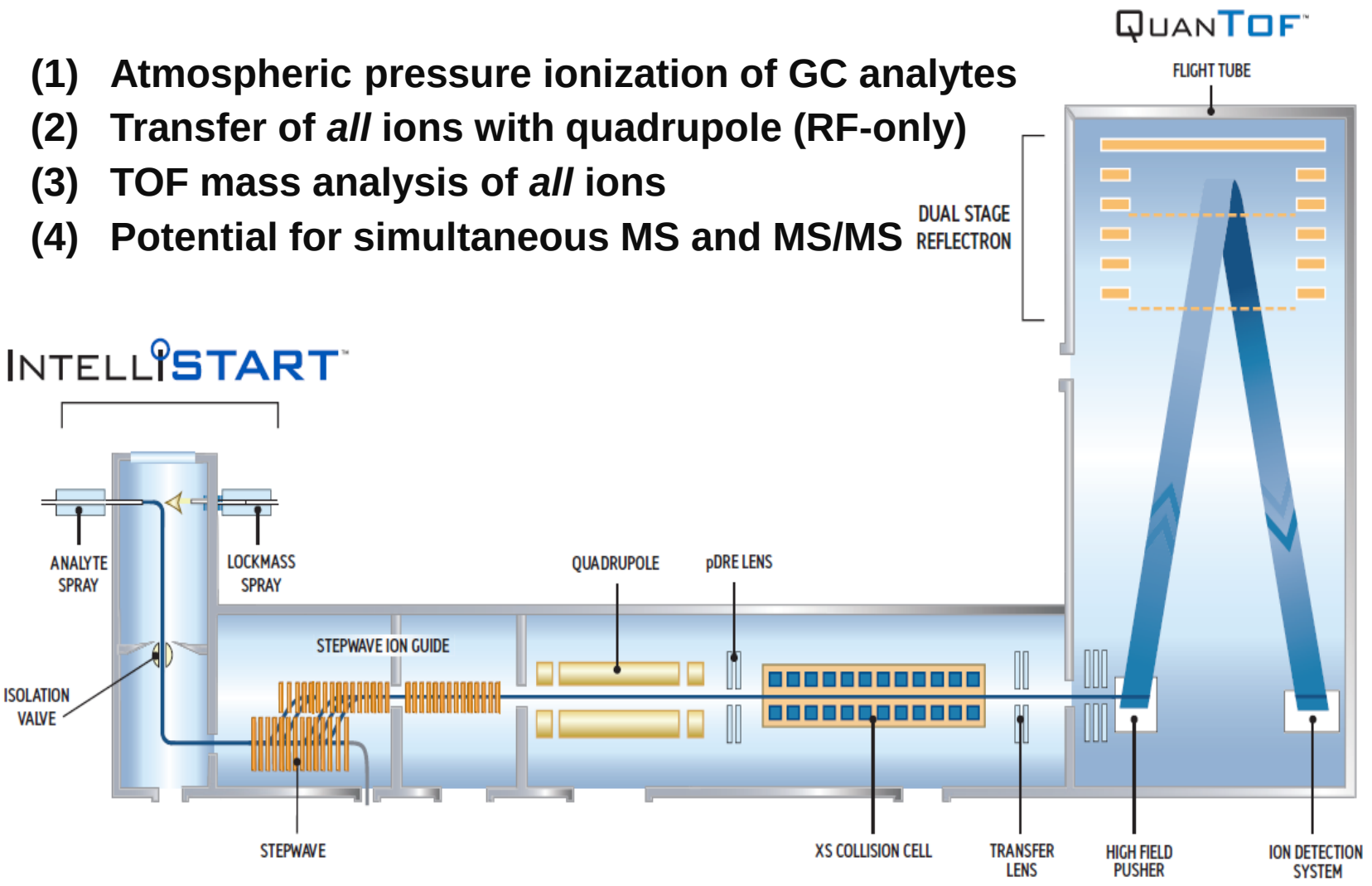
LC INSTRUMENT FOR GC

Atmospheric pressure ionization naturally compatible with GC

- No flow-related suppression
- APCI is a “soft” ionization technique
  - Predominantly molecular ions

Waters Xevo G2-XS

(1) Atmospheric pressure ionization of GC analytes
(2) Transfer of *all* ions with quadrupole (RF-only)
(3) TOF mass analysis of *all* ions
(4) Potential for simultaneous MS and MS/MS



MIXED-MODE IONIZATION

Charge Transfer:

$N_2^{\bullet+} + M \rightarrow M^{\bullet+} + N_2$

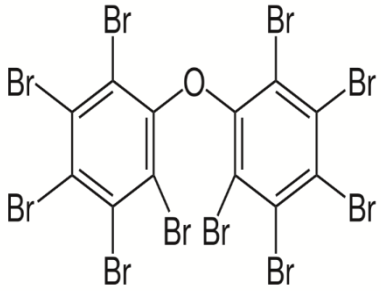
Proton Transfer:

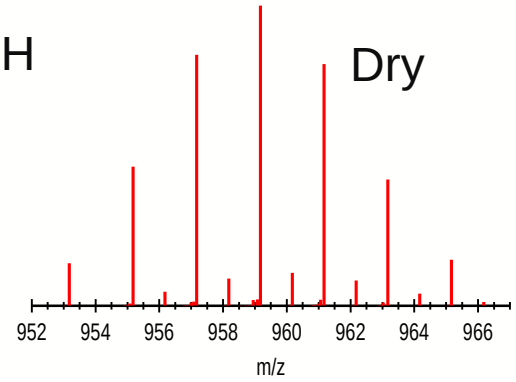
$N_2^{\bullet+} + H_2O \rightarrow H_2O^{\bullet+} + N_2$

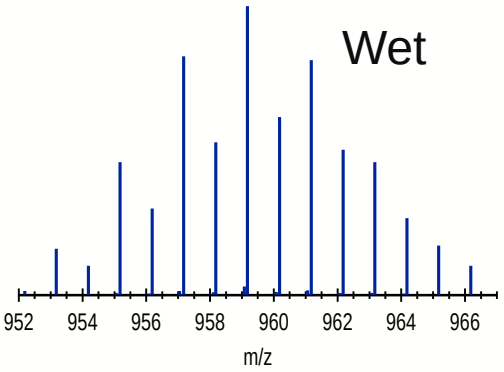
$H_2O^{\bullet+} + H_2O \rightarrow H_3O^{+} + OH$

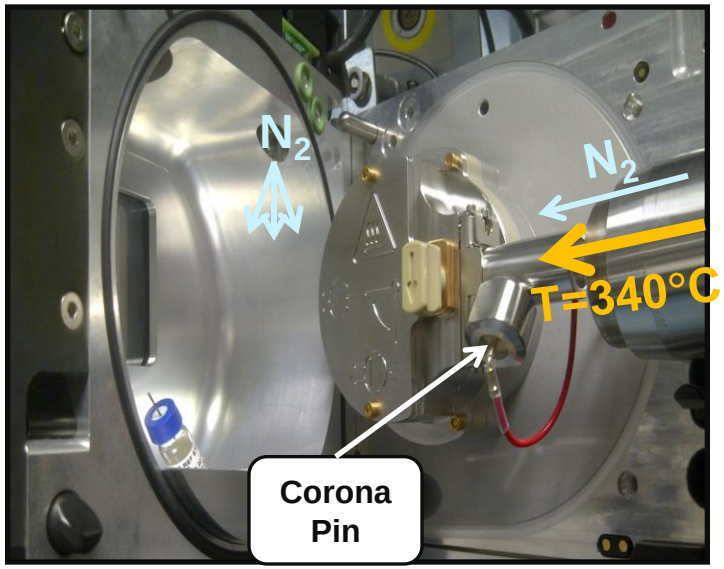
$H_3O^{+} + M \rightarrow H_2O + MH^{+}$

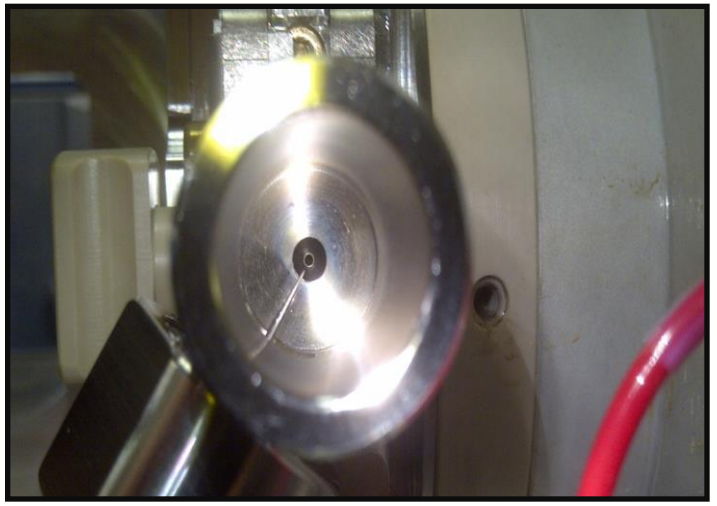
- Degree of protonation is variable day-to-day
- Particularly problematic during the summer
- Can lead to quantificaition issues







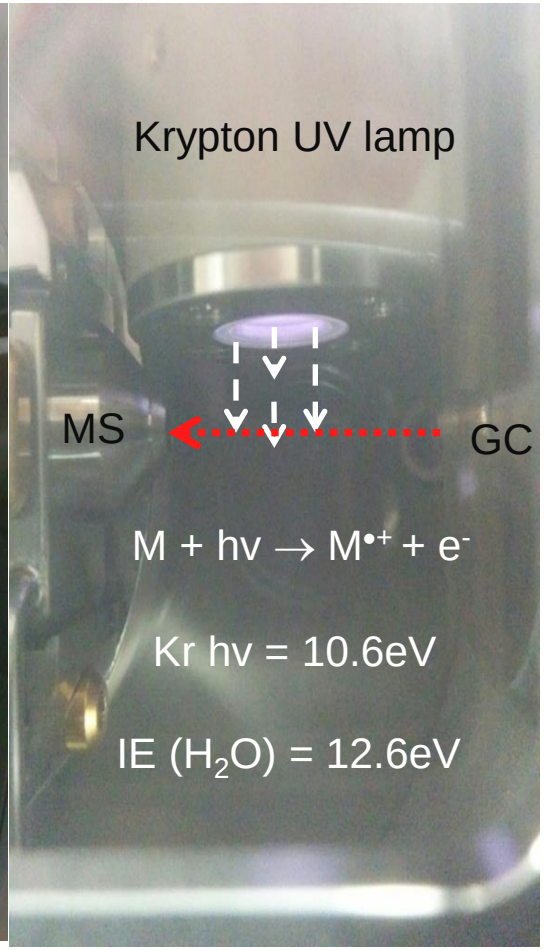




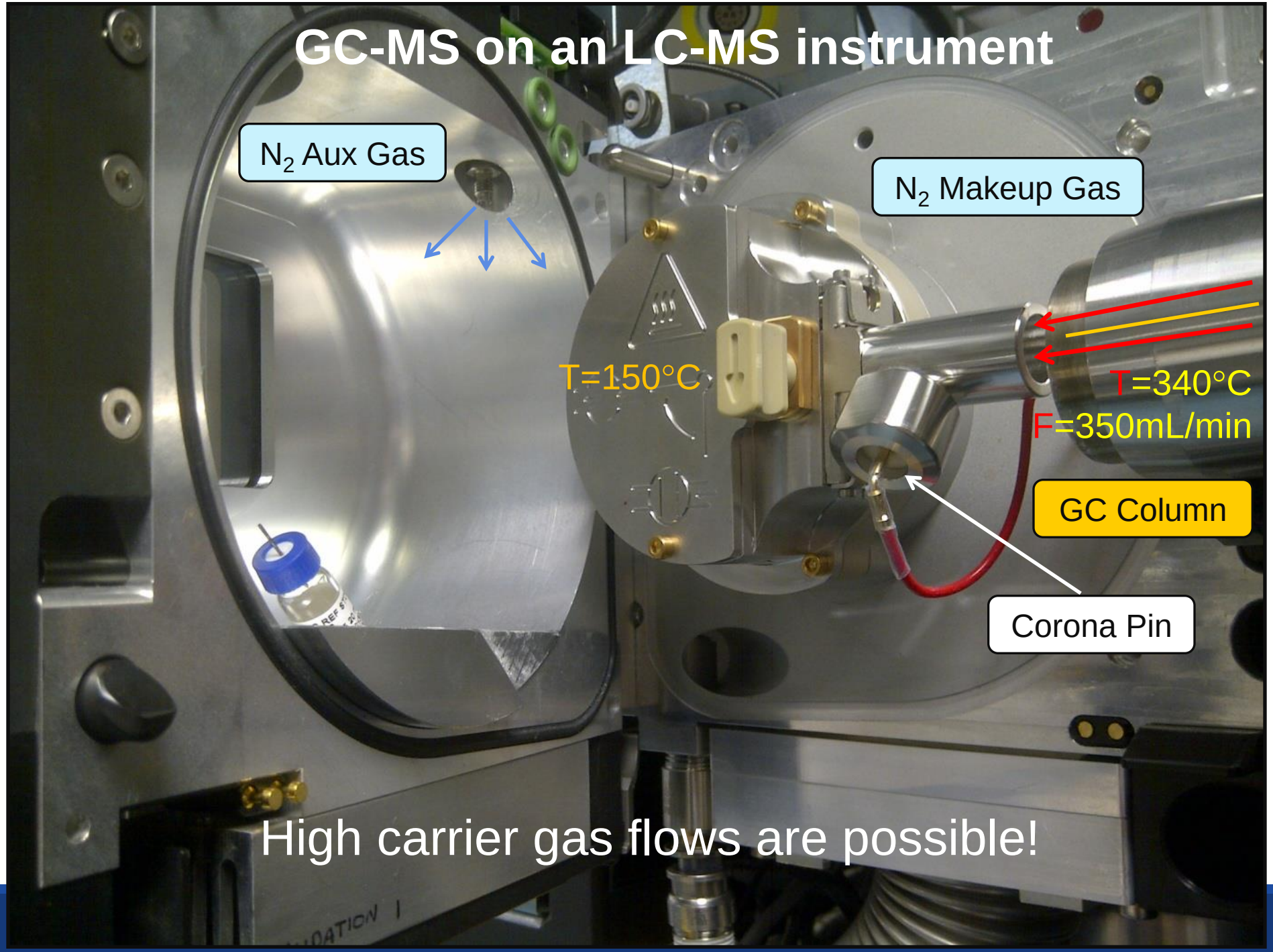
MODIFIED APGC SOURCE

- APCI ionizes a wide range of compounds
  - Chemical noise
  - Siloxane contamination
  - Mixed mode ionization
- Custom built APPI source for APGC
  - Reaction chamber removed
  - Replaced with ESI-type cone inlet
  - Hole drilled in top of APGC housing
  - Waters APPI lamp added
    - Kr, Xe, Ar

VLADISLAV LOBODIN,
Research Faculty
National High Magnetic Field Lab
Florida State University



GC-MS on an LC-MS instrument



High carrier gas flows are possible!

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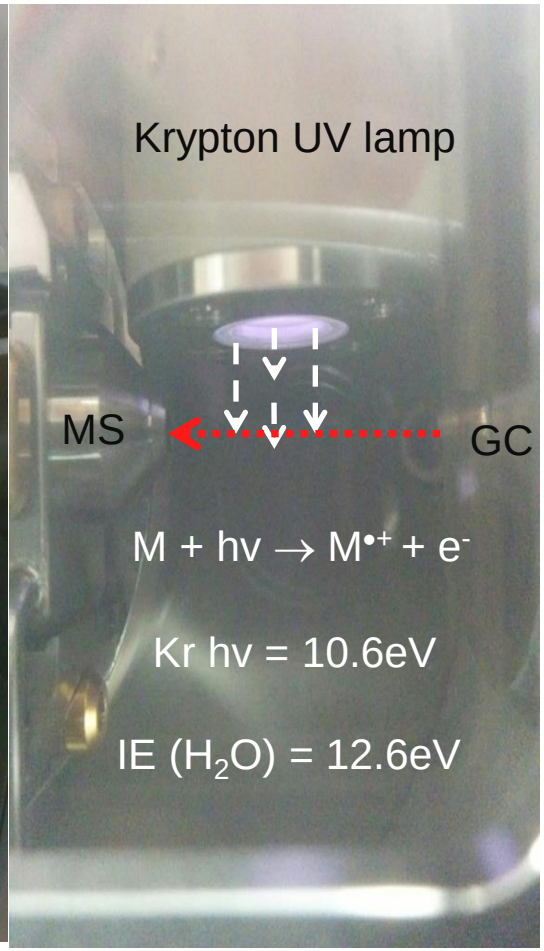
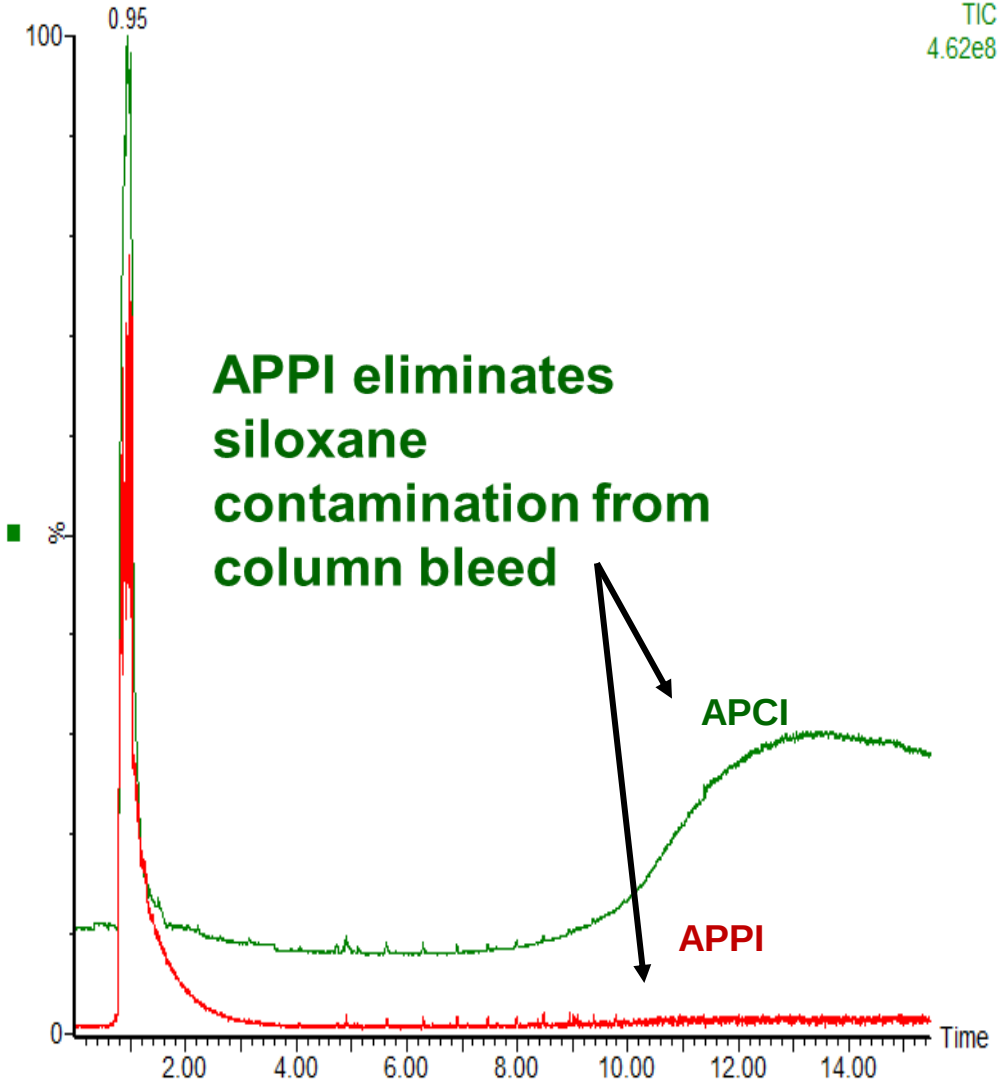
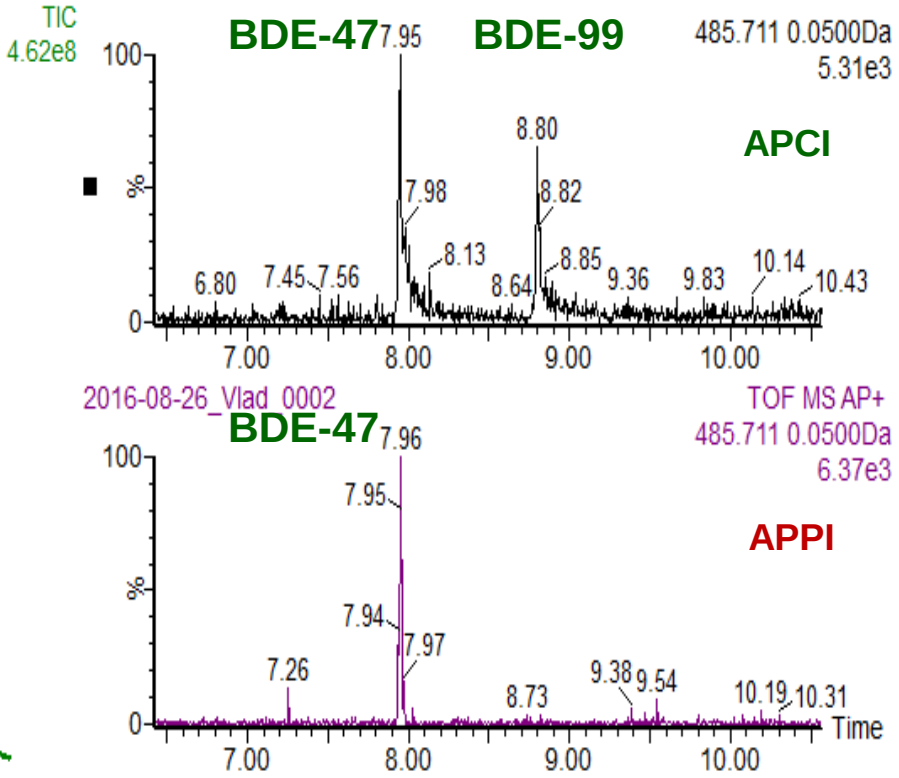


METHOD PERFORMANCE – SELECTIVITY



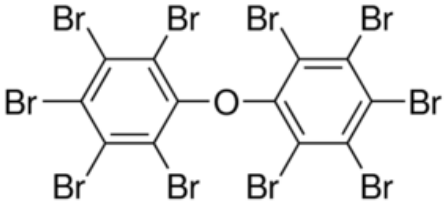


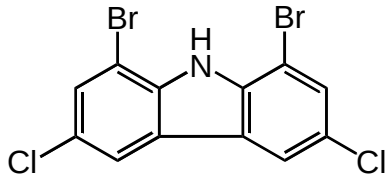
- Less chemical noise in individual mass channels due to enhanced selectivity
- No interference from dehalgenation products during ionization

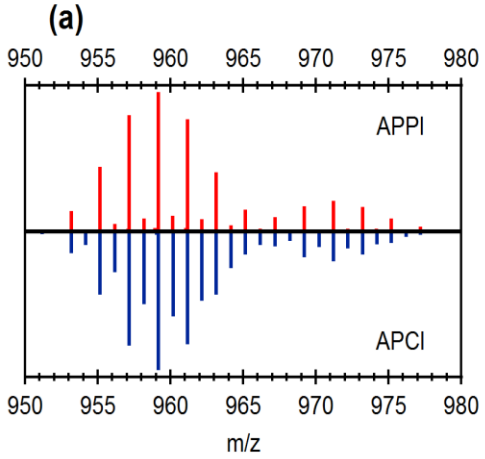
Prototype atmospheric pressure photoionization (APPI) source

Mixed mode ionization is reduced in GC-APPI

- APPI sensitivity comparable to APCI
- Single-mode ionization only
  - No protonation observed in APPI







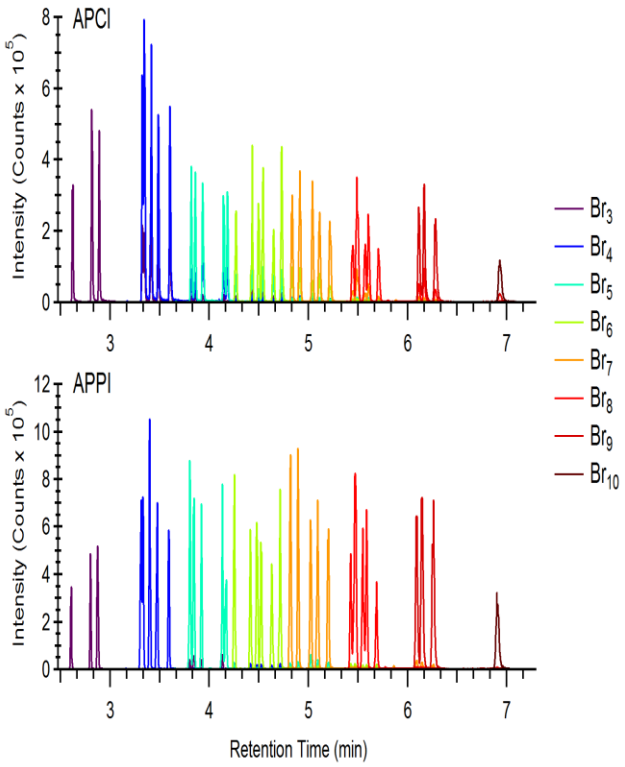


Photo-oxidation results in structure-diagnostic peaks

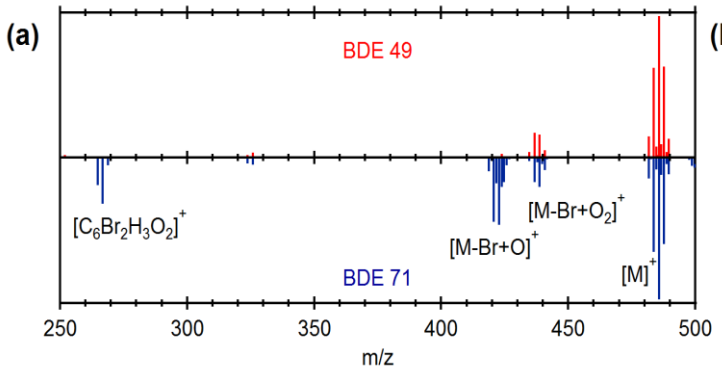
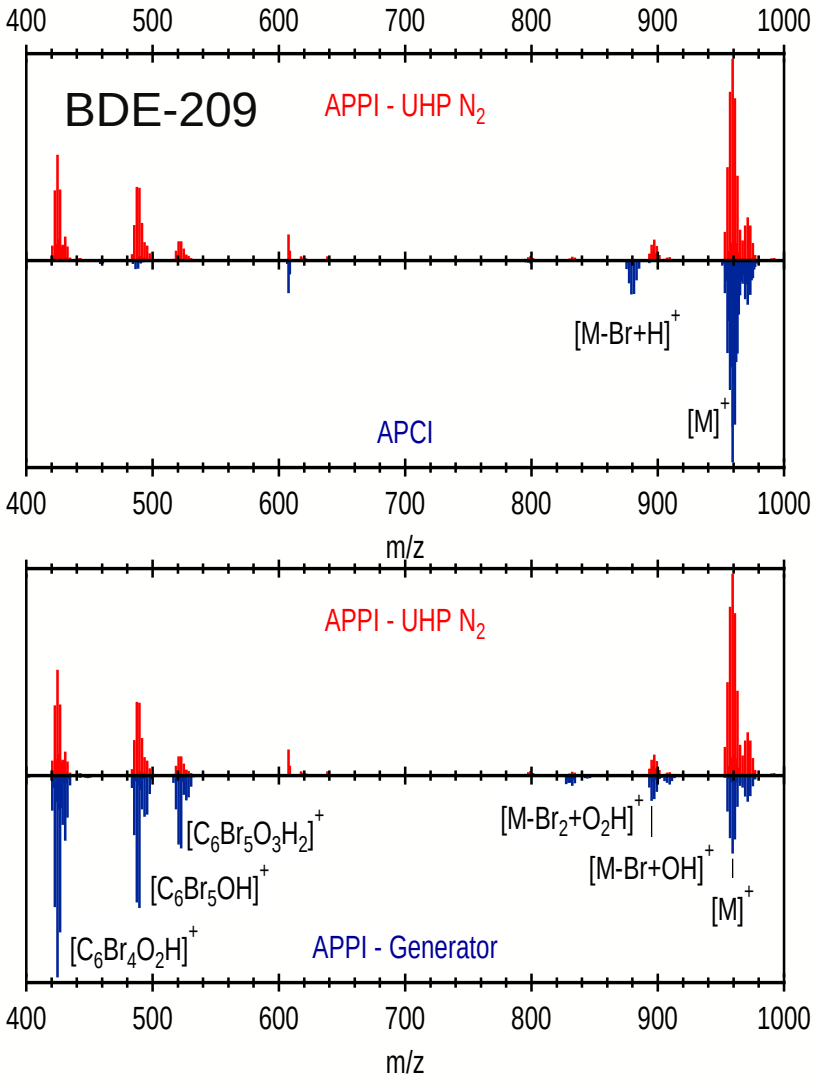
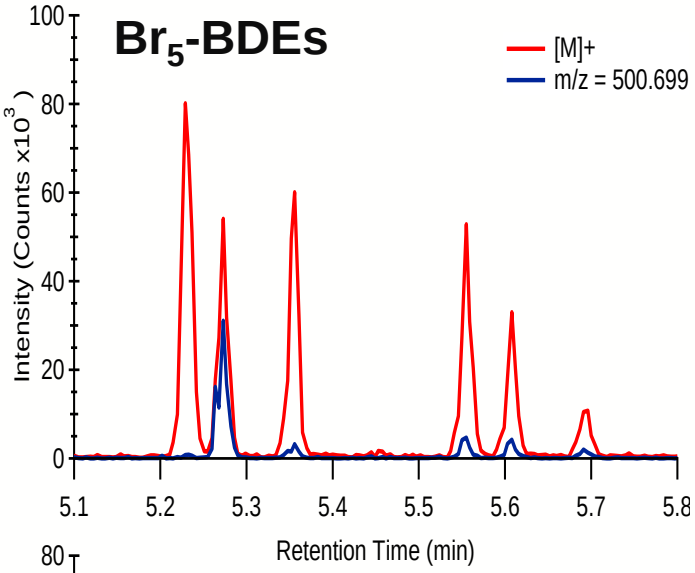


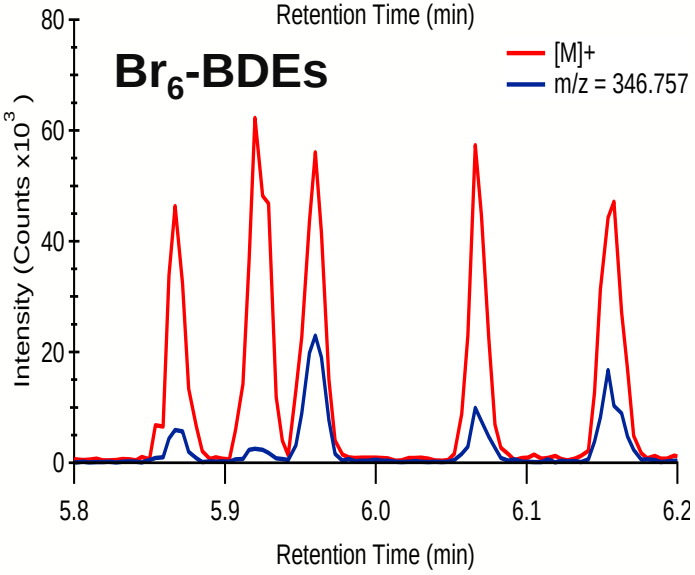
PHOTO-OXIDATION OF BDEs

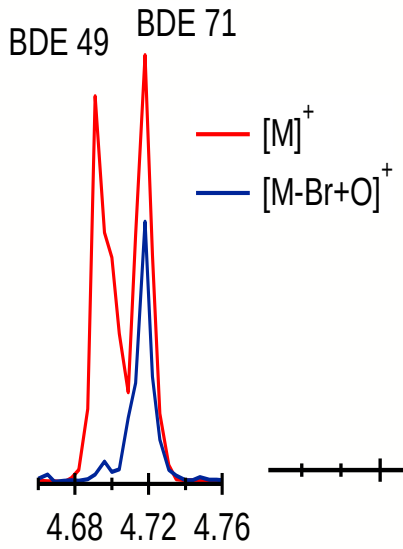


- Few ions other than charge-transfer and proton transfer products observed in APCI
- APCI in-source fragments primarily consist of debromination of protonated ions
- APPI produces photo-oxidation products and fragments
- Photo-oxidation is enhanced with increasing O_2 concentration
  - Ultrahigh purity N_2 from cylinder vs N_2 generator as make-up gas
- Can potentially be used for structural diagnostics at the expense of molecular ion intensity

ISOMER SPECIFIC OXIDATION



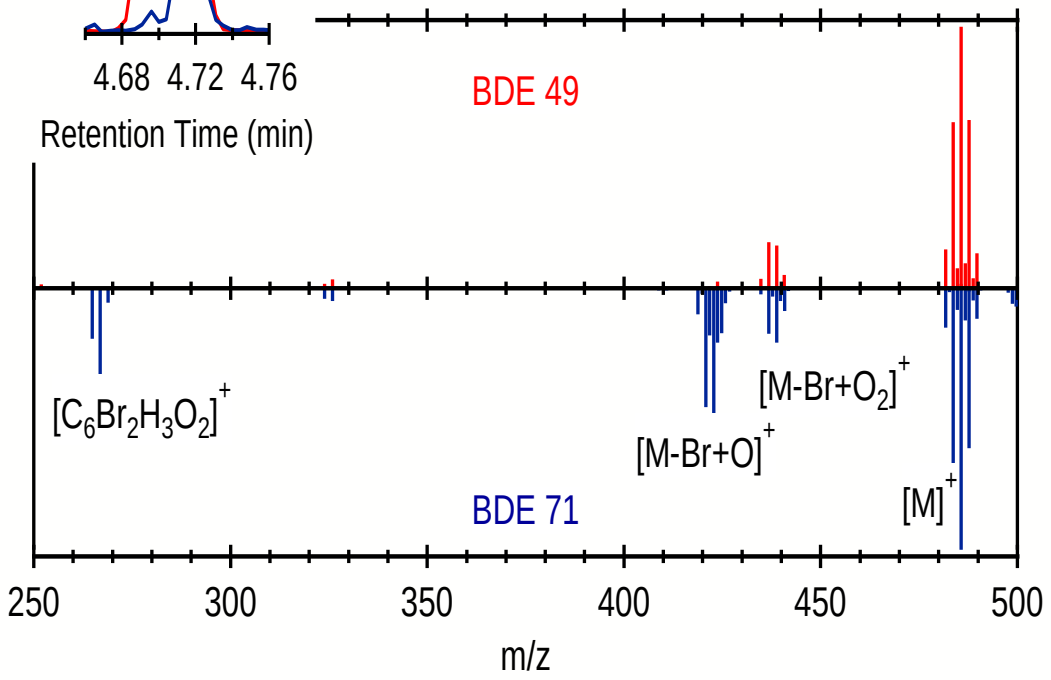




EPA Method 1614A (PBDE Analysis)

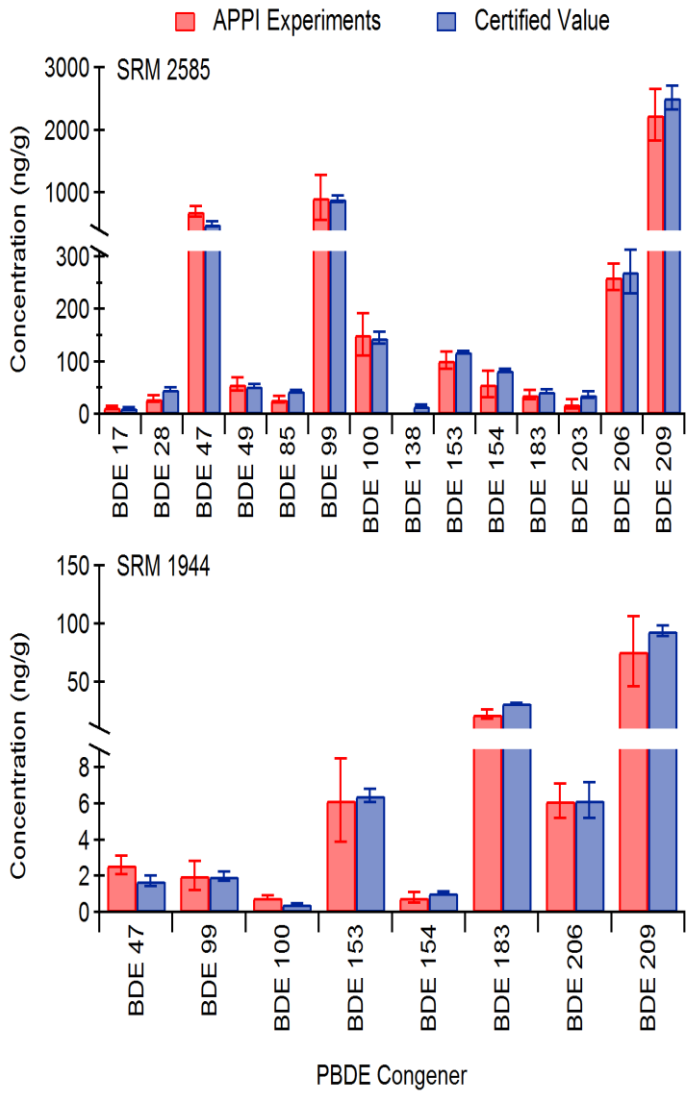
Critical separation is of BDE 49 & 71

<40% valley requirement



QUANTITATIVE RESULTS

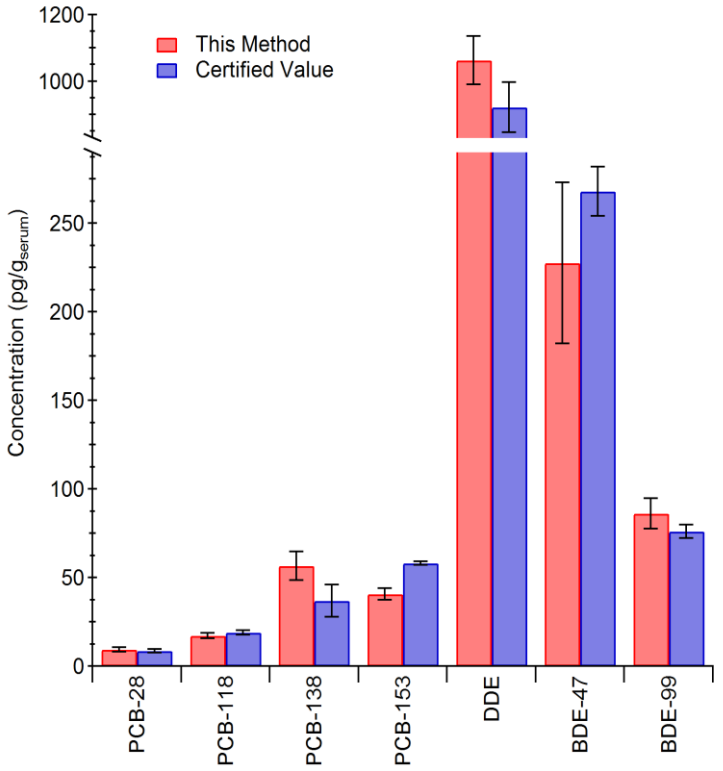
- APPI quantification of BDE congeners shows excellent agreement with NIST standard reference materials
  - SRM 2585 – Household Dust
  - SRM 1944 – New York/New Jersey waterway sediment
- Analysis performed using rapid GC method
  - RTX-1614 column (15 m x 0.25 mm x 0.1 µm)
  - Ramped from 90°C to 330 °C
  - Temperature program reflects max. instrument ramp rate
  - 10 min total analysis time
  - BDE-209 elutes in ~8 min
  - 3 mL/min He flow



METHOD PERFORMANCE

SRM 1957
Organic Contaminants in Human Serum

- Method is in excellent agreement with CRM certified values for a number of different compounds groups
- Low relative standard deviation



SUMMARY

- APPI is a new ionization source for the analysis of POPs by GC-MS
- APPI eliminates mixed-mode ionization issues experienced with APCI
- APPI can reduce chemical noise due to sample matrix and column bleed
- APPI has equivalent sensitivity to APCI, specifically for the analysis of BDEs and other selected halogenated POPs
- APPI can potentially differentiate between structural isomers with characteristic photo-ionization products
- APPI is quantitative
- Flows need to be optimized between column and MS entrance

Structural Determination of Polycyclic Aromatic Hydrocarbons by Ion Mobility Mass Spectrometry

Priscila M. Lalli, Ph.D.

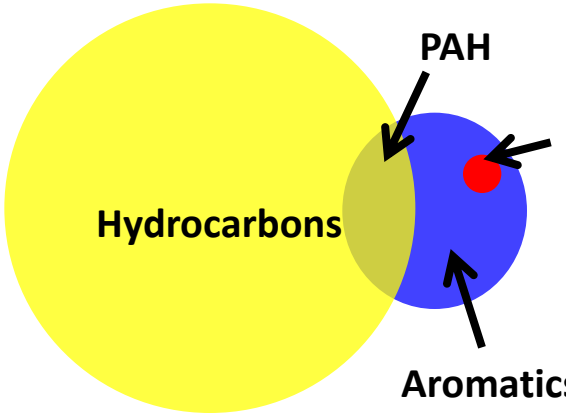
NATIONAL MAGLAB

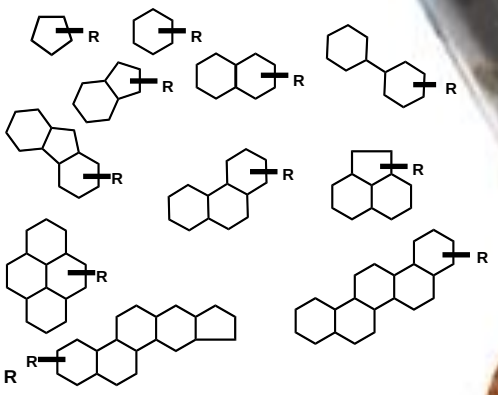
FLORIDA STATE UNIVERSITY 1851

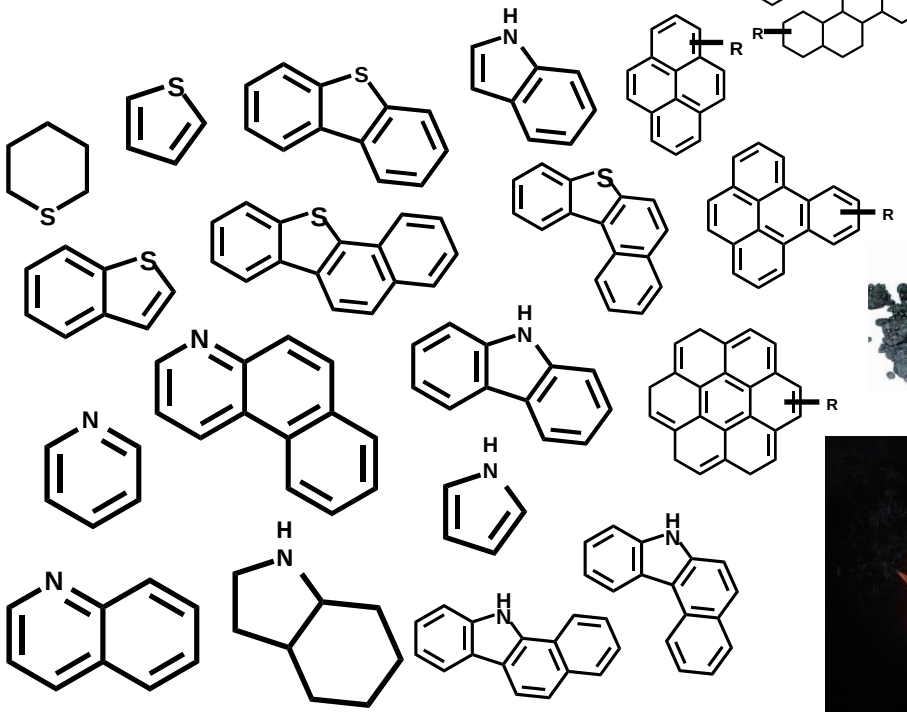
Future Fuels Institute FFI Florida State University

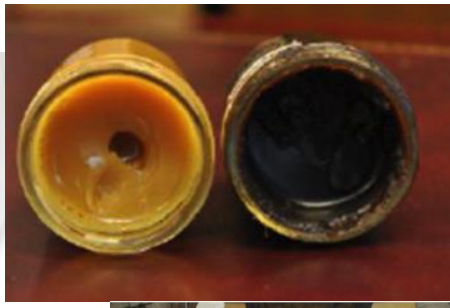
Petroleomics

Relate Chemistry to Production and Refinery Behavior



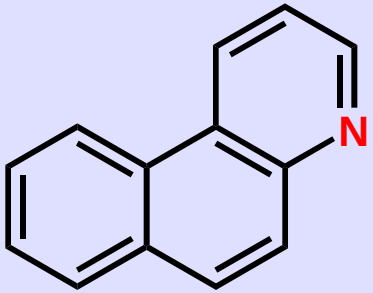




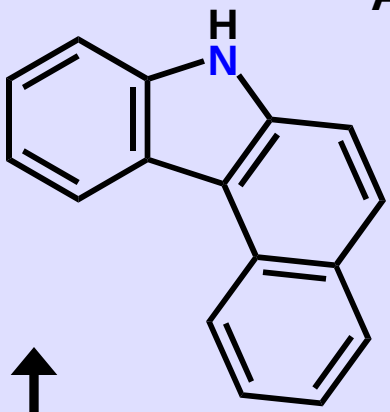


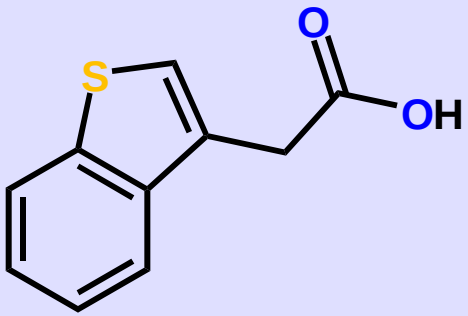
Electrospray Ionization (ESI)

Basic

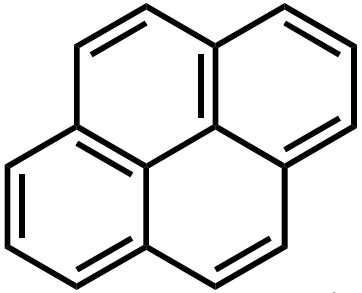


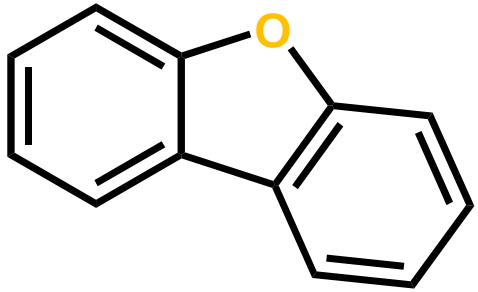
Acidic

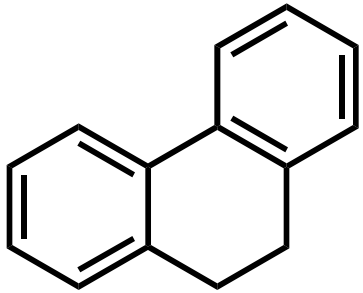


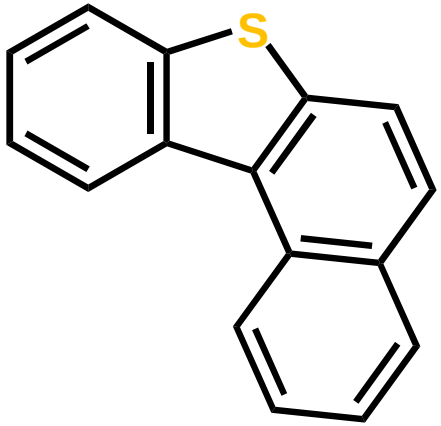


Atmospheric Pressure Photoionization (APPI)









Methods

Experimental Collision Cross Section (CCS)

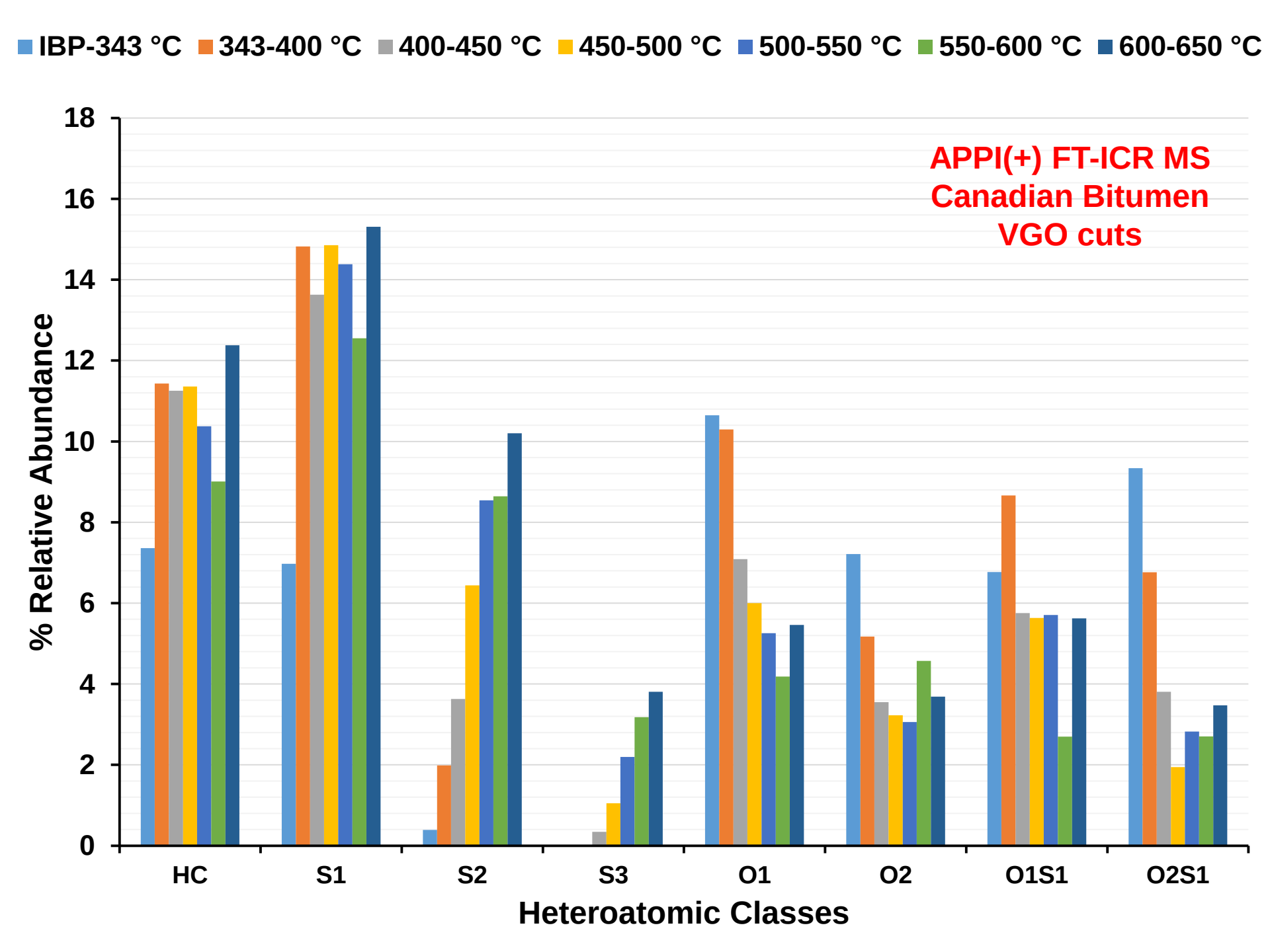
- 14 PAH model compounds
- APPI(+) Ion Mobility -TOF MS (Synapt G2-Si, Waters Corp.)
- Helium (3.4 mbar)
- IM cell calibration with polyalanine (with reported CCS from Henderson, S.C. *et al*. *J.Phys. Chem. B* **1999).**

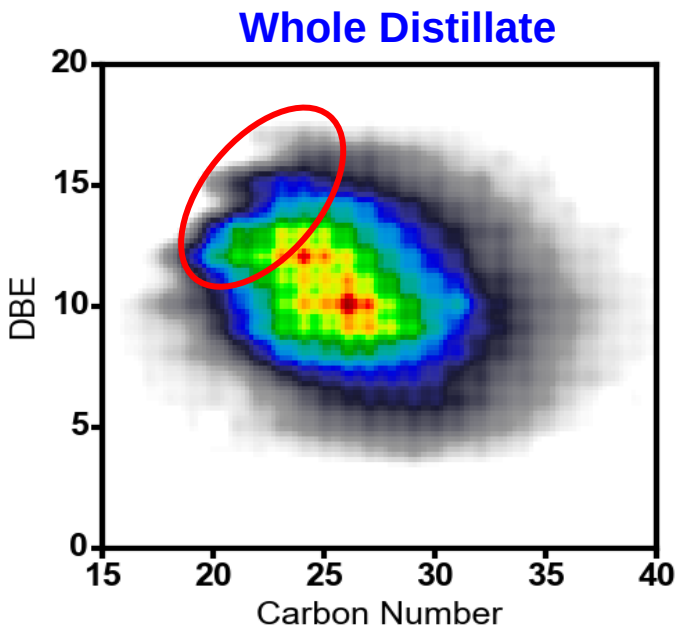
Theoretical Collision Cross Section

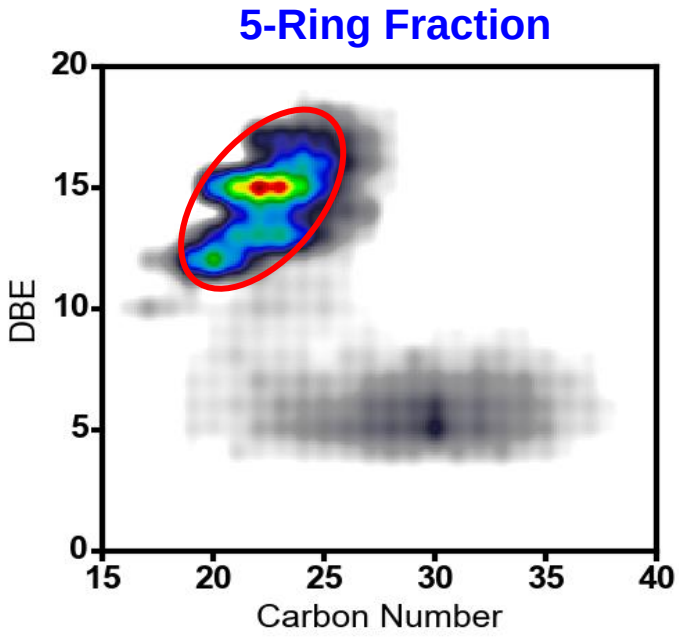
- Hypothetical Structures
- Structure optimization: Gaussian 04 (DFT B3LYP/6-311G(d,p)
- CCS calculation: Mobcal (Projection Approximation, Exact Hard Spheres Scattering Model (EHS) and Trajectory Method (TM).

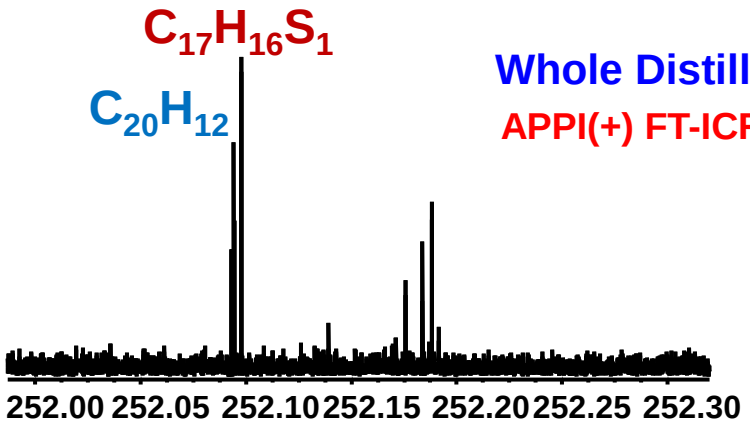
Fourier Transform Ion Cyclotron Resonance MS

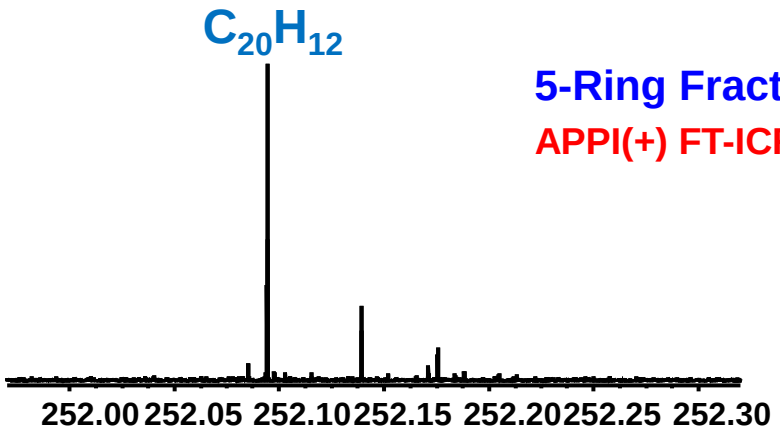
- APPI(+) FT-ICR MS @ 9.4 T (Rp ~ 800,000 at *m/z* 400; ~ 100-400 ppb mass error)

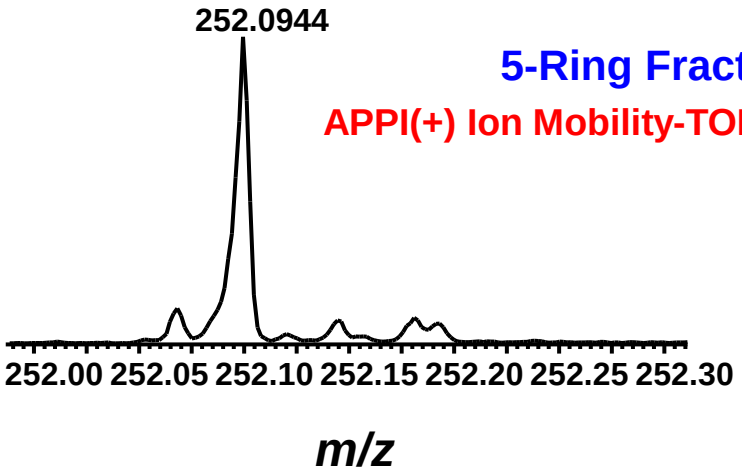

IBP-343 °C
343-400 °C
400-450 °C
450-500 °C
500-550 °C
550-600 °C
600-650 °C
APPI(+) FT-ICR MS
Canadian Bitumen
VGO cuts
% Relative Abundance
0
2
4
6
8
10
12
14
16
18
HC
S1
S2
S3
O1
O2
O1S1
O2S1
Heteroatomic Classes


Whole Distillate
DBE
Carbon Number


5-Ring Fraction
DBE
Carbon Number


C17H16S1
C20H12
Whole Distillate
APPI(+) FT-ICR MS
252.00 252.05 252.10 252.15 252.20 252.25 252.30


C20H12
5-Ring Fraction
APPI(+) FT-ICR MS
252.00 252.05 252.10 252.15 252.20 252.25 252.30

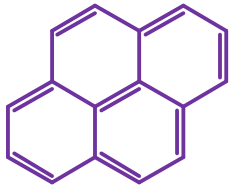

252.0944
5-Ring Fraction
APPI(+) Ion Mobility-TOF MS
252.00 252.05 252.10 252.15 252.20 252.25 252.30
m/z

Experimental Collision Cross Sections

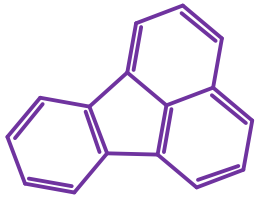
Model Compounds / Isomeric Sets

APPI (+) IM-MS

DBE = 12

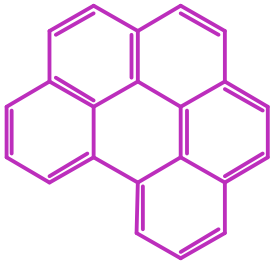


Pyrene - 83.95 Å²

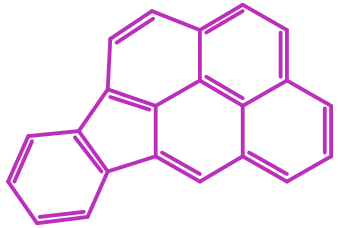


Fluoranthene – 84.99 Å²

DBE = 17



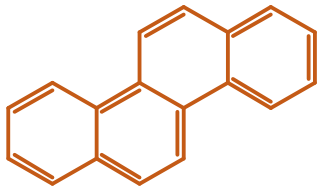
Benzo[ghi]perylene – 99.09 Å²



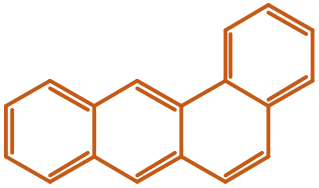
Indeno[1,2,3-cd]pyrene – 100.71 Å²

DBE = 13

Triphenylene – 90.42 Å²



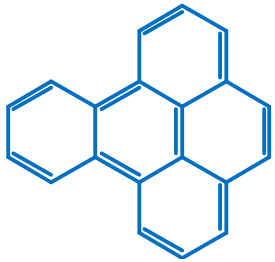
Chrysene – 91.15 Å²



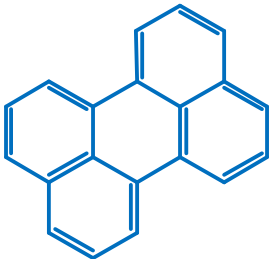
Benzo[a]anthracene – 91.51 Å²

Benzo[b]anthracene – 91.77 Å²

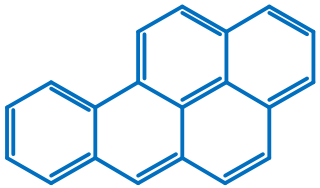
DBE = 15



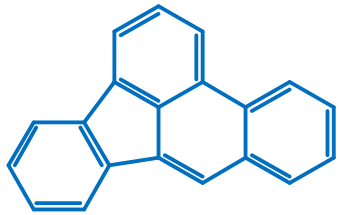
Benzo[e]pyrene
94.66 Å²



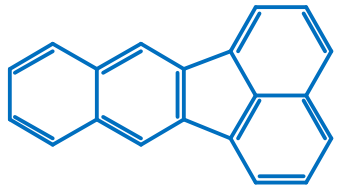
Perylene
95.12 Å²



Benzo[a]pyrene
95.23 Å²



Benzo[b]fluoranthene
96.14 Å²



Benzo[k]fluoranthene
96.64 Å²

Collision Cross Section

Standard Deviation: 0.01 – 0.10%

Experimental Collision Cross Sections for Sample

m/z	Molecular Formula	DBE	Experimental $CCS_{(He)}$ (Å²)	Standard Deviation
202.2560	$C_{16}H_{10}$	12	84.78	0.03
254.1096	$C_{20}H_{14}$	14	96.13	0.06
252.0939	$C_{20}H_{12}$	15	94.95	0.04
276.0939	$C_{22}H_{12}$	17	100.13	0.10

Fluoranthene (84.99 Å²)

Not 9-Phenylanthracene (98.89 Å²)

Benzo[e]pyrene or Perylene

Inconclusive

Experimental and Theoretical Collision Cross Sections

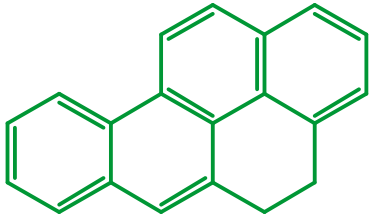
Isomeric set $C_{20}H_{12}$, DBE = 15

Name	PA (Å²)	EHS (Å²)	TM (Å²)	Experimental $CCS_{(He)}$ (Å²)	Standard Deviation
Benzo[e]pyrene	93.75	96.79	91.49	94.66	0.04
Perylene	93.89	96.66	93.24	95.12	0.06
Benzo[a]pyrene	94.89	97.91	92.55	95.23	0.05
Benzo[b]fluoranthene	96.77	100.28	94.12	96.14	0.03
Benzo[k]fluoranthene	97.7	101.54	95.26	96.64	0.04

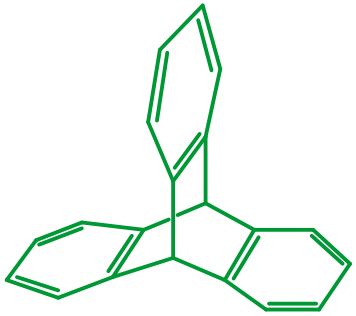
PA method: best agreement with experimental CCS with % deviations of 1.0 to 3.0 %,

Theoretical Collision Cross Sections

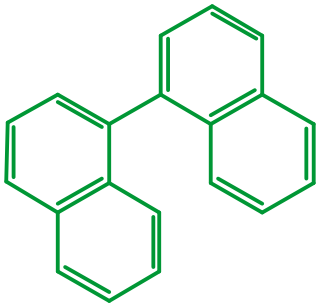
Hypothetical Structures ($C_{20}H_{14}$, DBE = 14)



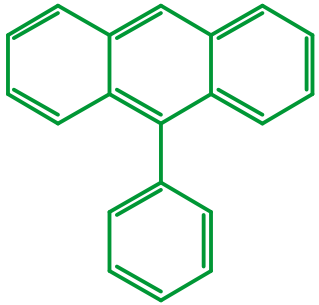
4,5-dihydrobenzo[pqr]tetraphene
95.51 Å²



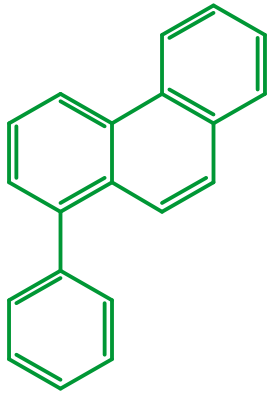
Trypticene
98.32 Å²



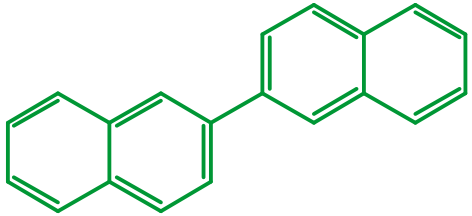
1,1-PR-binaphthyl
98.77 Å²



9-Phenylanthracene
99.75 Å²



1-Phenylanthracene
100.08 Å²



2,2-binaphthyl
103.18 Å²

Sample: 96.13 Å²

Conclusion

Ion mobility mass spectrometry was able to give insight into the structure of PAHs in a VGO cut from Canadian bitumen by comparison of experimental $CCS_{(He)}$ of ions in the sample with those of model compounds and/or by comparison with theoretical $CCS_{(He)}$ calculated for hypothetical structures.

PAHs with more peri-condensed aromatic rings were found to be more compact than those linearly fused.

PAHs with a more rounded shape are more compact than those with elongated structures.

PAHs with an island structure are more compact than their isomers with archipelago structure.

IVG Institute for Combustion and Gas Dynamics Thermodynamics

UNIVERSITÄT DUISBURG ESSEN

Open-Minded

Photoionization Workshop

Isomer-resolved Species Identification and Quantification by Synchrotron-based Photoionization Mass Spectrometry

Thomas Bierkandt and Tina Kasper

65th ASMS Conference on Mass Spectrometry and Allied Topics
June 4 – 8, 2017, Indianapolis, Indiana

June 5, 2017

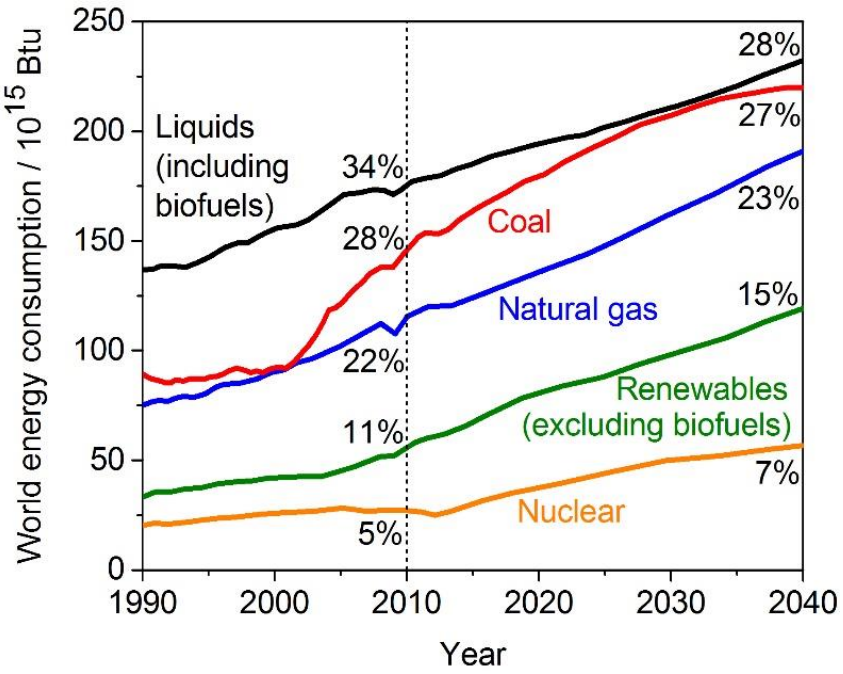
Combustion processes and world energy consumption

- Currently more than 80% of world energy use supplied by fossil fuels
- Fossil fuels also in 2040 most important primary energy carrier

www.nationalgeographic.de

www.bbc.com

EIA, International Energy Outlook 2013



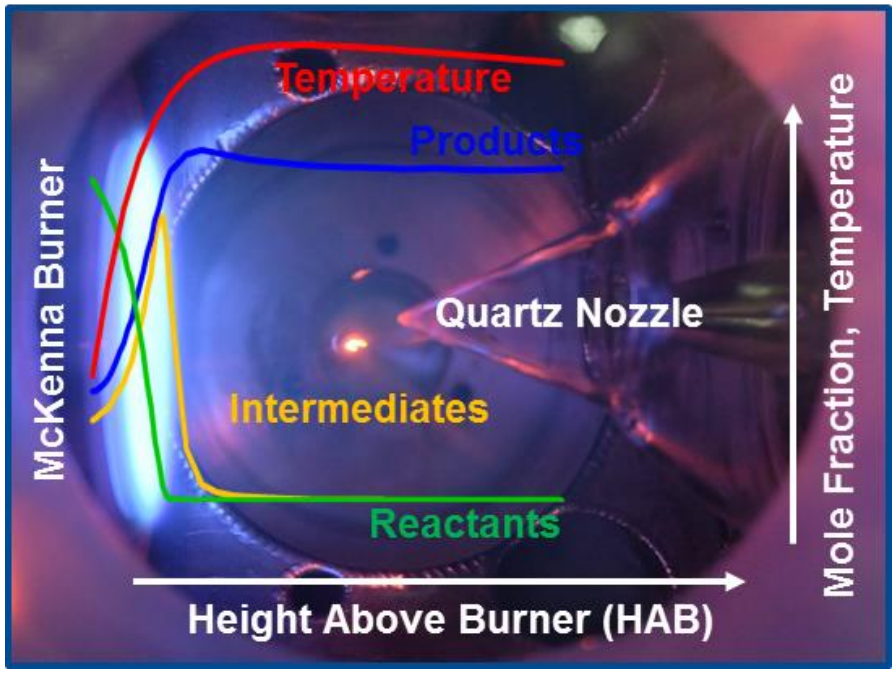
- Combustion is a major source of air borne pollutants such as NOx, VOCs, PAHs and soot
- Pollutants are fuel-dependent

→ Development of alternative combustion strategies and use of biofuels →

Understanding combustion processes is of crucial interest

Combustion is a complicated mix of chemistry and gas dynamics

Laminar premixed low-pressure flames



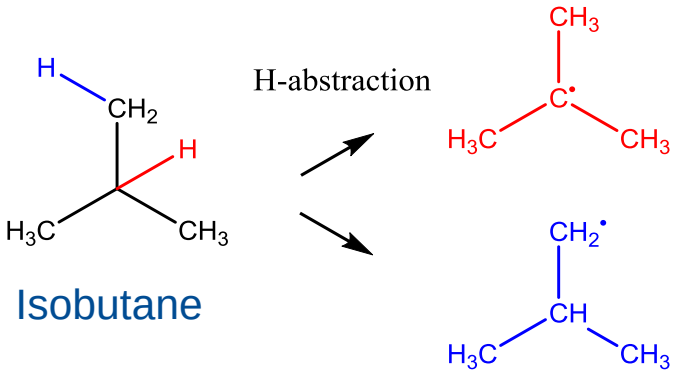
Chemical composition:

- Which species are present?
  - Key reaction species and highly reactive radicals
- How large are their concentrations?

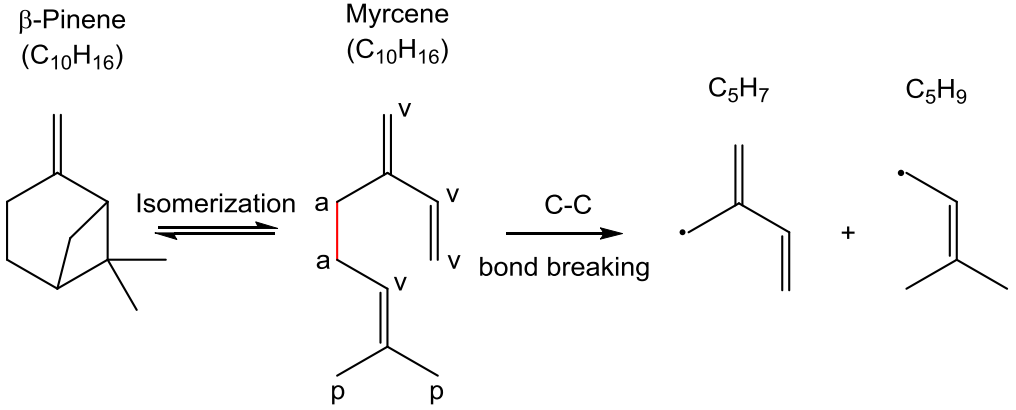
Reaction kinetics:

- Which species react with each other?
- How fast are those reactions?

Combustion kinetics of monoterpenes:
Poster on Wednesday (WP 122)

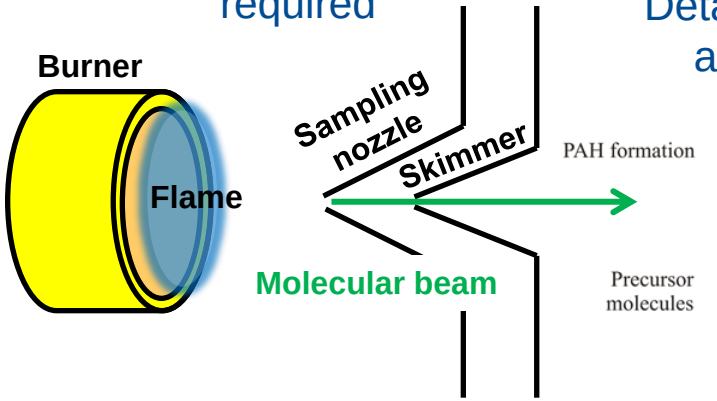


Isobutane

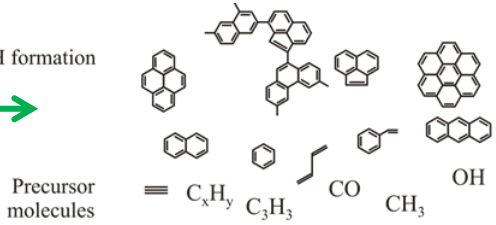


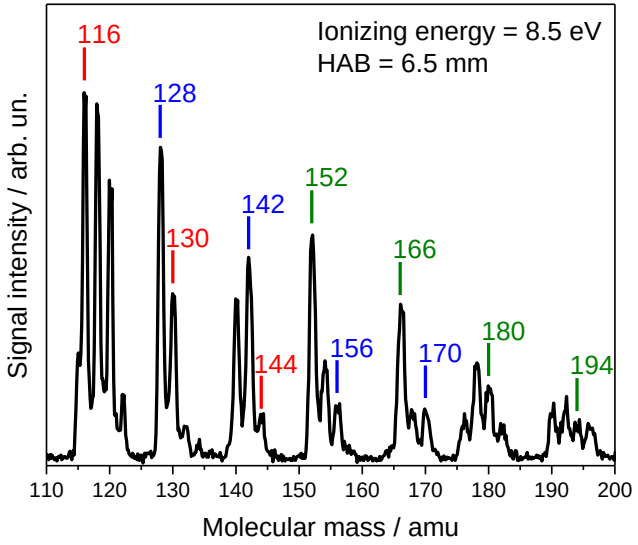
Challenges in flame sampling

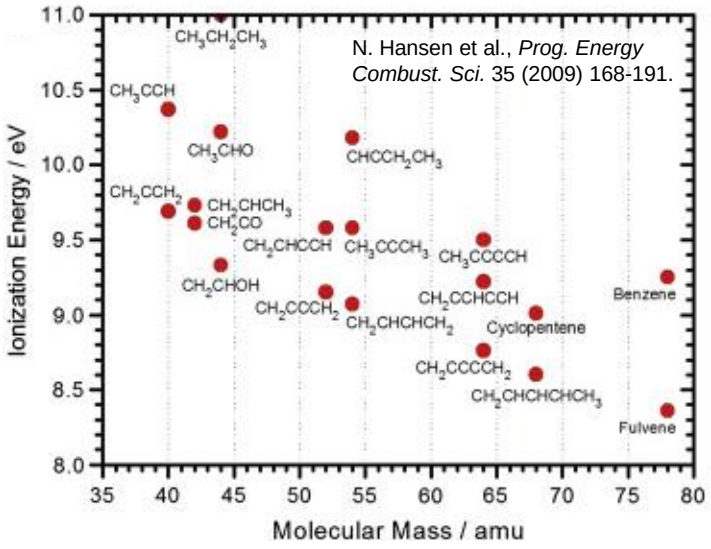
Methods for observing key reaction species (radicals) are required



Details of the chemistry are very important





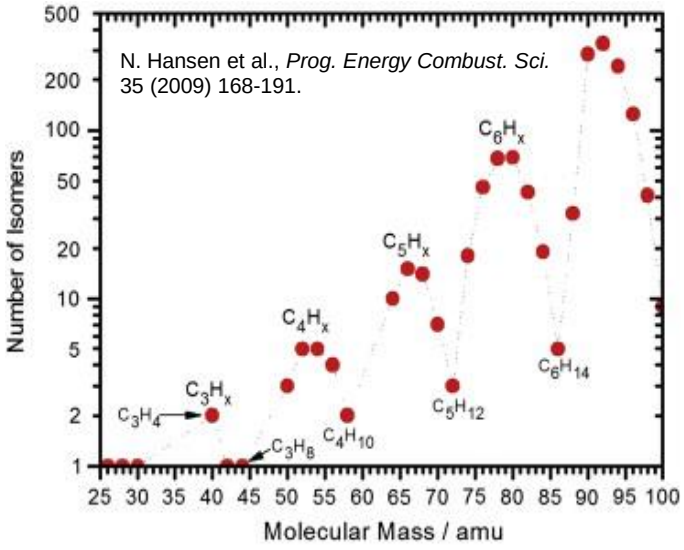


Wanted:

Identification of different isomers

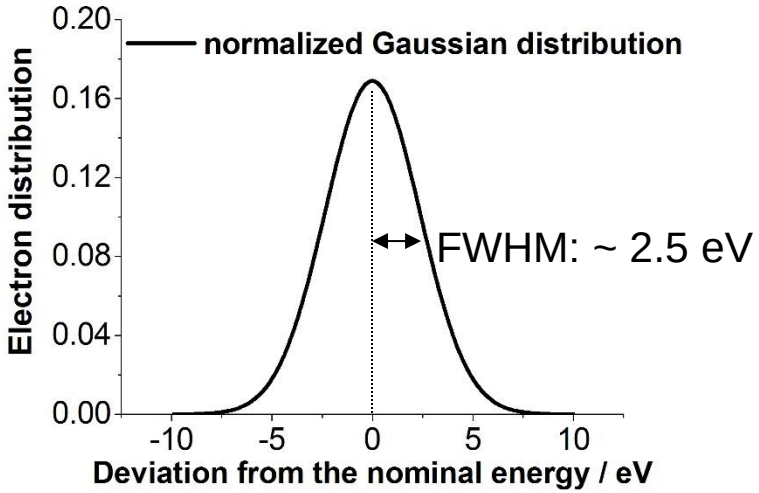
and

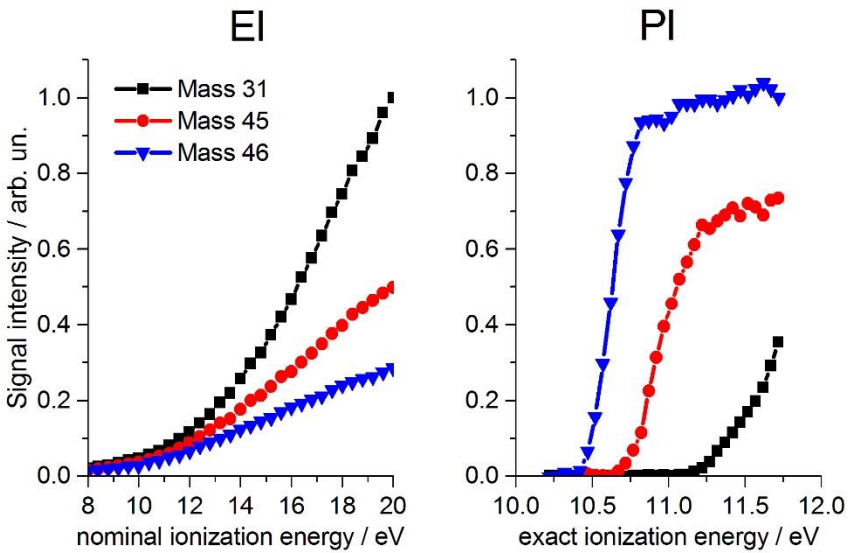
rapid tunability from 5-16 eV (VUV)



Ionization methods in flame-sampling molecular-beam mass spectrometry

	Electron ionization (EI)	Single-photon ionization (SPI)
Selectivity	No	High
Energy resolution (E/ΔE)	Low (< 20)	High (10000 for VUV lasers)
Fragmentation	Can be a problem	"soft ionization"
Tunability	Fast	Limited and time-consuming
Beam	Very high flux (continuous)	High flux (pulsed, low repetition rate)





Is there a light source which combines the best of both worlds?

Synchrotron radiation

Synchrotron-based flame chemistry experiments

ALS
- Premixed flame
- Counter-flow diffusion flame
- Jet-stirred reactor

NSRL
- Premixed flame
- Counter-flow diffusion flame
- Pyrolysis flow reactor
- Jet-stirred reactor

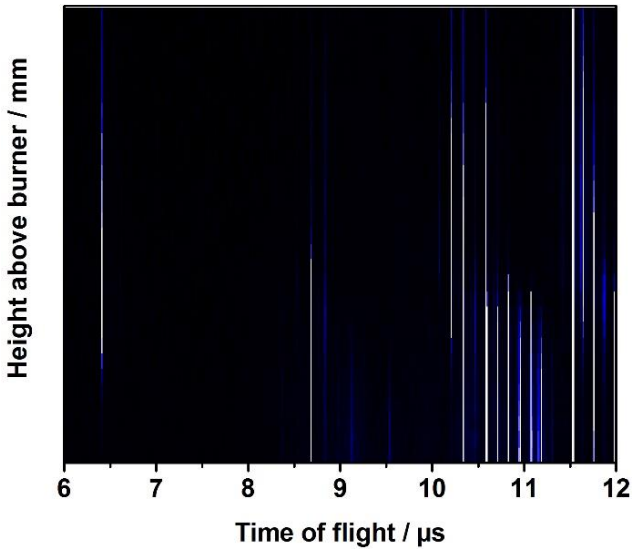
Soleil/SLS
- Premixed flame
- Pyrolysis reactor

BESSY
- Premixed flame

2002 **2003** **2013** **2018**

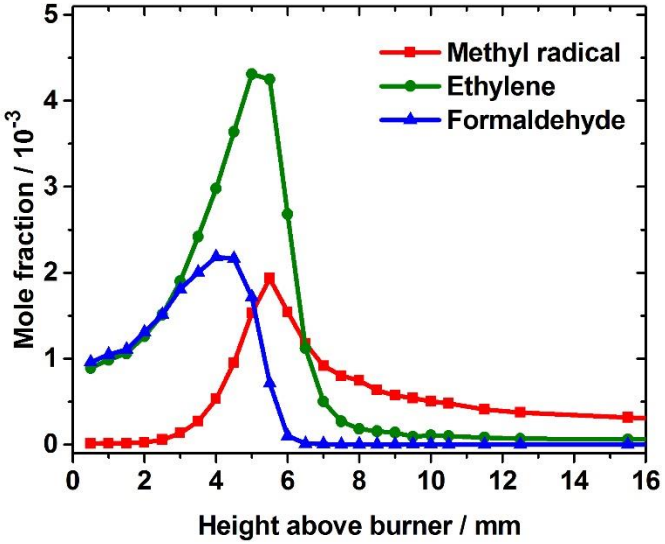
	ALS	NSRL	SLS	Soleil	BESSY
Photon flux [1/s]	10^{14}	10^{12}	10^{11}	10^{11}	10^{11}
E/ΔE	300	2000	4000	200000	85000
Energy range [eV]	7-30	7-20	5-30	5-40	6-40
m/Δm	3500	3000	300	300	<10000
Technique	PIMS	PIMS	PEPICO	PEPICO	PIMS

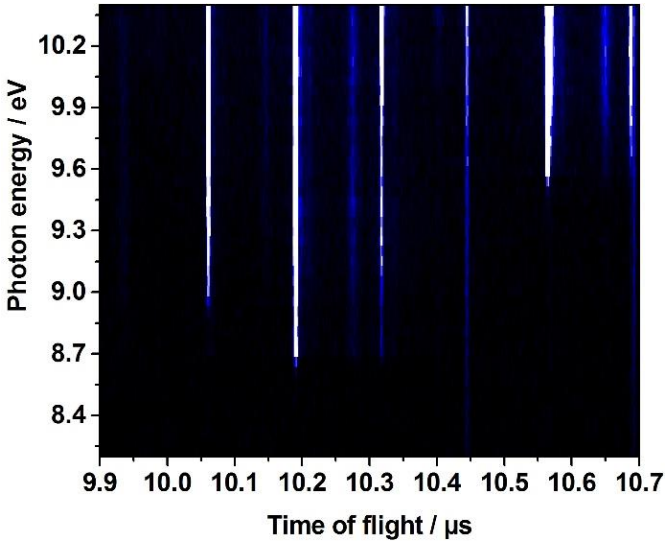
Species identification and quantification



variation of burner position

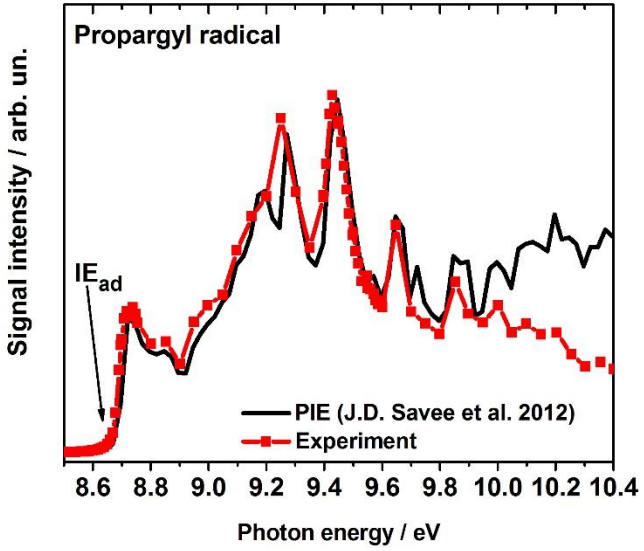
photon energy constant



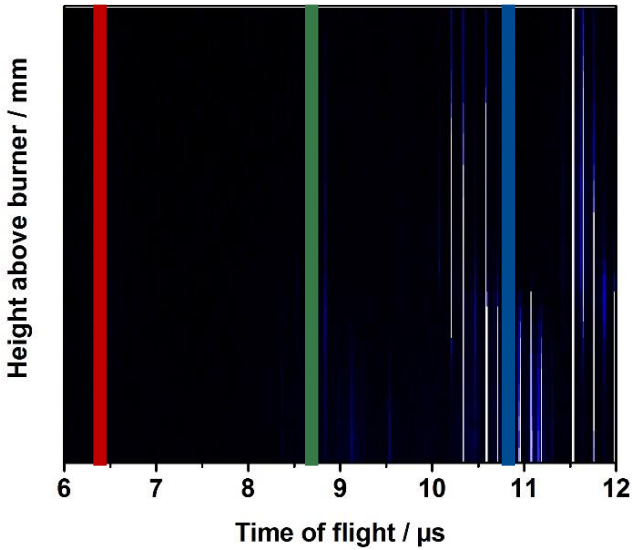


variation of photon energy

burner position constant

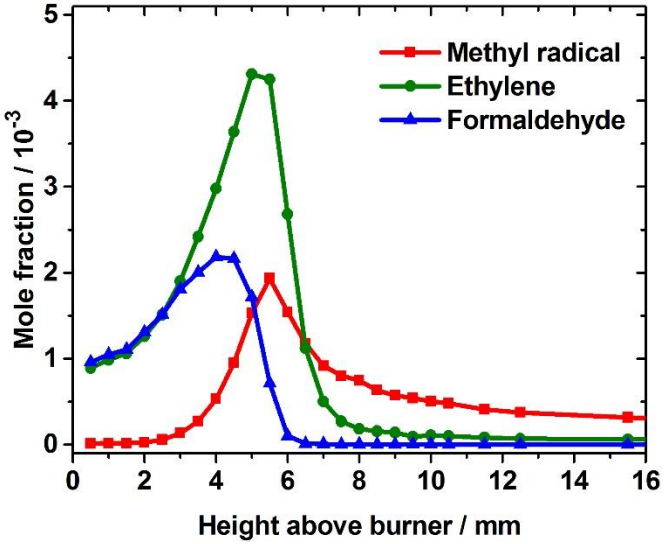


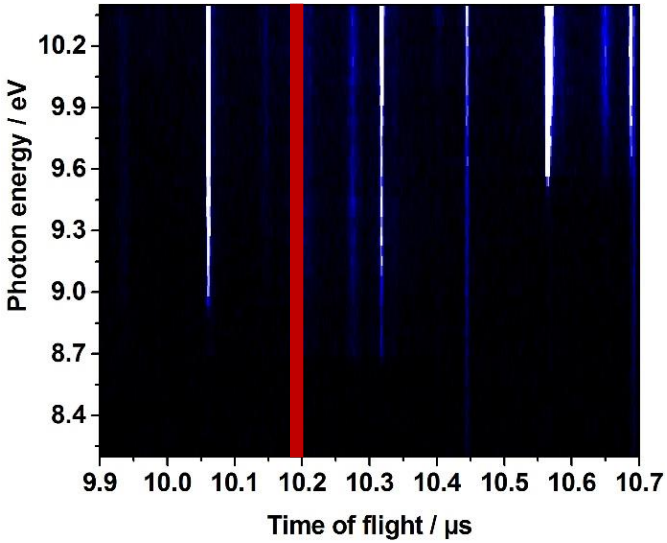
Species identification and quantification



variation of burner position

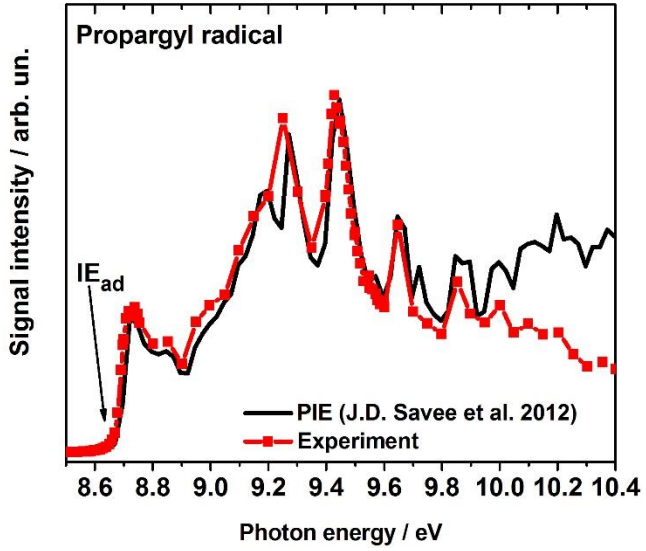
photon energy constant



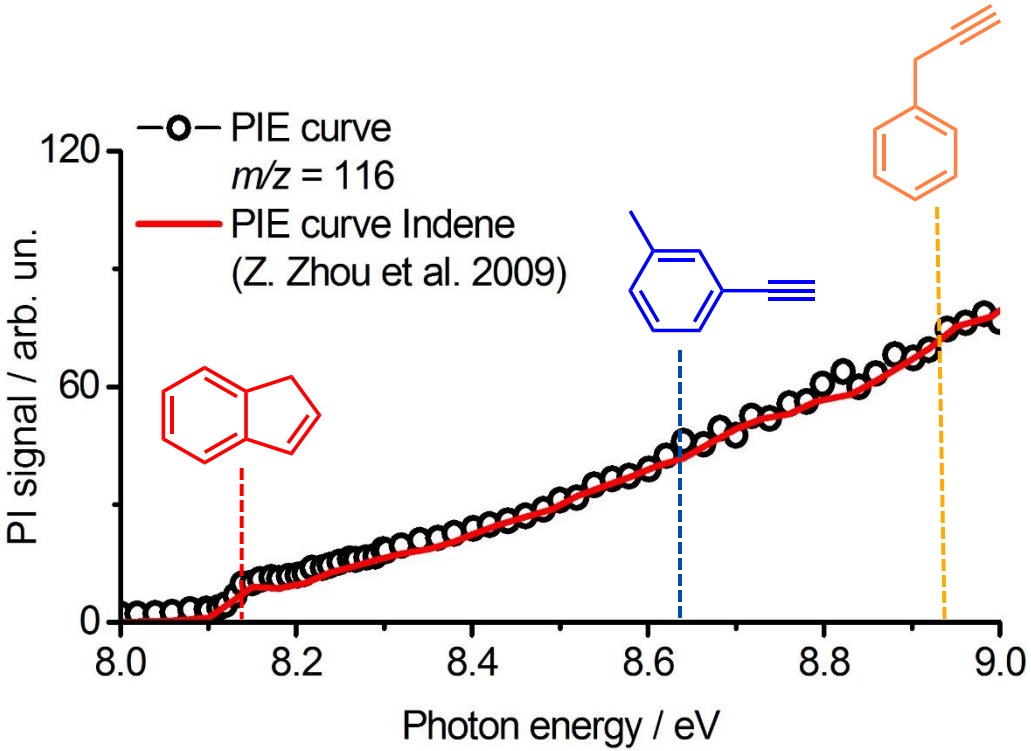


variation of photon energy

burner position constant



Isomer resolution – the big advantage of synchrotron radiation for ionization

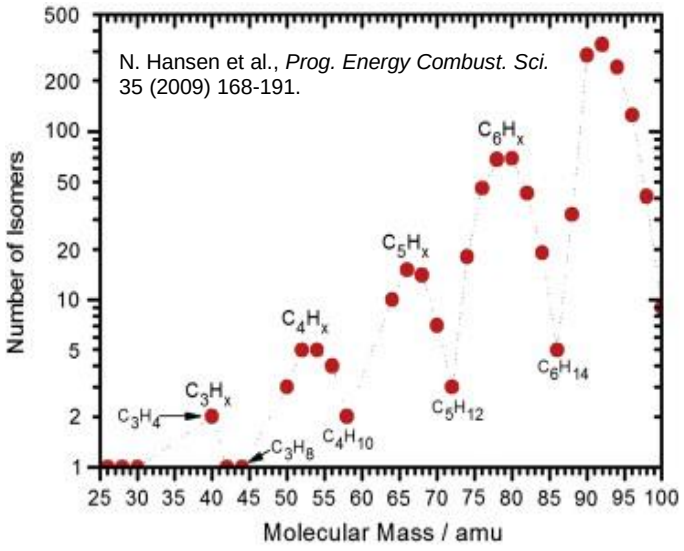


- Number of isomers increases with m/z
- Isomers react differently

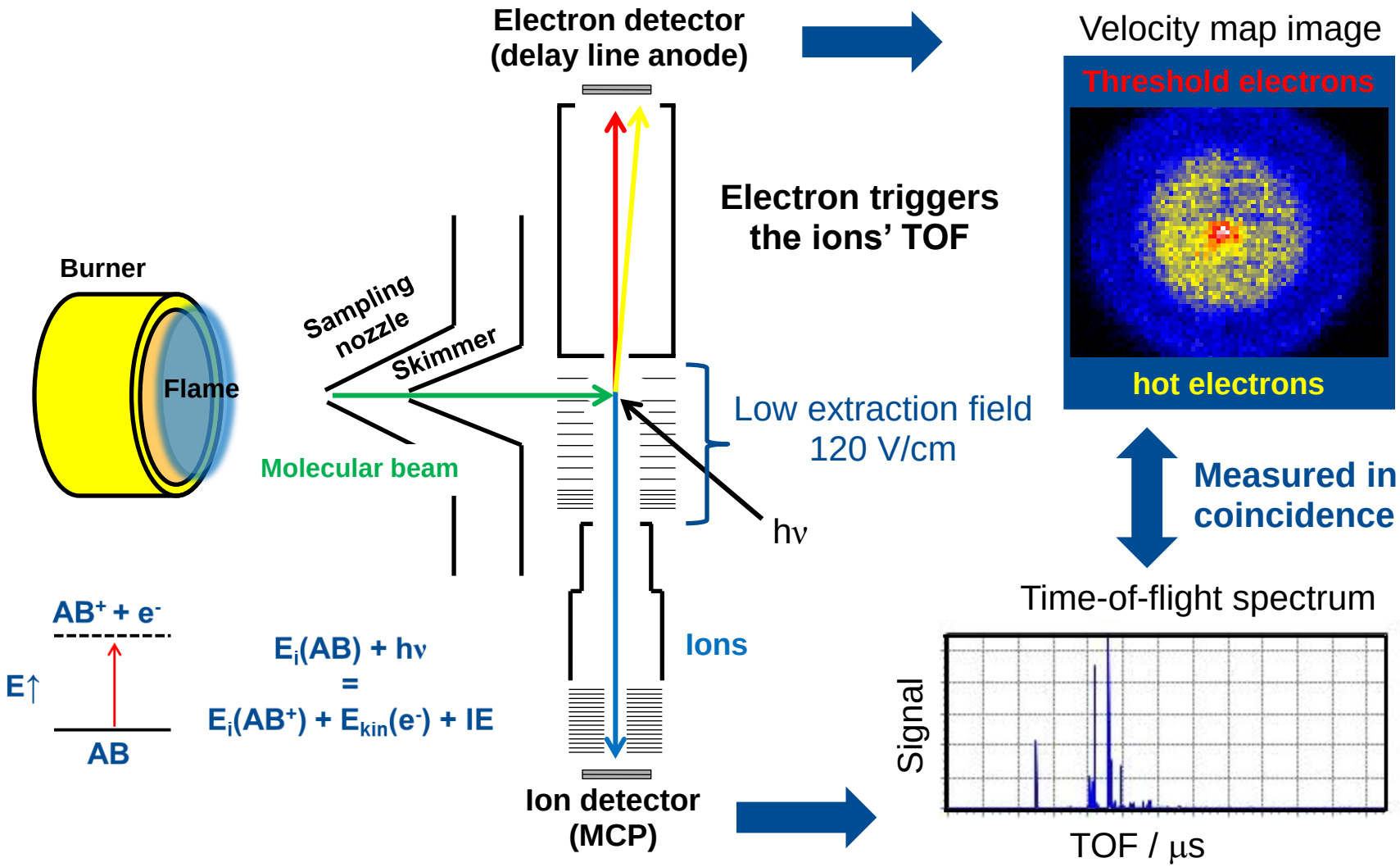
How can PEPICO improve isomer resolution?

Example: C_9H_8 isomers

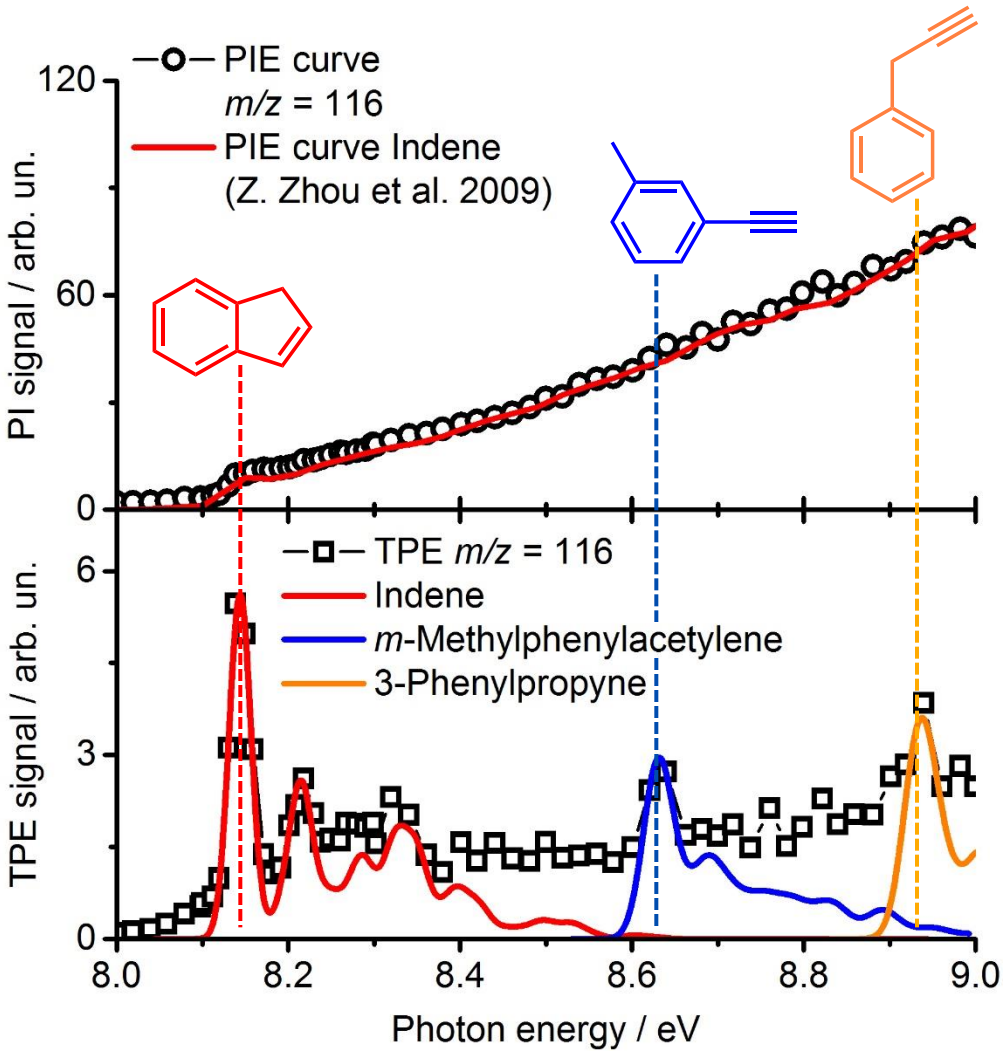
- Photoionization efficiency (PIE) curve
  - Good signal-to-noise
  - Detection limit: $x_i \sim 10^{-7}$
  - First onset can be assigned to indene
  - Larger isomers have typically similar PIE curves
  - Only one isomer identified



iPEPICO: imaging photoelectron photoion coincidence spectroscopy



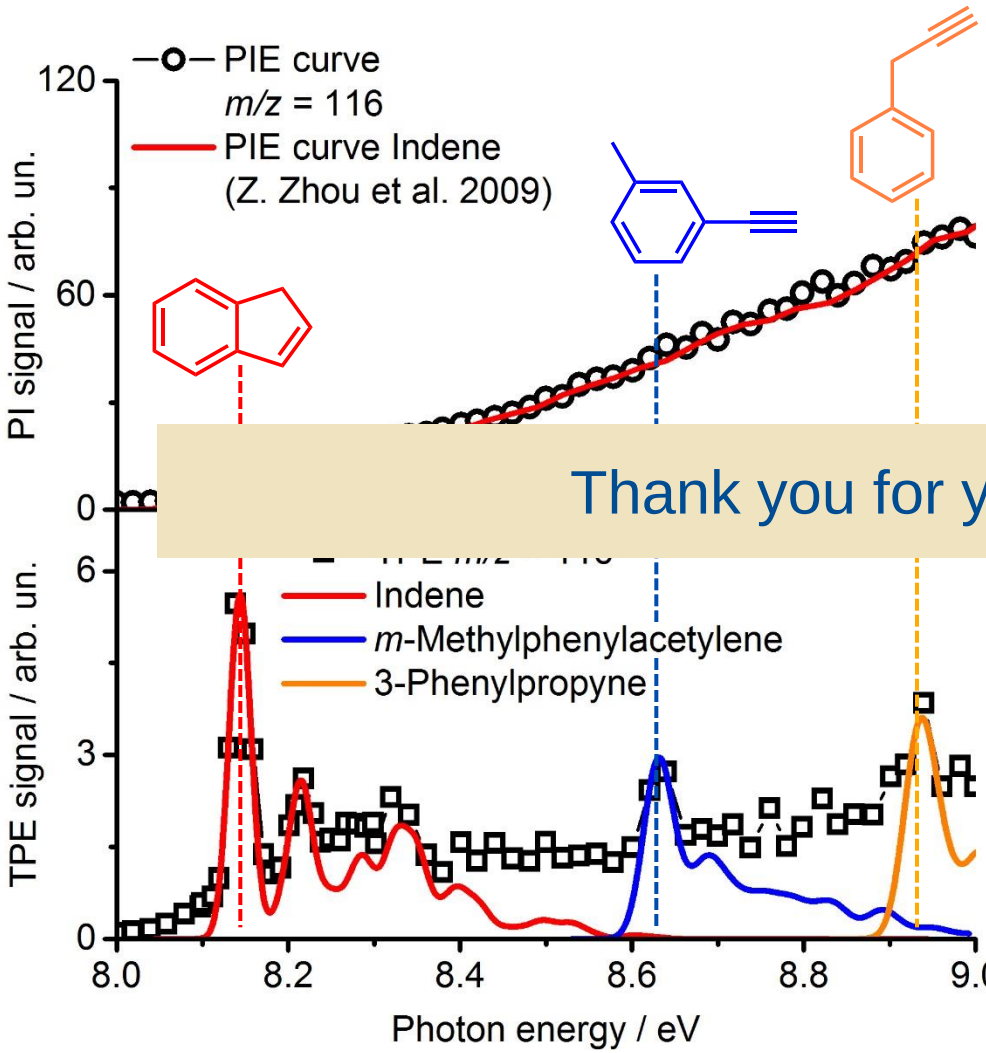
ms-TPES help to identify isomers



Example: C_8H_9 isomers

- Photoionization efficiency (PIE) curve
  - First onset can be assigned to indene
  - Only one isomer identified
- ms-TPES
  - Fingerprint of each species
  - Three isomers instead of one
  - Measuring threshold photoelectrons increases the selectivity
  - Not for all species because higher averaging times

ms-TPES help to identify isomers



Example: C_8H_9 isomers

- Photoionization efficiency (PIE) curve
  - First onset can be assigned to indene
  - Only one isomer identified

Thank you for your attention

- Fingerprint of each species
- Three isomers instead of one
- Measuring threshold photoelectrons increases the selectivity
- Not for all species because higher averaging times

Vacuum Photoionization Mass Spectrometry

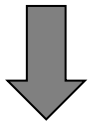
An approach for online analysis of complex mixtures

Author: Sven Ehlert, Andreas Walte

ASMS Photoionization Workshop June 2017

Basic idea of Vacuum Photo Ionization Mass Spectrometry

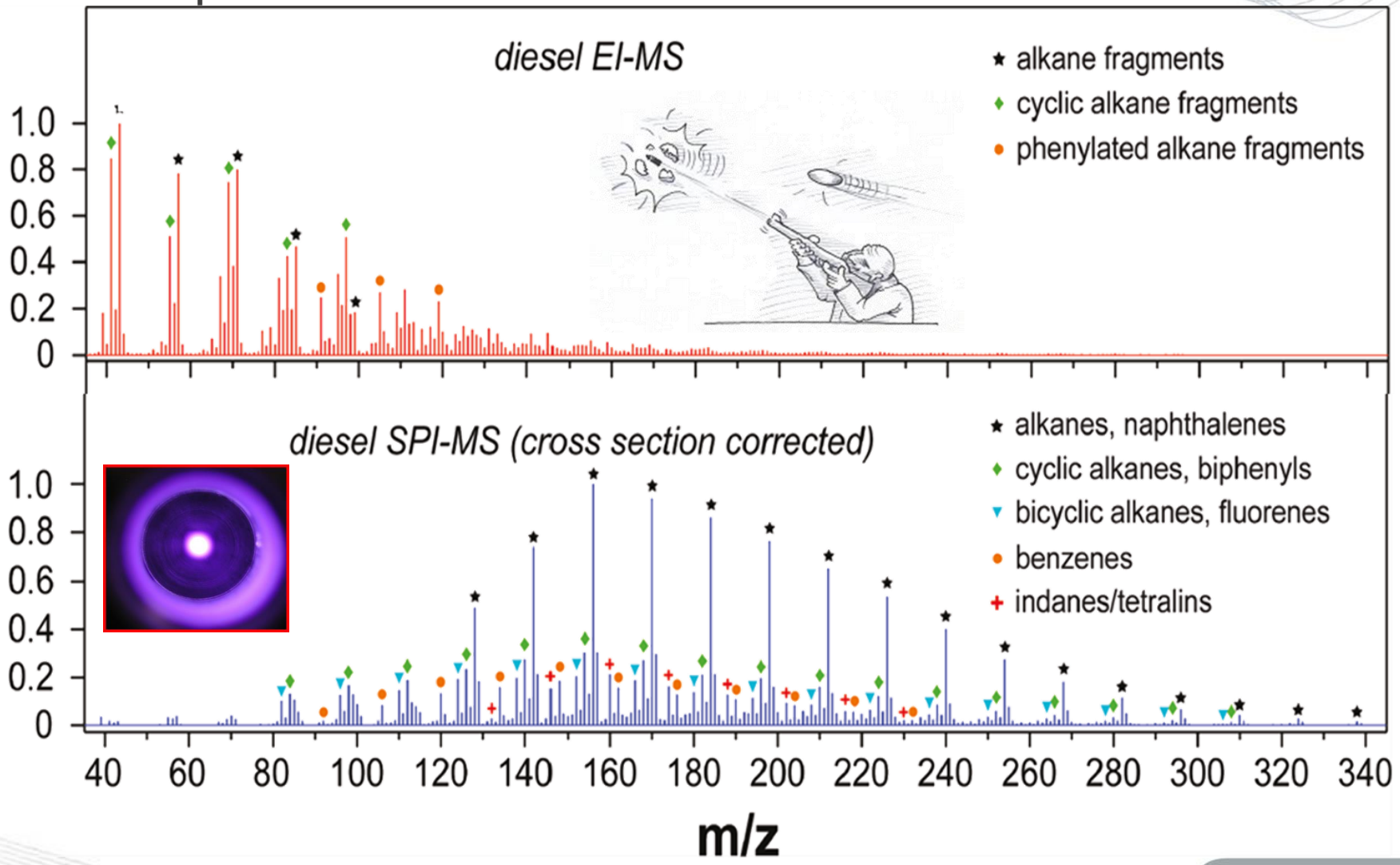
PIMS - Soft photo ionization in <u>vacuum</u>
(no fragmentation as in
EI-MS and no matrix effects as in CI-MS)



direct MS analysis
(including effective matrix suppression e.g. N_2, O_2…)

Introduction:
Photo ionization

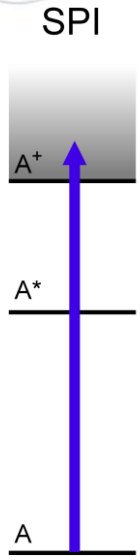
Mass spectra of Diesel

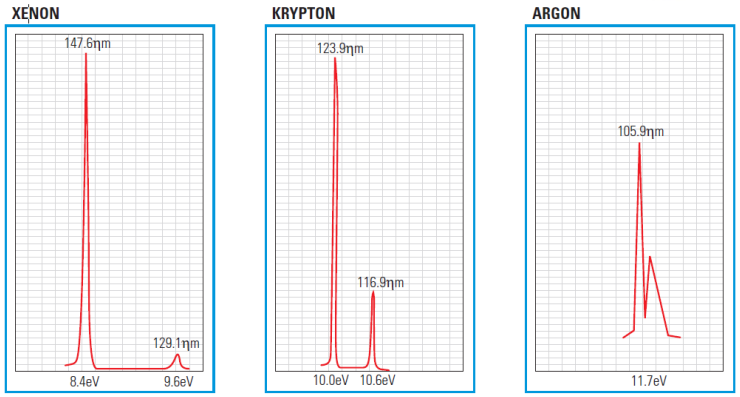


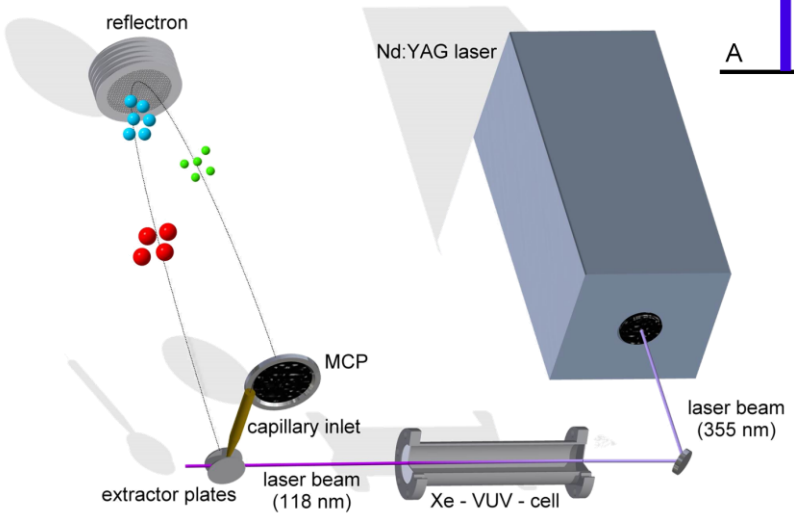
Introduction:
Photo ionization - SPI

Vacuum UV Single Photon Ionization (SPI)

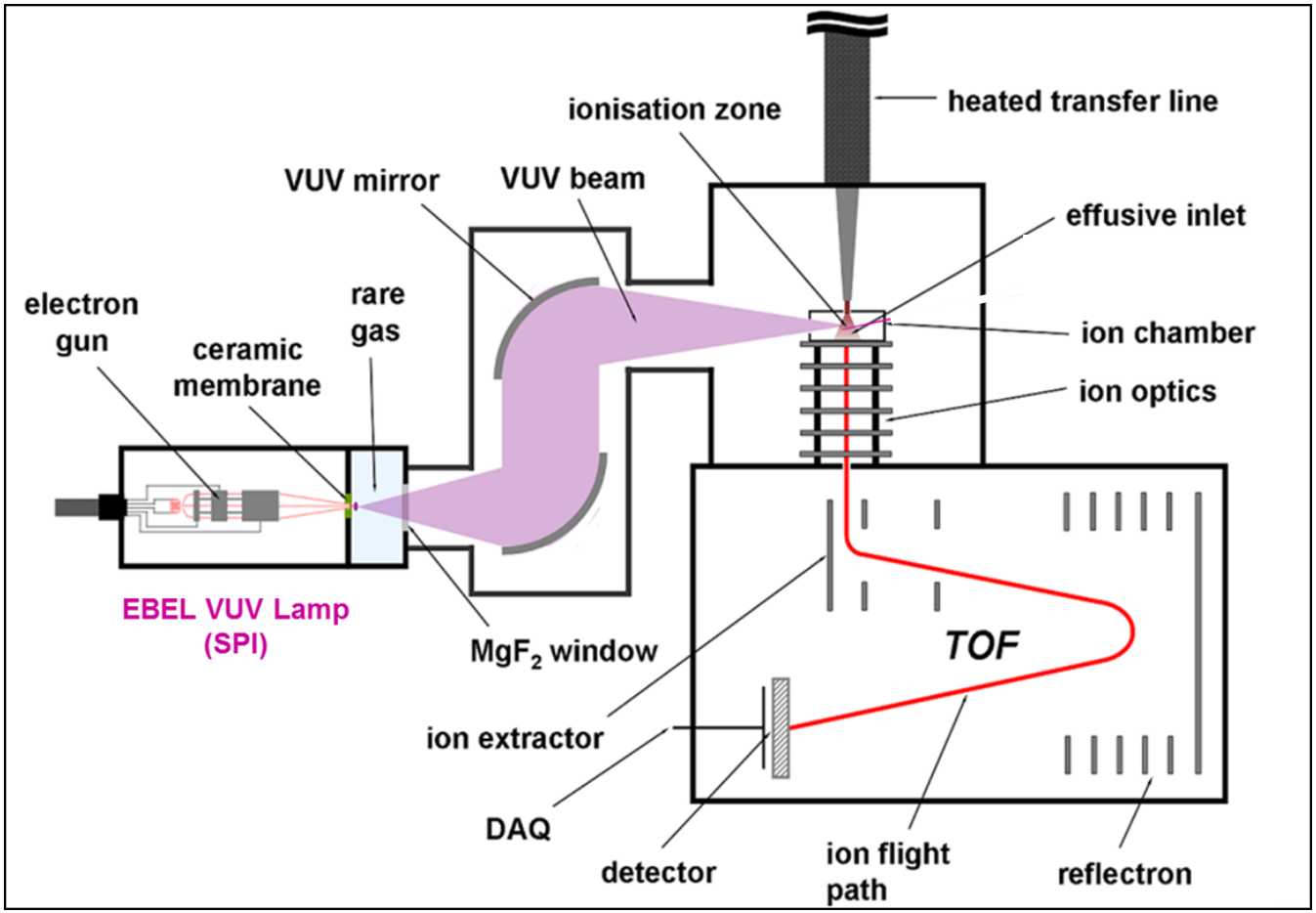
- incoherent VUV radiation (excimer lamp, e.g. 9.8 eV [126nm]), glow discharge lamps, e.g. filled with Kr, 10.0 & 10.6eV [123.9 & 116.9nm], or deuterium lamps, e.g. 10.8….3.1eV [115…400nm])
- ionization with laser photons (118 nm ,10.5 eV)
- soft ionization of most organic compounds
- ppb on-line concentration range







SPI-Lamp Setup

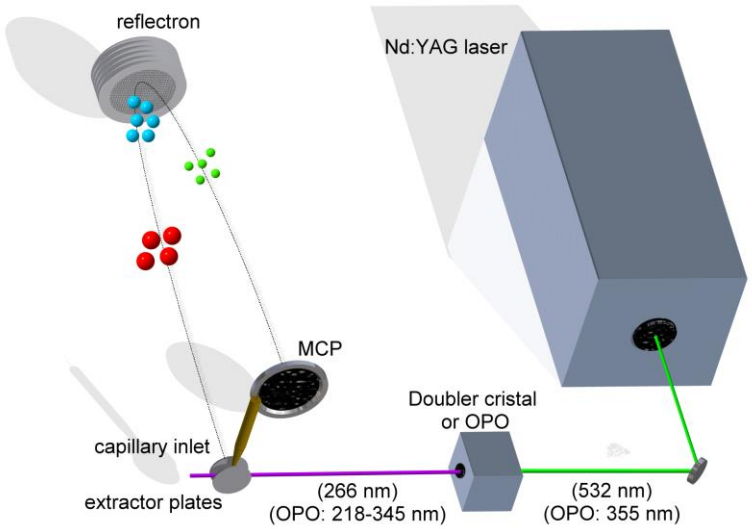


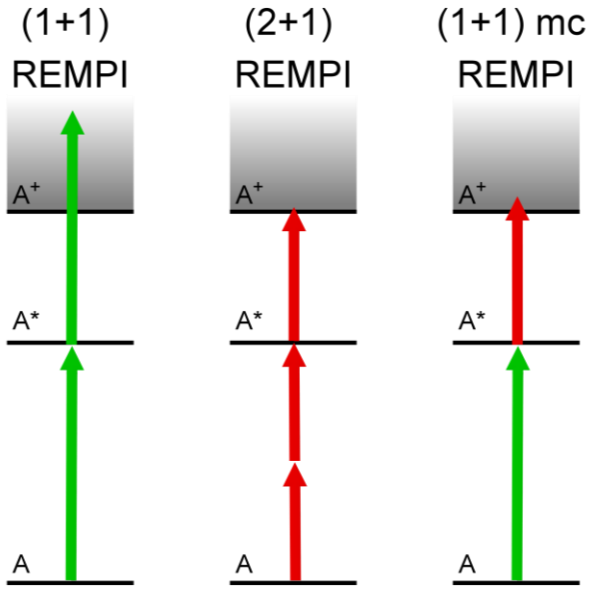
SPI-MS setup with EBEL VUV – Light Source

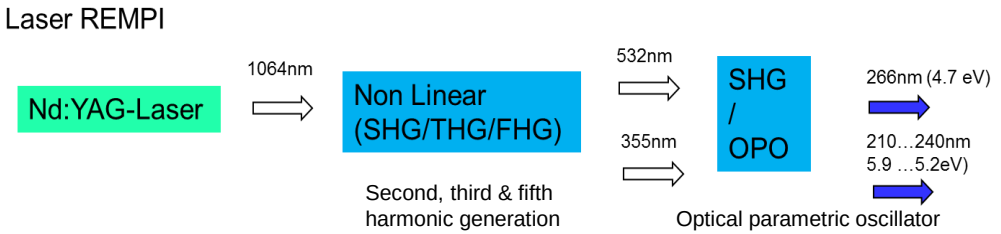
Introduction:
Photo ionization - REMPI

Resonance-Enhanced Multiphoton Ionization (REMPI)

- ionization by UV laser pulses (210-270 nm, ~10^7 W/cm²)
- highly efficient soft two-photon ionization of aromatics
- ppb/ppt on-line concentration range

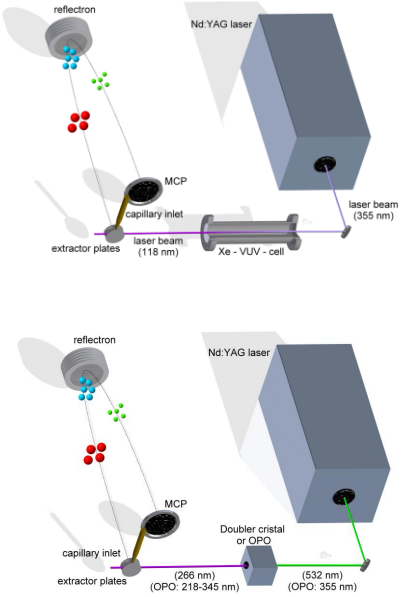




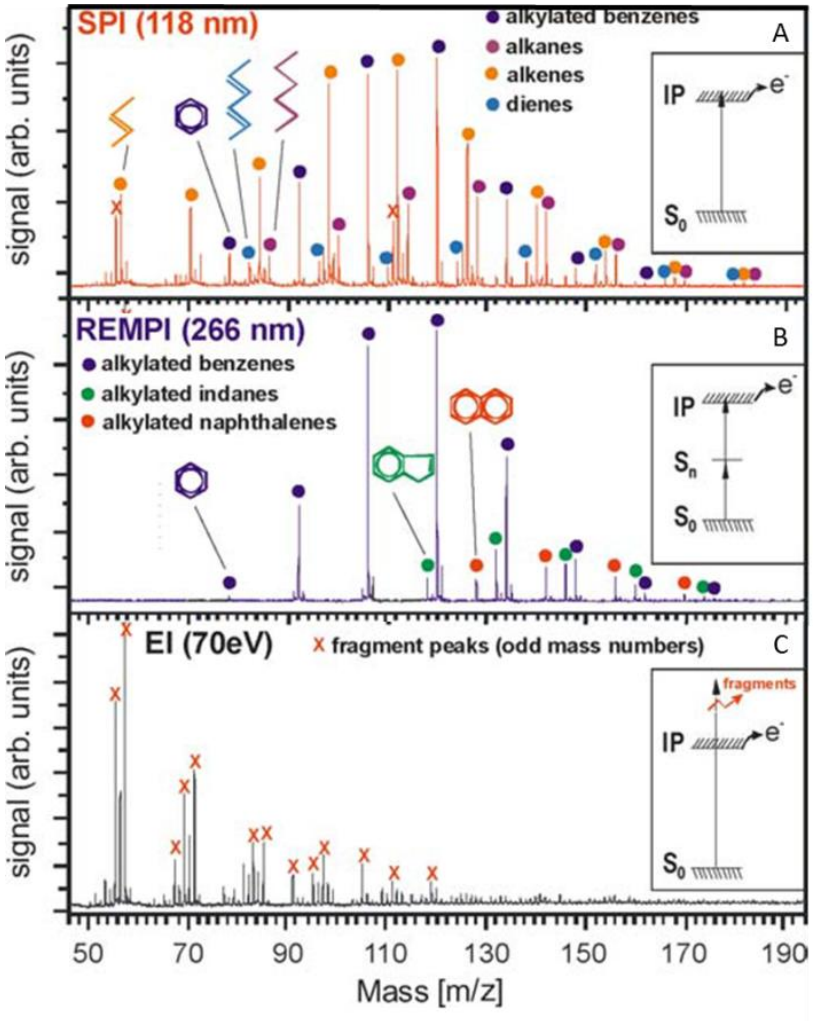


Introduction:

Photo ionization - SPI and REMPI



Mass spectra of Diesel



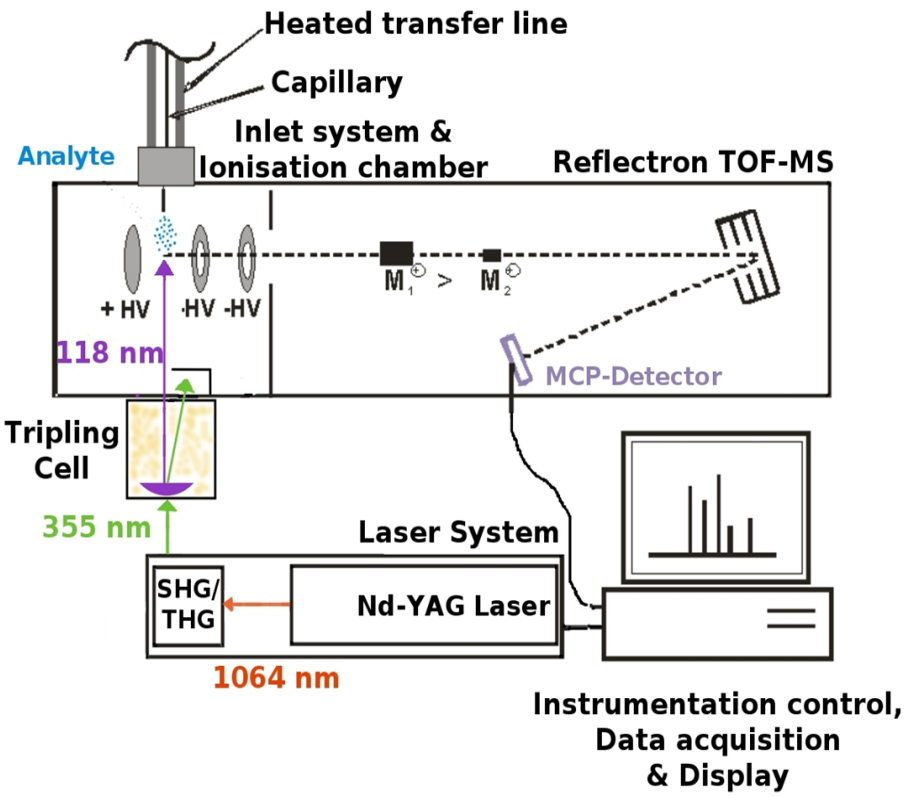
fragment-free/less overview

especially selective for aromatic compounds

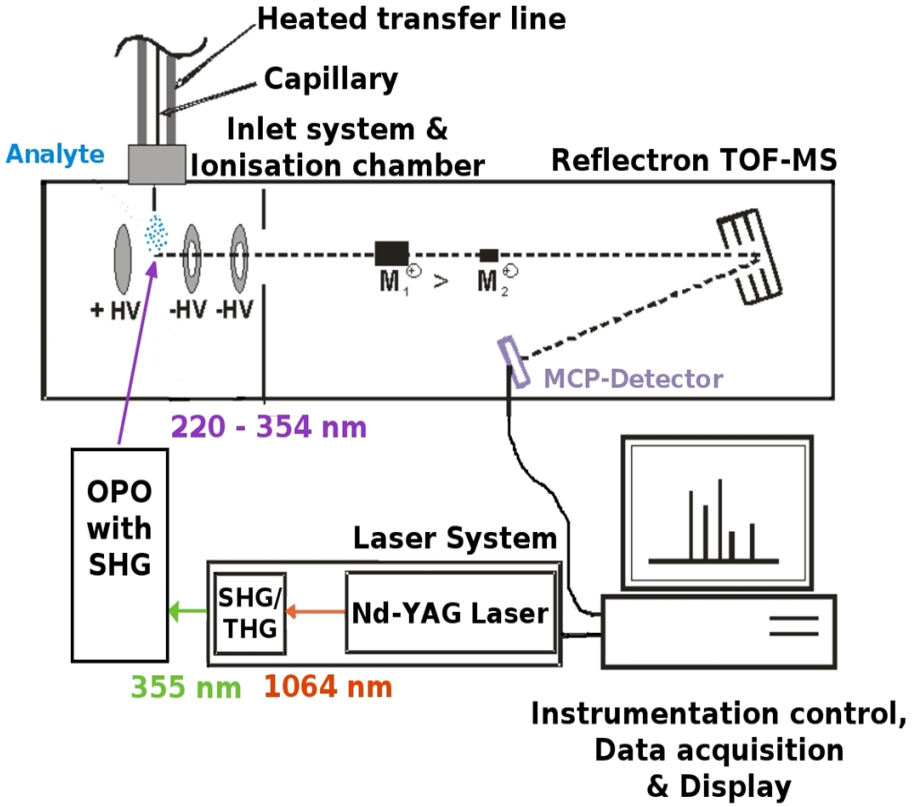
heavy fragmentation

Laser Setup

SPI-Setup



REMPI-Setup



Products & Applications

LM2X-PHOTO-TOF-MS

SMOKE ANALYZER

Lamp VUV SPI Source

TG-PIMS

THERMOGRAVIMETRY- PHOTOIONIZATION MS

Lamp VUV SPI Source

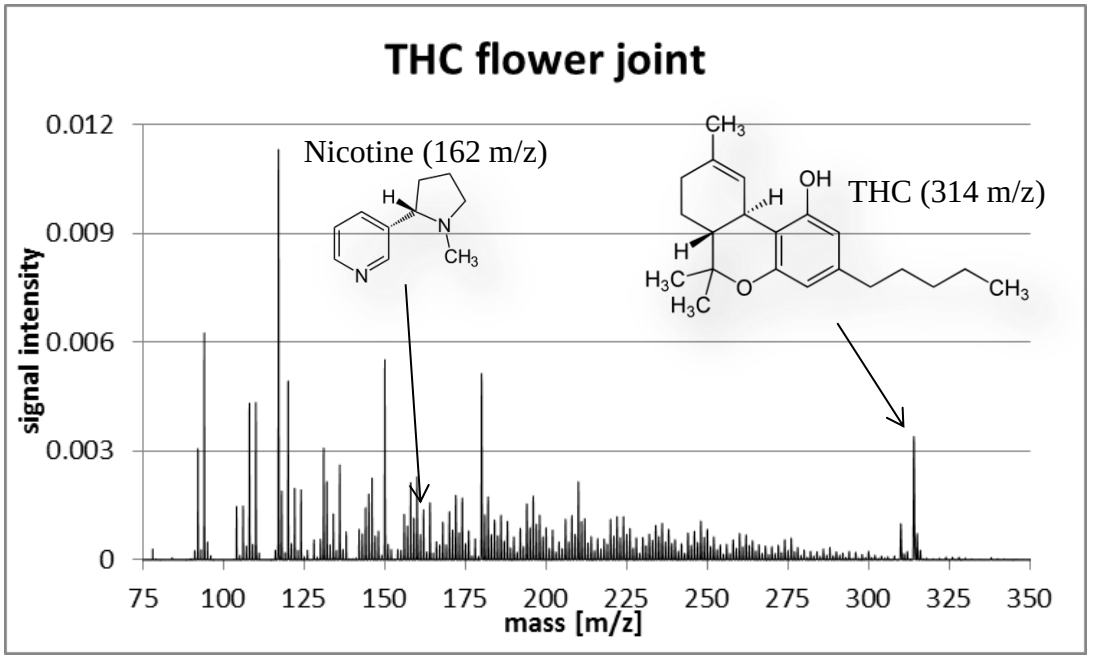
PHOTO-TOF-MS

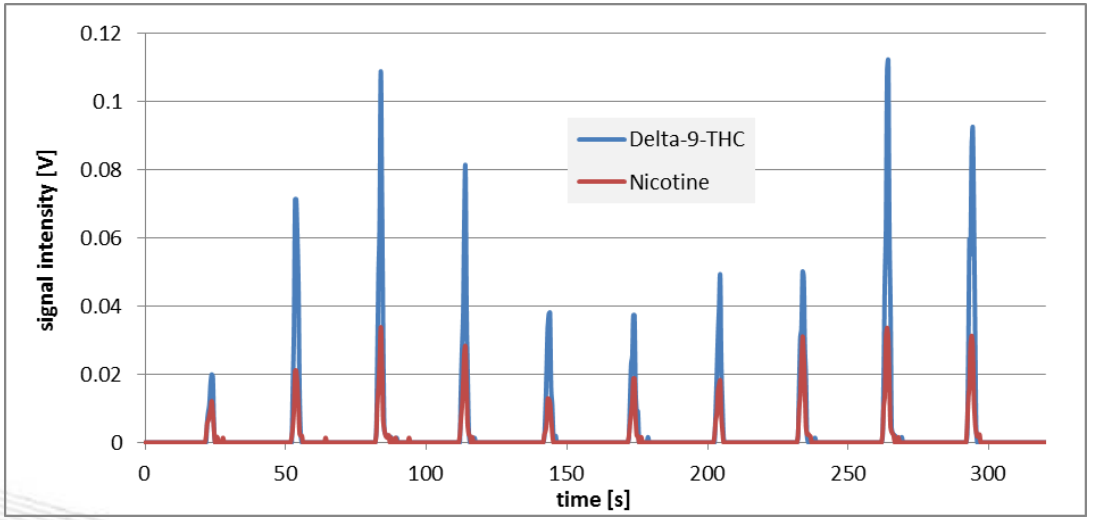
CUSTOMIZED GAS ANALYZER

Lamp or Laser VUV SPI

fixed or tuneable Laser REMPI

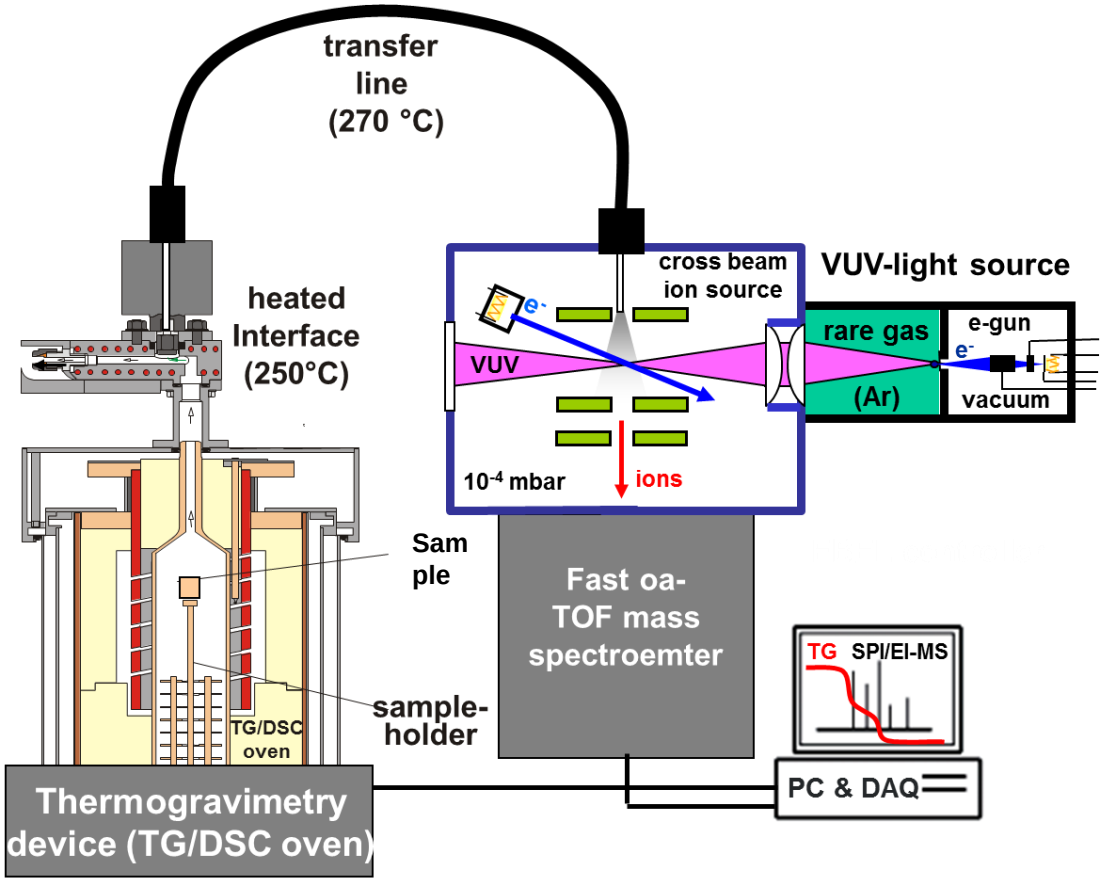
Application: Tobacco & Marihuana





Applications

Thermogravimetry–PIMS device

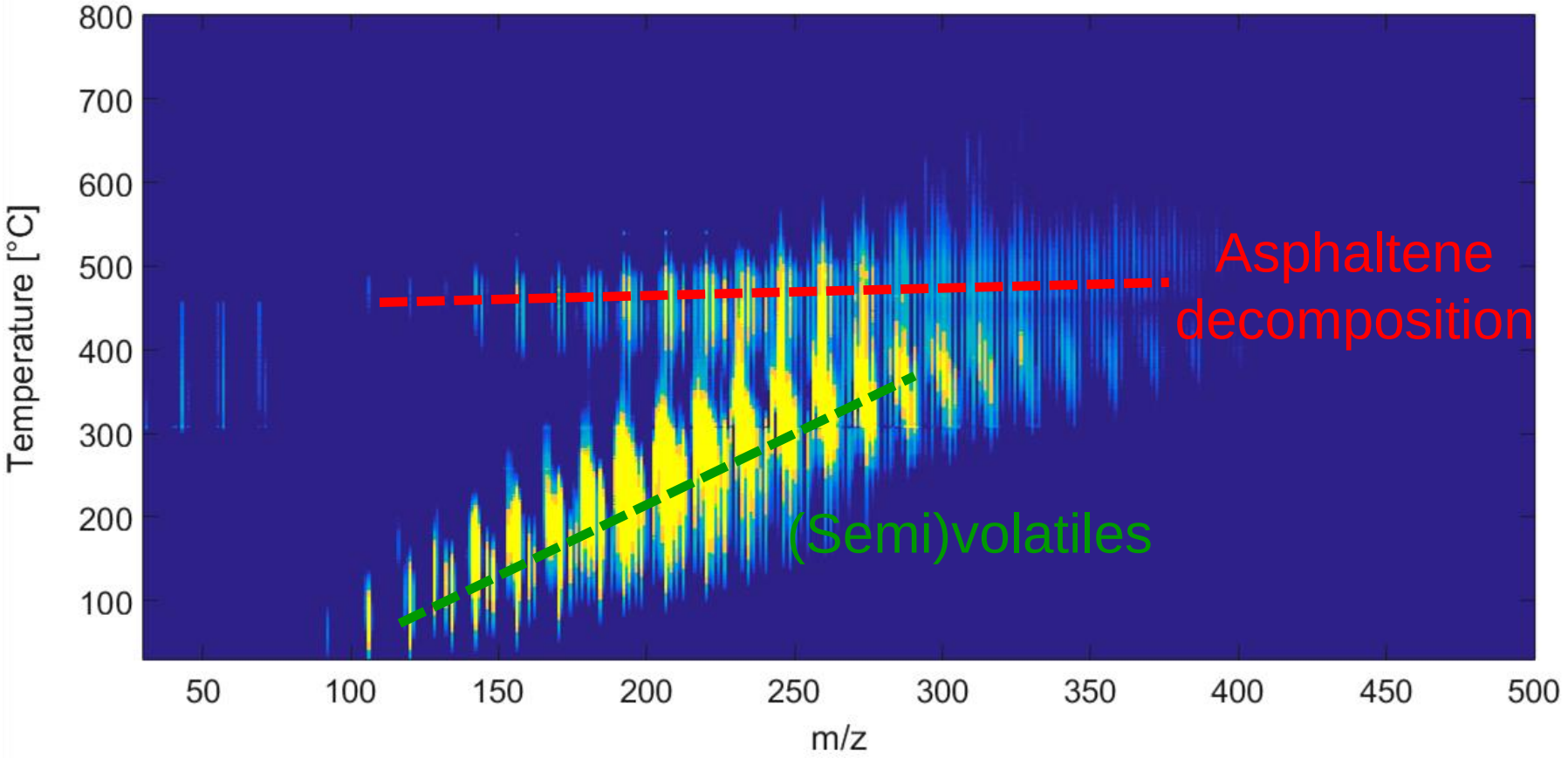


Applications

Thermogravimetry–PIMS device

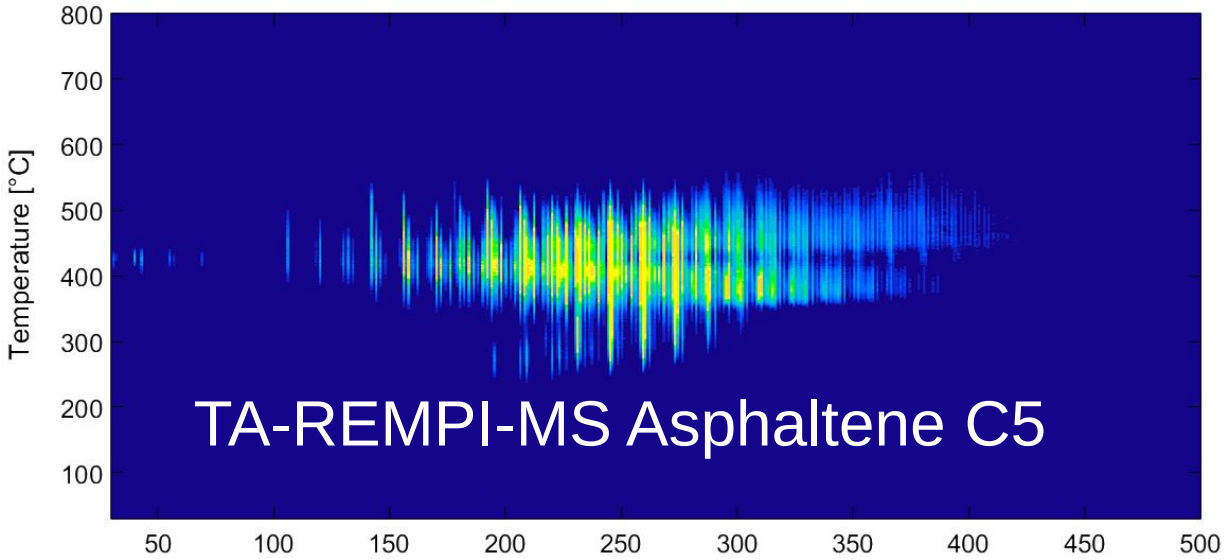
Applications

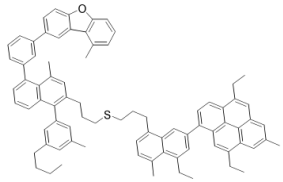
Analysis of oil (R820 crude oil):
Thermogravimetry–PIMS device

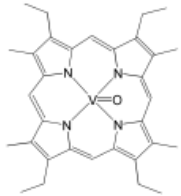


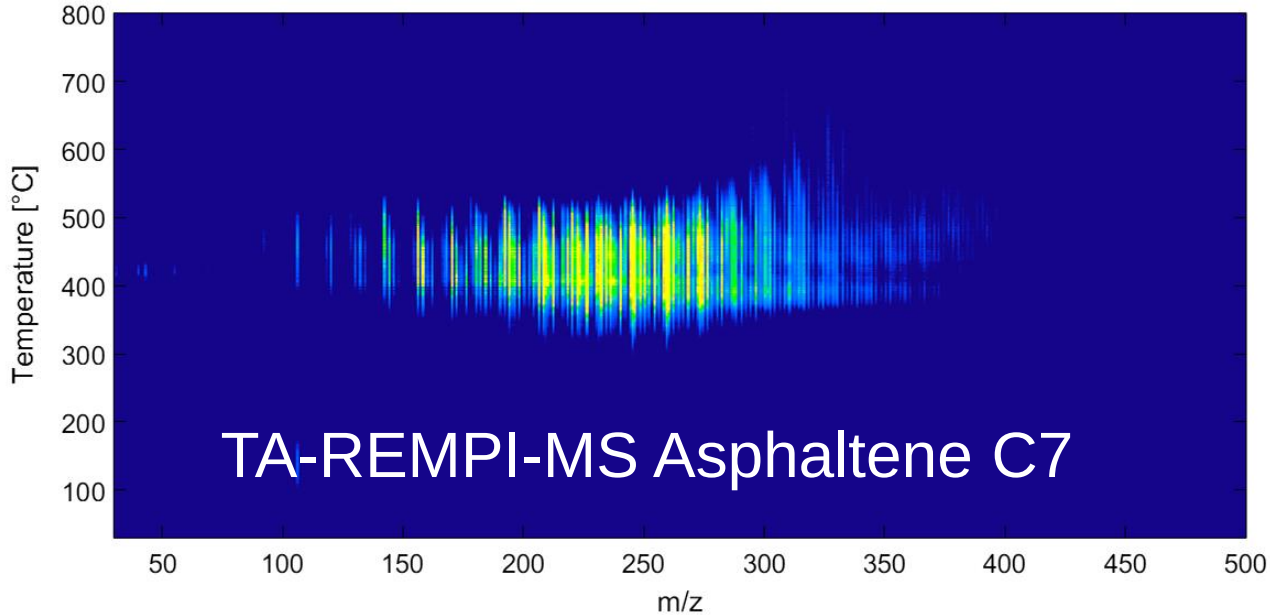
Applications

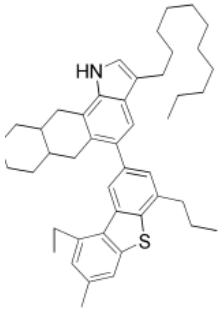
Analysis of Asphaltene (C5/C7)





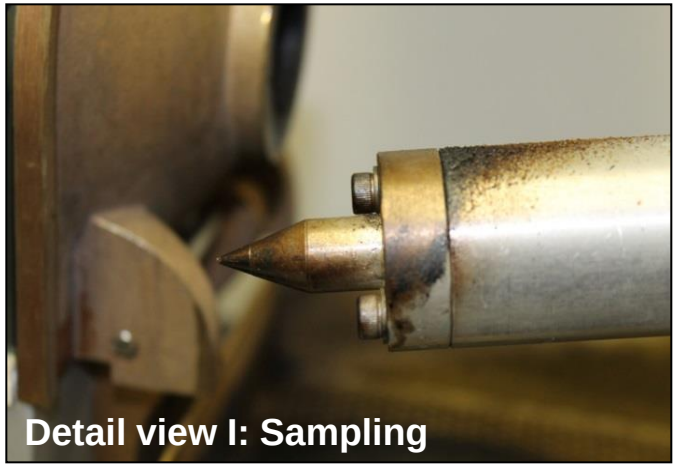






Applications

Experimental setup for roasting test at University of Rostock


Detail view I: Sampling

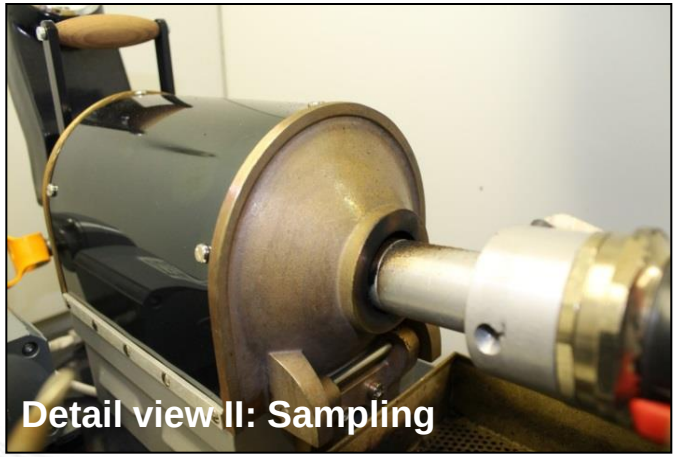

Detail view II: Sampling

PHOTO-**TOF-MS**

CUSTOMIZED GAS ANALYZER

Applications

photonion

Experimental setup for roasting test at University of Rostock

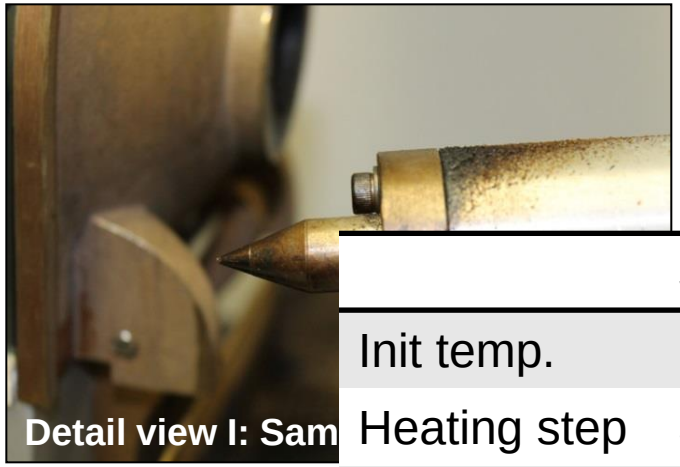
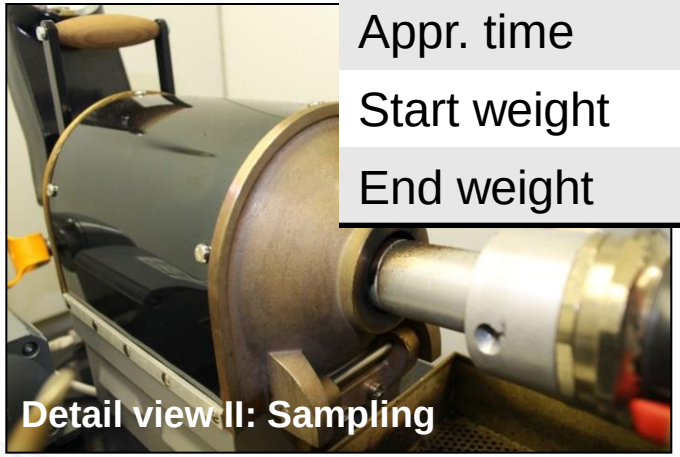


PHOTO-**TOF-MS**

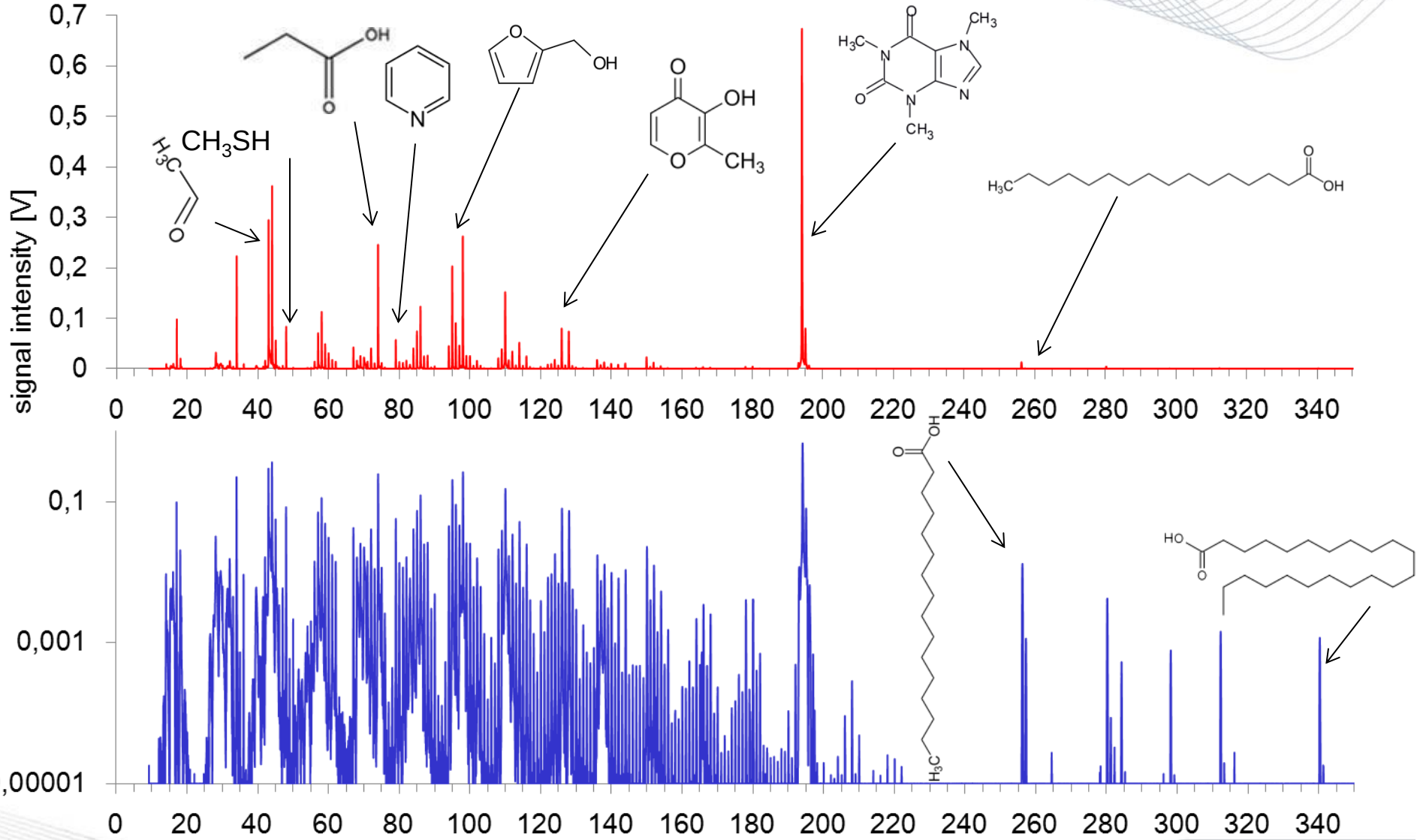
CUSTOMIZED GAS ANALYZER

	Slow	Normal	Fast
Init temp.	200°C	200°C	200°C
Heating step	3,5	4	6
Appr. time	20 min	11 min	6 min
Start weight	100 g	100 g	100 g
End weight	66-73 g	71-75 g	70-78 g



Applications

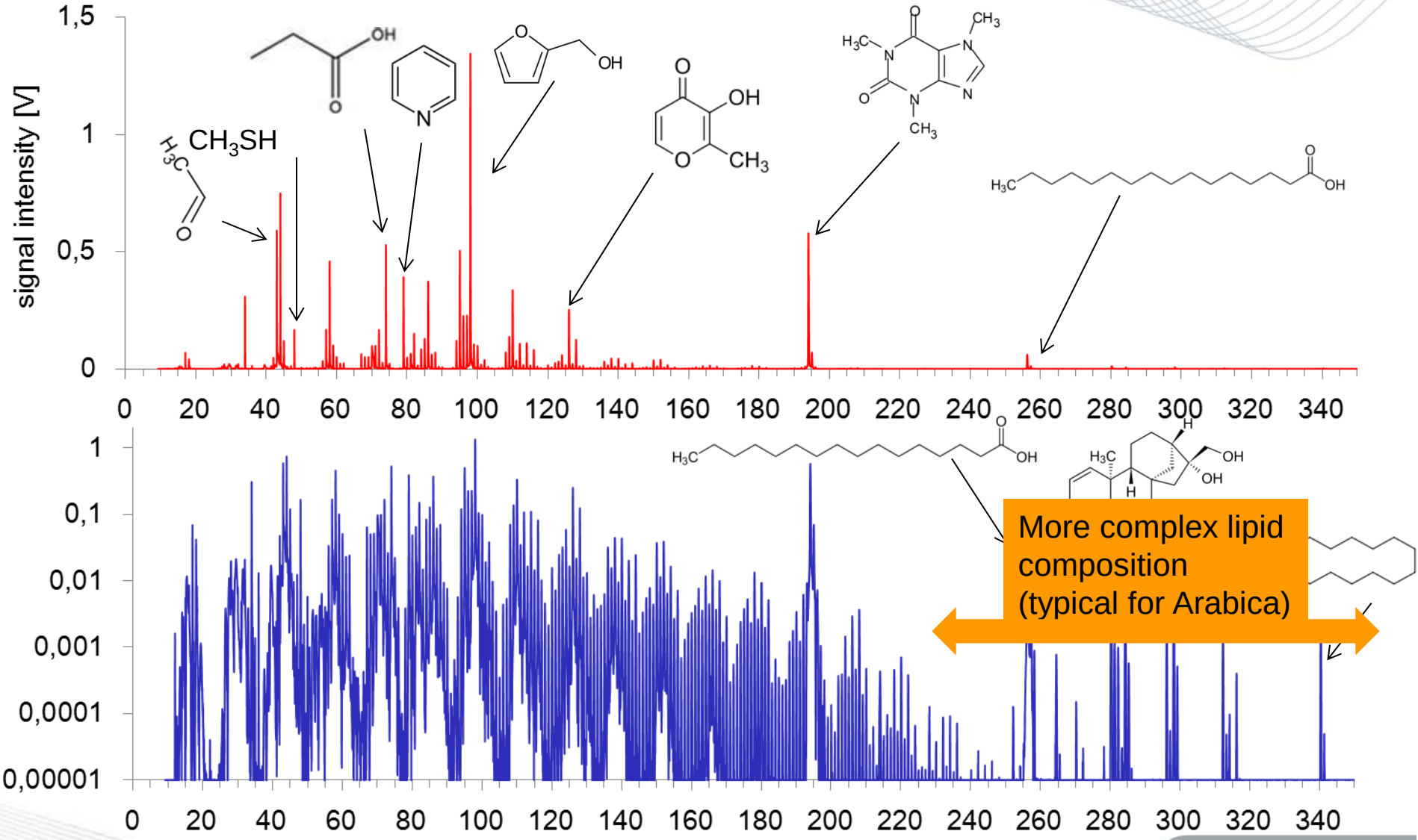
SPI mass spectrum of Robusta coffee roast gas (lin. & log scale)



molecular mass m/z

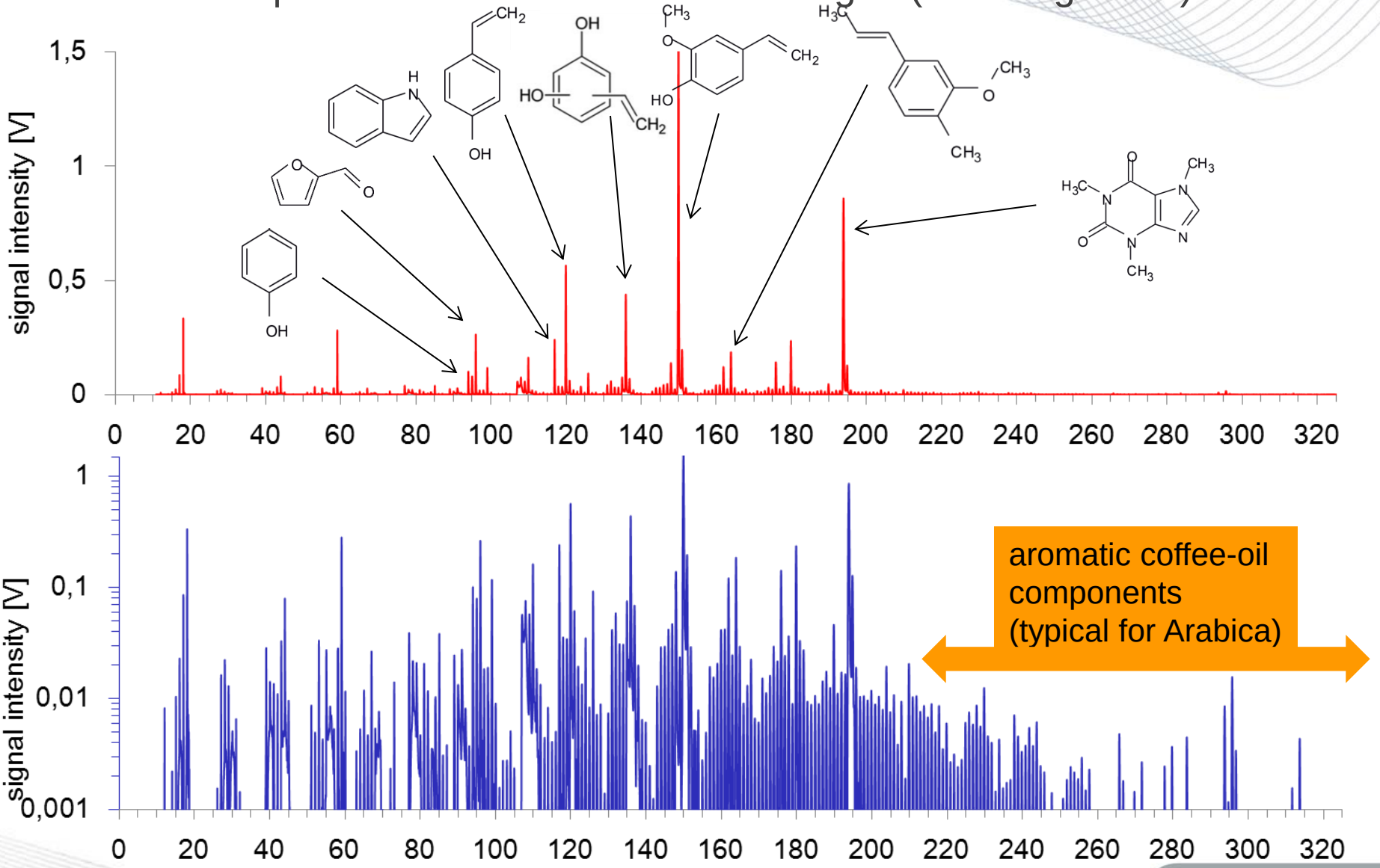
Applications

SPI mass spectrum of Arabica coffee roast gas (lin. & log scale)



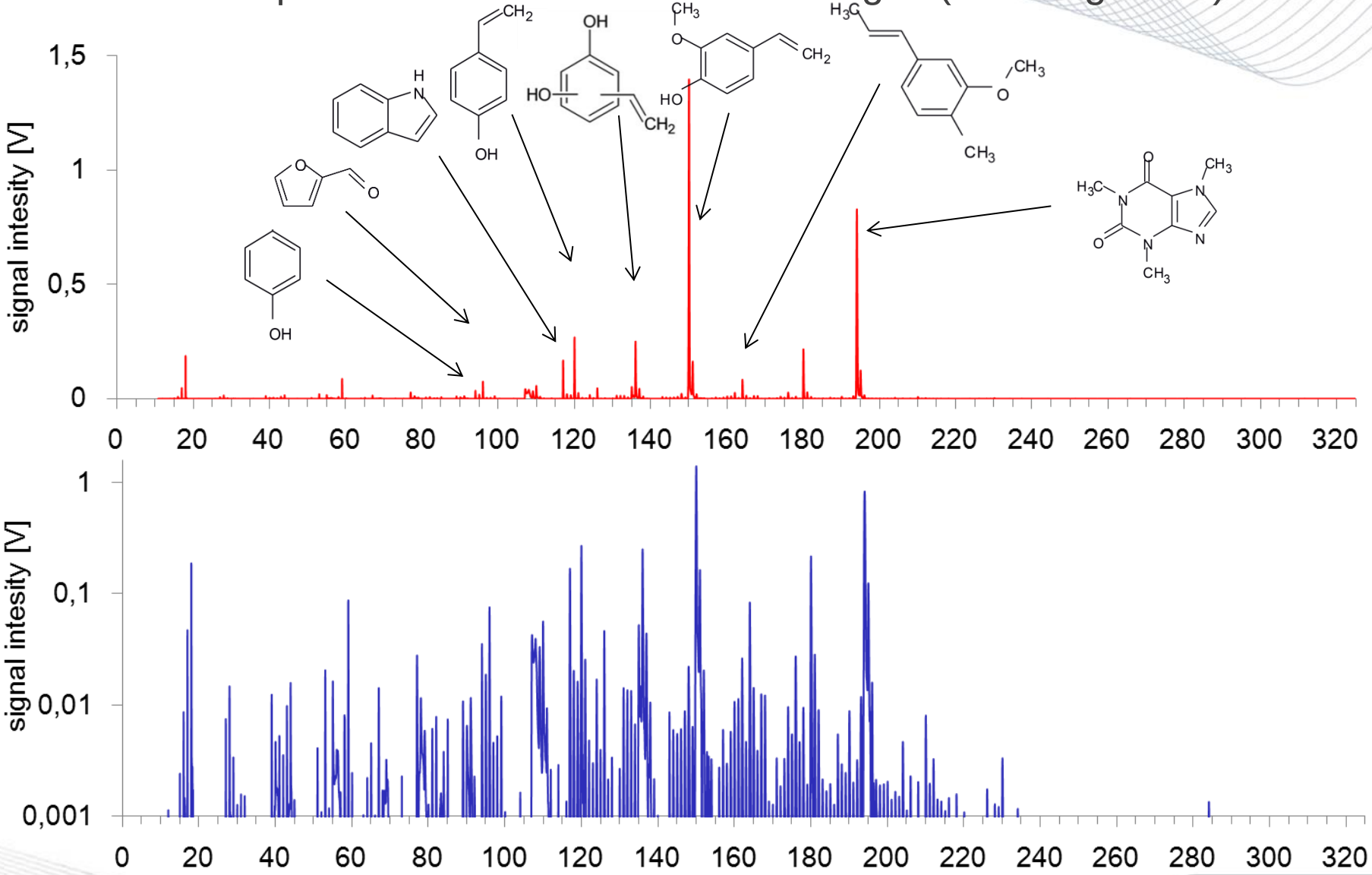
Applications

REMPI mass spectrum of Arabica coffee roast gas (lin. & log scale)



Applications

REMPI mass spectrum of Robusta coffee roast gas (lin. & log scale)



Further Application

- **Analysis of environmental gases and aerosol particle**
  Online Laser Desorption-Multiphoton Postionization Mass Spectrometry of Individual Aerosol Particles; Anal. Chem., 2008, 80 (23), pp 8991–9004
  Hyphenation of a EC / OC thermal–optical carbon analyzer to photo-ionization time-of-flight mass spectrometry: an off-line aerosol mass spectrometric approach for characterization of primary and secondary particulate matter; Atmos. Meas. Tech., 8, 3337-3353, 2015

- **Engine emission (ship diesel, car engine…)**
  Gas phase carbonyl compounds in ship emissions: Differences between diesel fuel and heavy fuel oil operation Original Research Article; Atmospheric Environment, Volume 94, September 2014, Pages 467-478
  Real-time analysis of aromatics in combustion engine exhaust by resonance-enhanced multiphoton ionisation time-of-flight mass spectrometry (REMPI-TOF-MS); Analytical and Bioanalytical Chemistry July 2012, Volume 404, Issue 1, pp 273–276

- **Pyrolysis Experiments (e.g. wood combustion…)**
  Online Analysis of Biomass Pyrolysis Tar by Photoionization Mass Spectrometry; Energy & Fuels 2016 30 (3), 1555-1563
  On-Line Process Analysis of Biomass Flash Pyrolysis Gases Enabled by Soft Photoionization Mass Spectrometry; Energy Fuels, 2012, 26 (1), pp 701–711

PHOTO-**TOF-MS**
CUSTOMIZED GAS ANALYZER

TG-PIMS
THERMOGRAVIMETRY- PHOTOIONIZATION MS

LM2X-PHOTO-**TOF-MS**
SMOKE ANALYZER

Thank you for your attention!

More Info: www.photonion.de

PHOTO-**TOF-MS**
CUSTOMIZED GAS ANALYZER

TG-PIMS
THERMOGRAVIMETRY- PHOTOIONIZATION MS

LM2X-PHOTO-**TOF-MS**
SMOKE ANALYZER

A4a: Not yet, but is a good idea.

A4b: Waters: the AP source has an extra holder in the source which can be used for dopants.

A4c: Dopant can be used to tune selectivity

Q5: Is Waters going to commercialize GC-APPI systems?

A5: It is still under investigation, but not in the near future.

Q6: Can APPI also be used to measure organic sulfur compounds (e.g. PAH with sulfur)?

A6a: Yes, it is very good for ionizing organic sulfur compounds. In general less polar compounds can be better ionized by APPI than by ESI.

A6b: Isobaric compounds can be separated by IMS

Q7: Is it possible to do quantitative work with synchrotron-PI or other vacuum PI?

A7a: Yes, the relative ionization efficiency has to be determined. Databases of photoionization cross sections are available.

A7b: An easy approach to obtain photoionization cross sections is to use a gas chromtography to separate many compounds with known concentrations and use PI-MS to detect.

Q8: Different PI sources were shown, is there a standard best source?

A8: There are less expensive sources (glow discharge) and more expensive ones (Laser SPI, REMPI). What source to choose depends on the application, e.g. what is the required detection limit in the application.

We made reference to asking questions using the app, but the first contributor from the audience commented that it is quicker to speak than type, so we decided not to use the app. Anyway for that size of audience it seemed not to make sense. We heard positive feedback from many attendees. We intend to distribute a pdf version of this report to the interest group members upon agreement of the speakers.
The planning process for next year's workshop is already in progress.

The briefing material is attached.

Eleanor and Ralf