Highly time-resolved two-dimensional mapping of the molecular combustion and pyrolysis product concentrations during a puff in a burning cigarette

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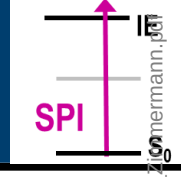
3 BAT Ltd.
Southampton, UK

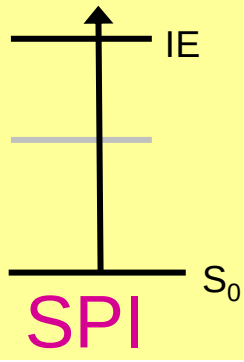
Introduction: Photo ionization - SPI and REMPI



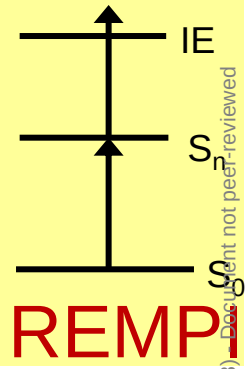
PIMS - Soft photo ionisation in vacuum (no fragmentation as in EI-M… …analysis

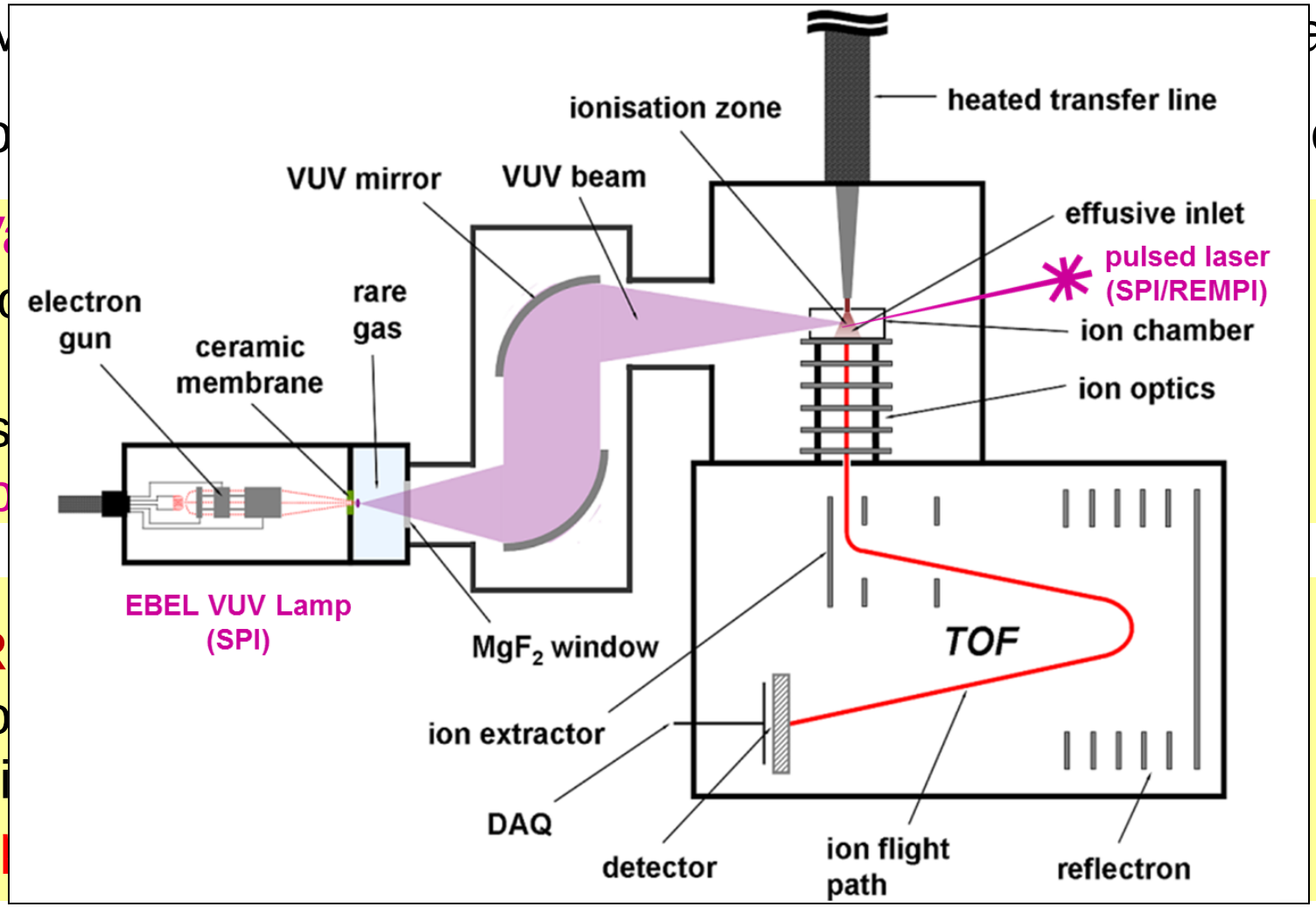
Two… …e applied:

a) V…
- i…
- s…
- p…



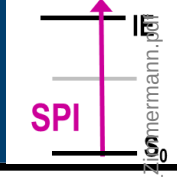
b) R…
- io…
- hi…
- pl…





➔ Mass analysis by time-of-flight (TOFMS), ion trap (ITMS) etc.

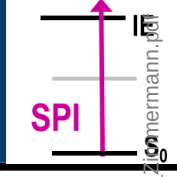
Introduction: Photo ionization - SPI and REMPI



Why using (vacuum-) photo ionization for fast on-line monitoring?

- + **soft ionization** (fragmentation-free ionization of many tobacco smoke chemicals and reduced fragmentation of labile compounds)
- + **SPI - universal ionization** (incl. alkanes), IE-threshold selectivity
- + **REMPI**: **selective** for **aromatic** compounds
- + two easily **switchable** laser PI techniques: REMPI & SPI (+EI)
- + **sensitive and fast**: ppb concent. in sub-second time resolution
- + no **matrix effects**: "physical ionization"

Introduction: Photo ionization - SPI and REMPI



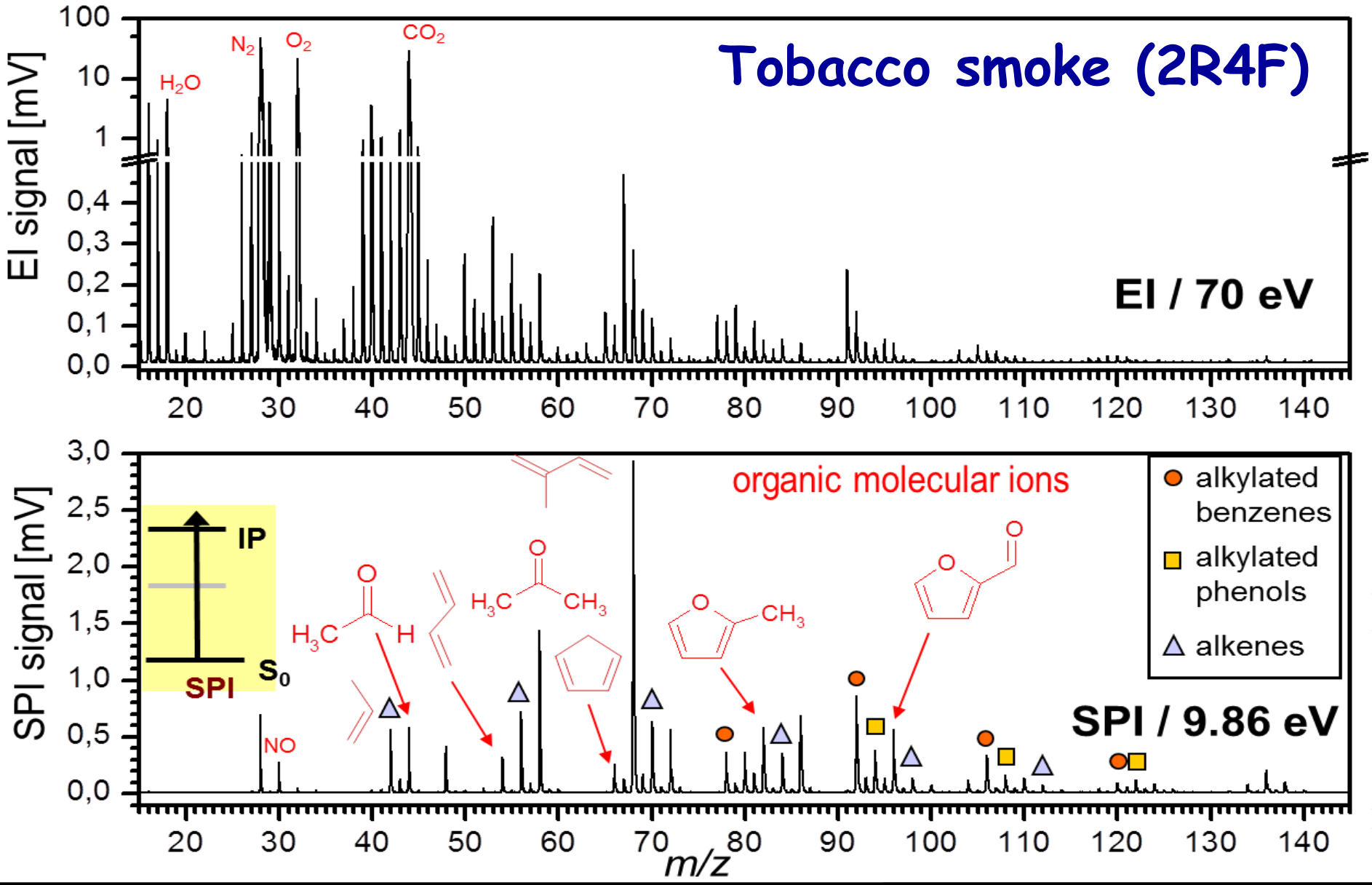
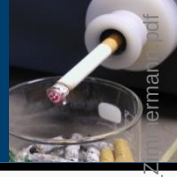
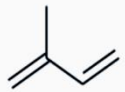


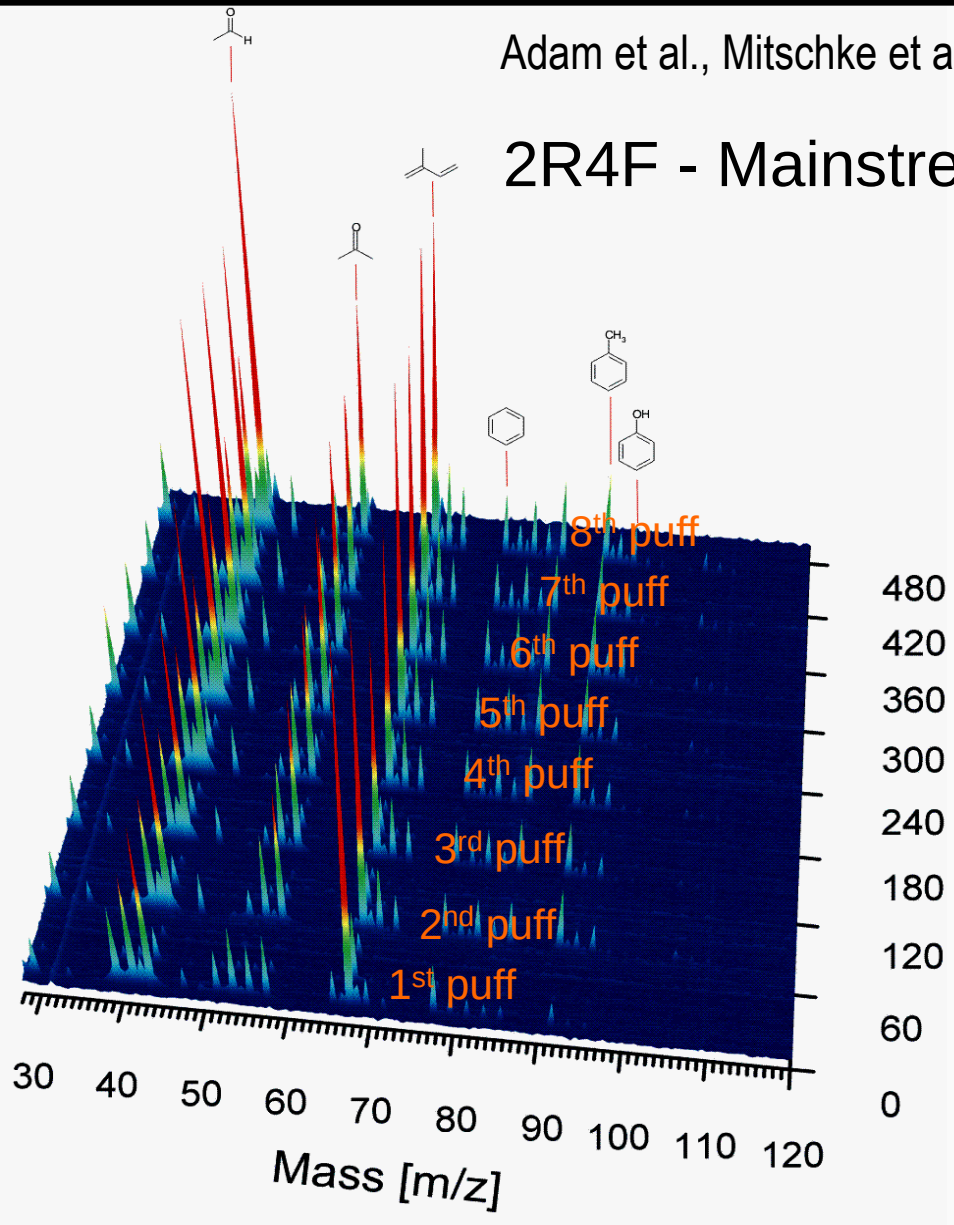
Photo ionization – mass spectrometry: On-line tobacco smoke analysis



Adam et al., Mitschke et al., Streibel et al.



2R4F - Mainstream



2R4F - Sidestream

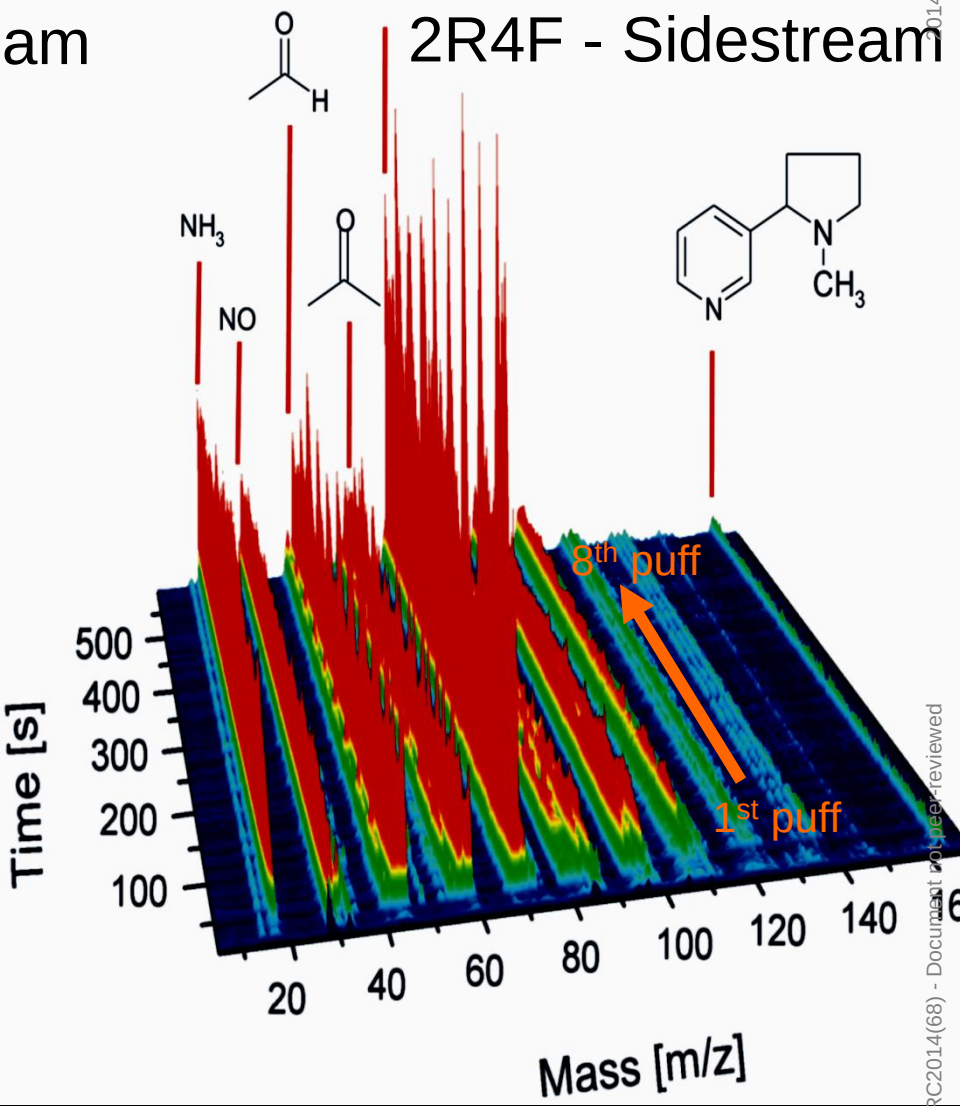
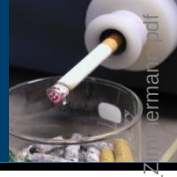


Photo ionization – mass spectrometry: On-line tobacco smoke analysis



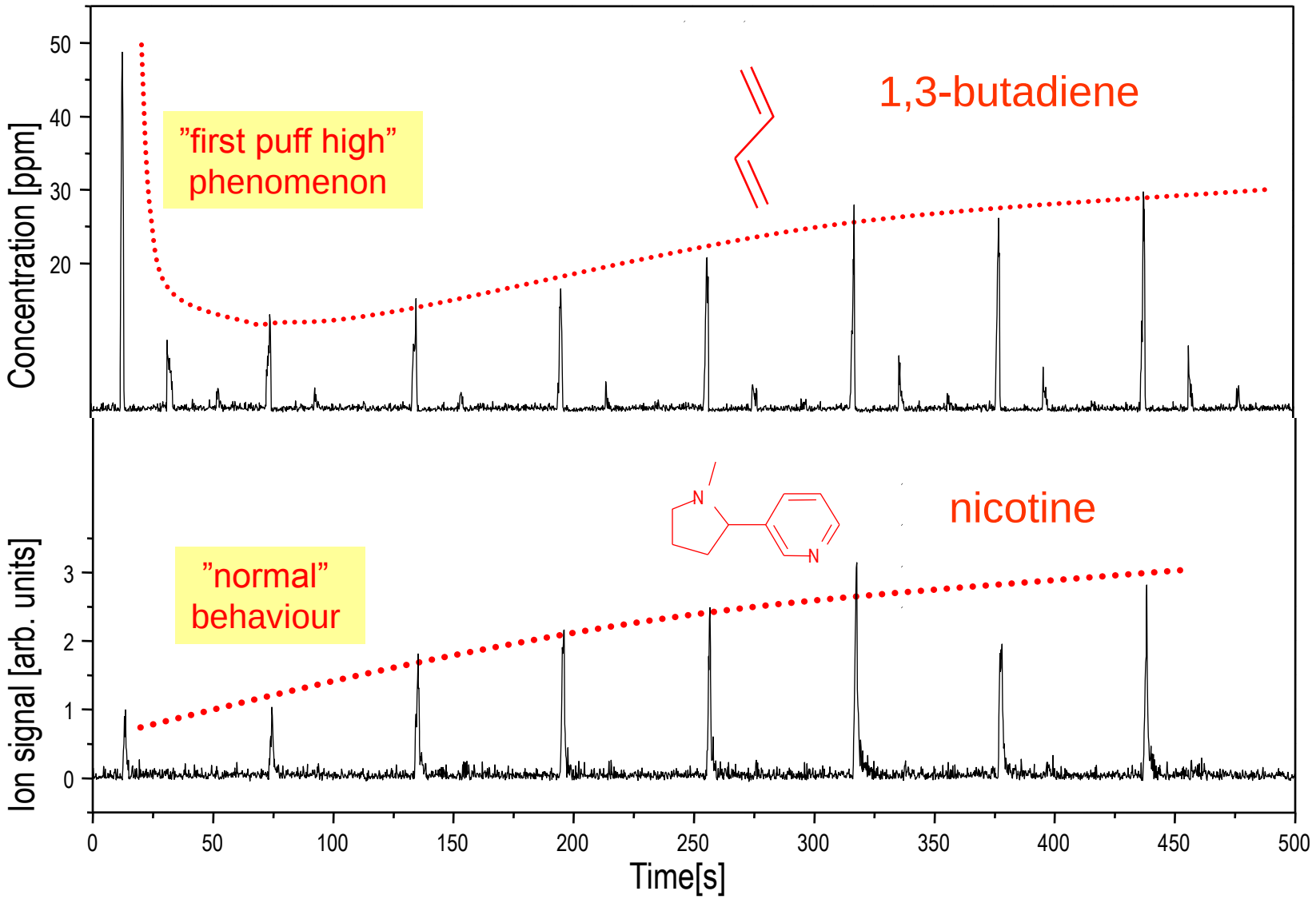


Photo ionization – mass spectrometry: On-line tobacco smoke analysis

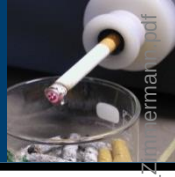


Photo ionization MS smoke profiler for Industrial applications (Borgwaldt KC)

- **Integrated smoke machine – SPI-TOFMS system (programmable profiles: ISO, intense, human, e-cig.) for industrial routine & research**
- **Quantitative puff-resolved on-line analysis of tobacco smoke toxicants (e.g., isoprene, butadiene, benzene, acetaldehyde)**
- **Analysis of e-cigarette and heat-not-burn product smoke composition**

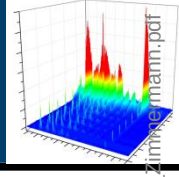
- Easy to use integrated system (smoke machine)
- Compact oa-TOFMS mass analyzer (R~900)
- Different VUV-lamps for SPI ion source
- EI ion source

Stand-alone photo ionization MS for flexible applications (Photonion GmbH)

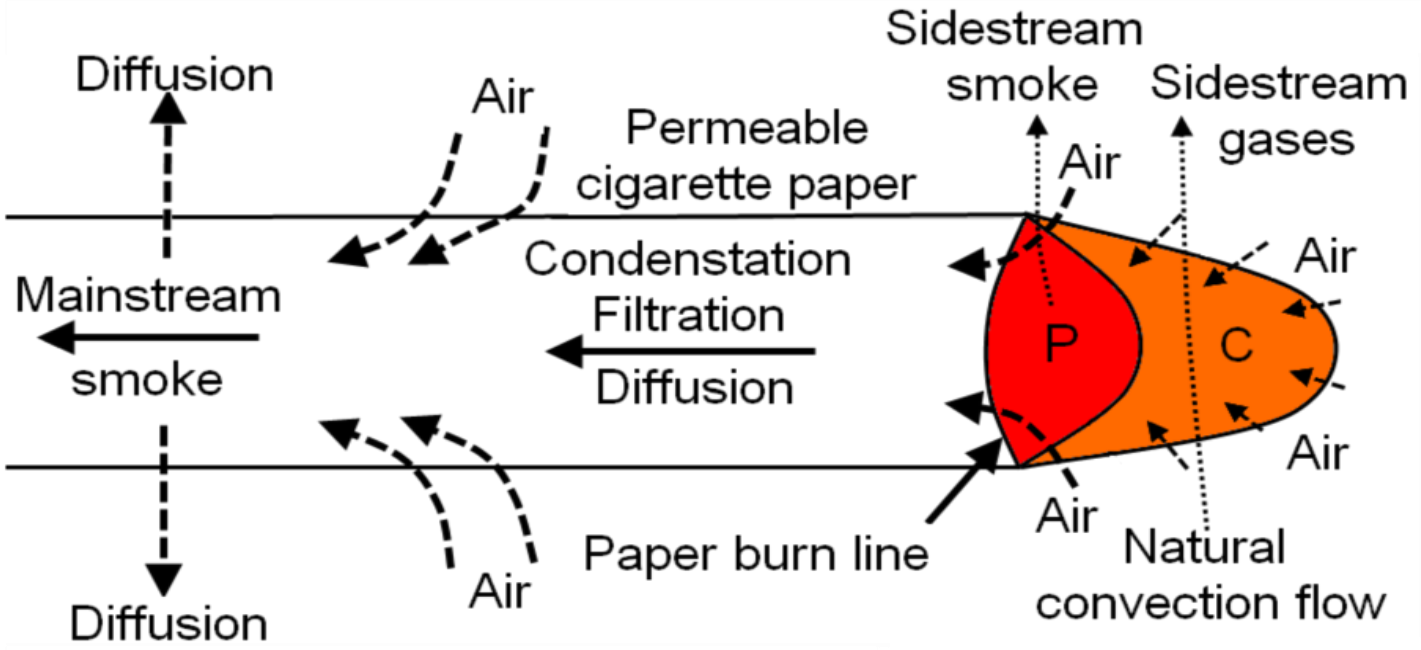
- **Flexible, ultra-high performance PI-TOFMS system for research and industrial process analysis**
- **System can be coupled to:**
  - **Thermal analysis,**
  - **µ-probe sampling device,**
  - **Smoking machine,**
  - **Human smoking analyzer (Gas/PM)**
  - **Smoke particle matter analyzer**
  - **Fast gas chromatography pre-separation (puff- resoved)**

- High flexibility and sensitivity
- Direct Reflectron TOF mass analyzer (R~2000)
- REMPI, laser-SPI and VUV lamp SPI source
- EI ion source and switchable ionization
- Multiple coupling options.

Application of PI-MS for analysis of pyrolysis & combustion products within the cigarette



- Research Cigarettes: Well defined model-system for solid state combustion
- Tobacco: Bio mass consisting mainly of Celluloses ("glucose-polymer") and Lignin ("phenolic-polymer") with alkaloid content(nicotine)
- Very reproducible "automated" machine smoking (ISO-testing): One bell-shaped puff (35 ml/2s) per minute



P = Pyrolysis/ Distillation zone

C = Combustion zone

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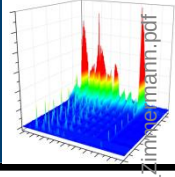

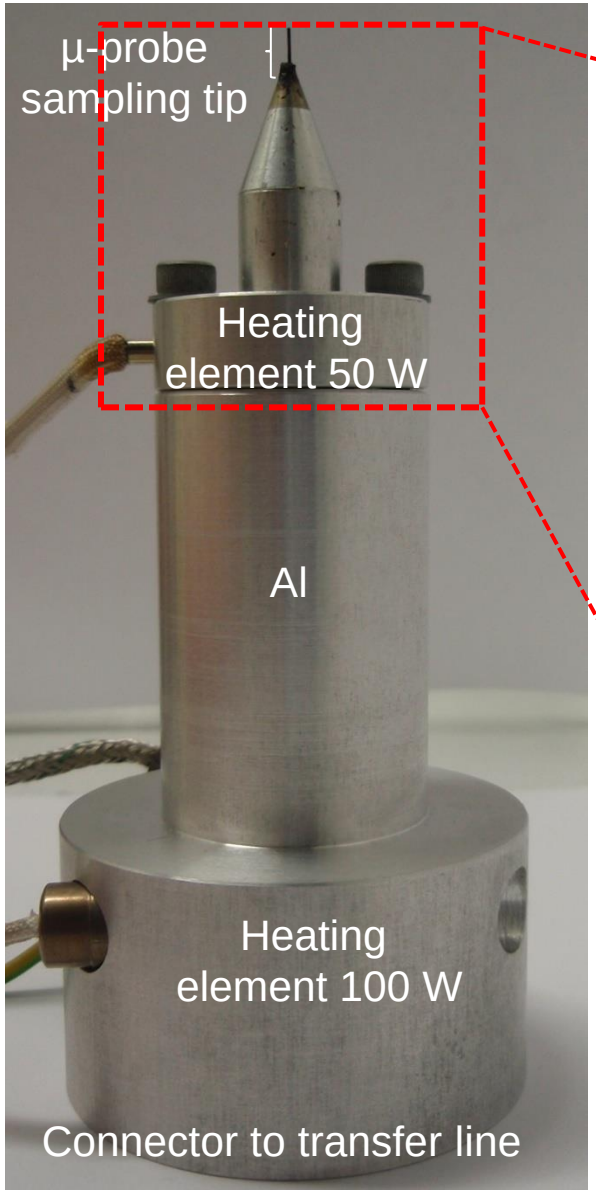

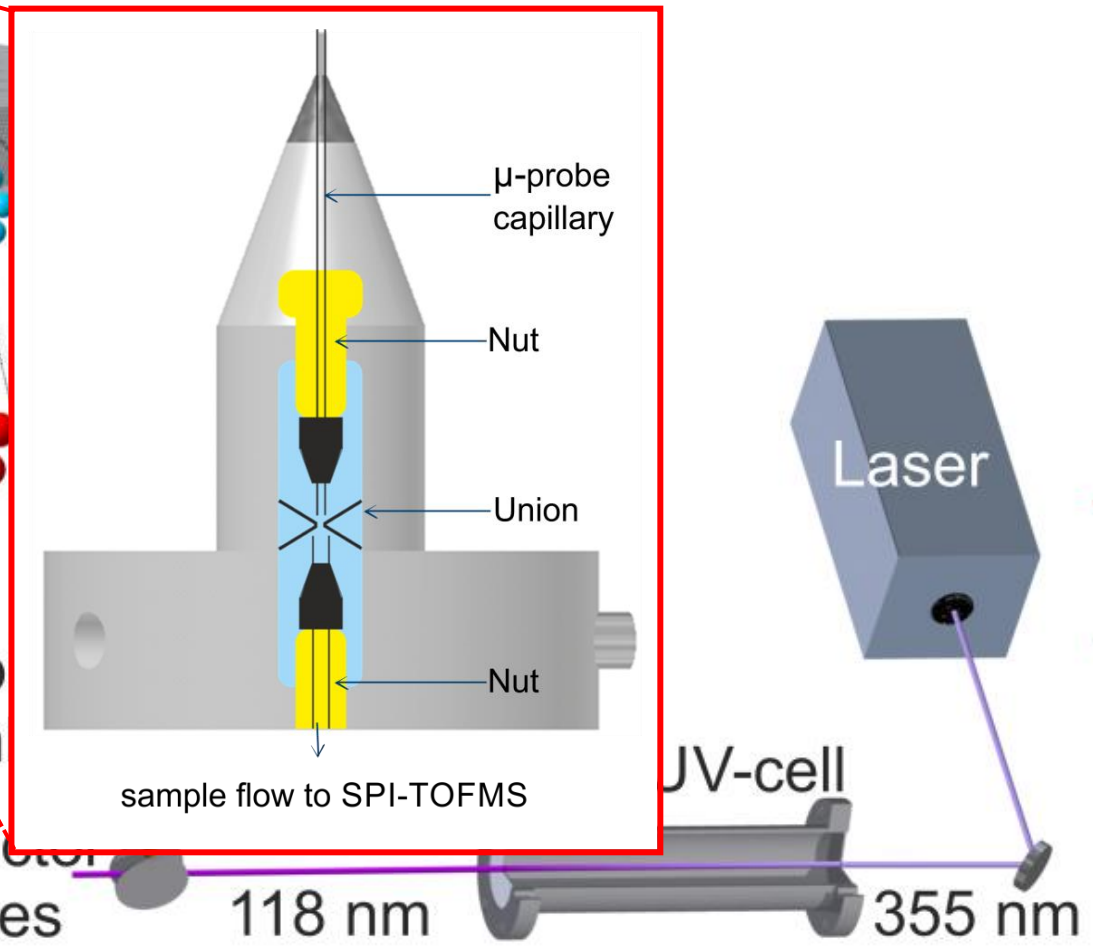

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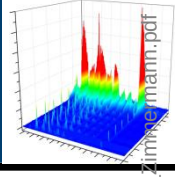

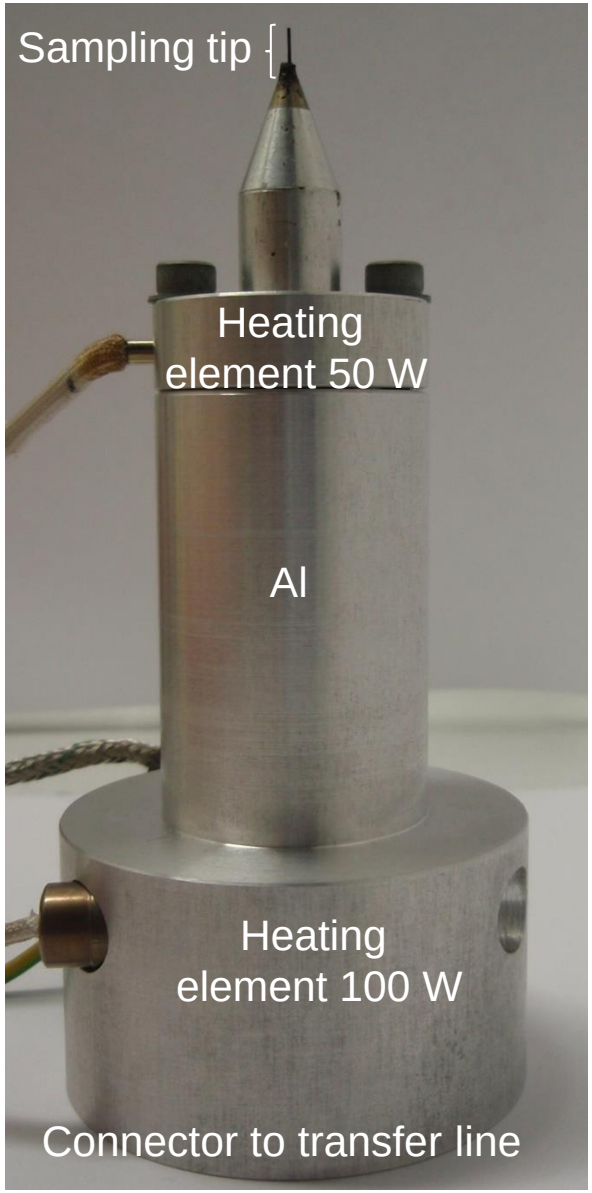

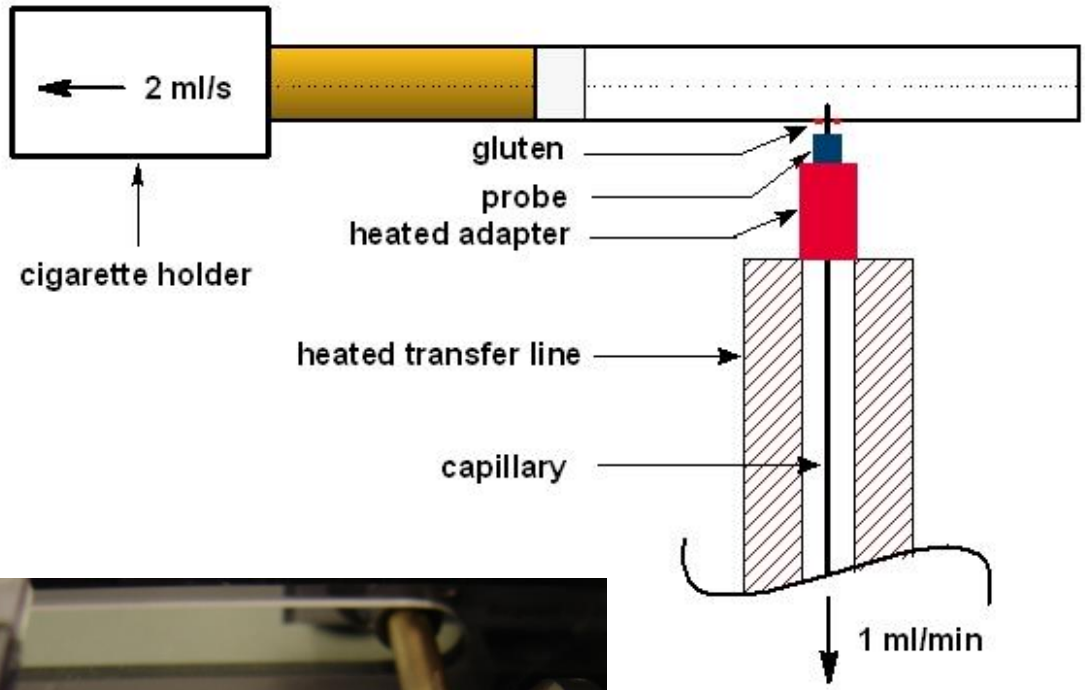

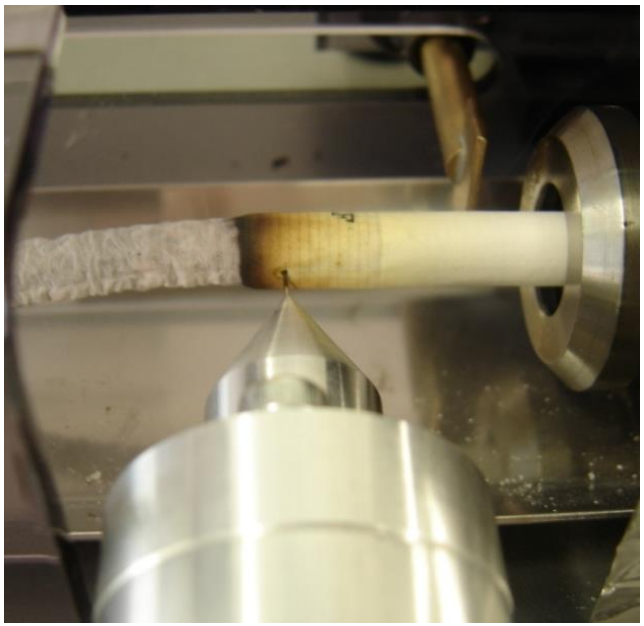

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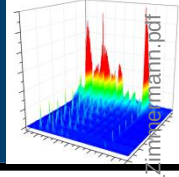
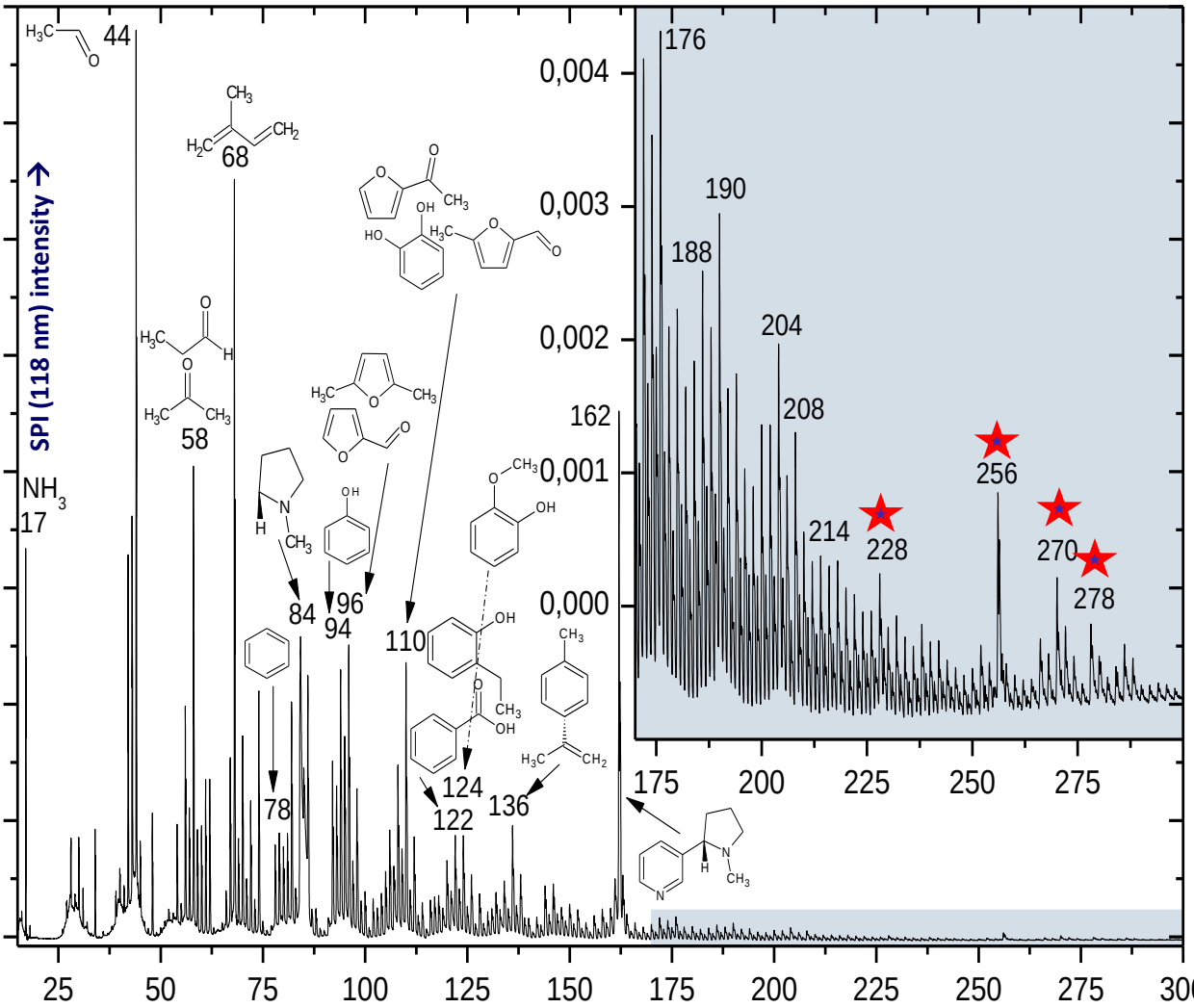


Rich pyrolysis/combustion product spectrum: Masses up to 300 m/z detectable

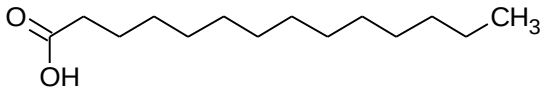


[R. Hertz et al. Anal. Chim. Acta, 2012 (714) 104-113]

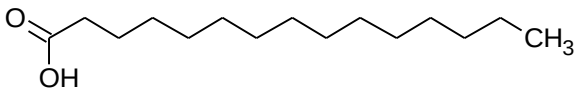
SPI: Universal ionization:

➔ For example: Higher molecular weight signature of fatty acids ★

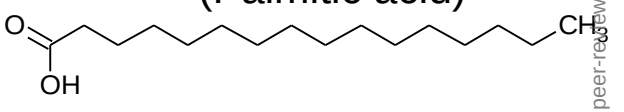
mass 228 Tetradecanoic acid



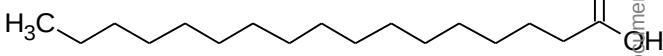
mass 242 Pentadecanoic acid



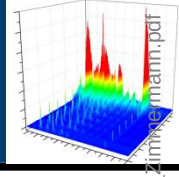
mass 256 Hexadecanoic acid (Palmitic acid)



mass 270 Heptadecanoic acid

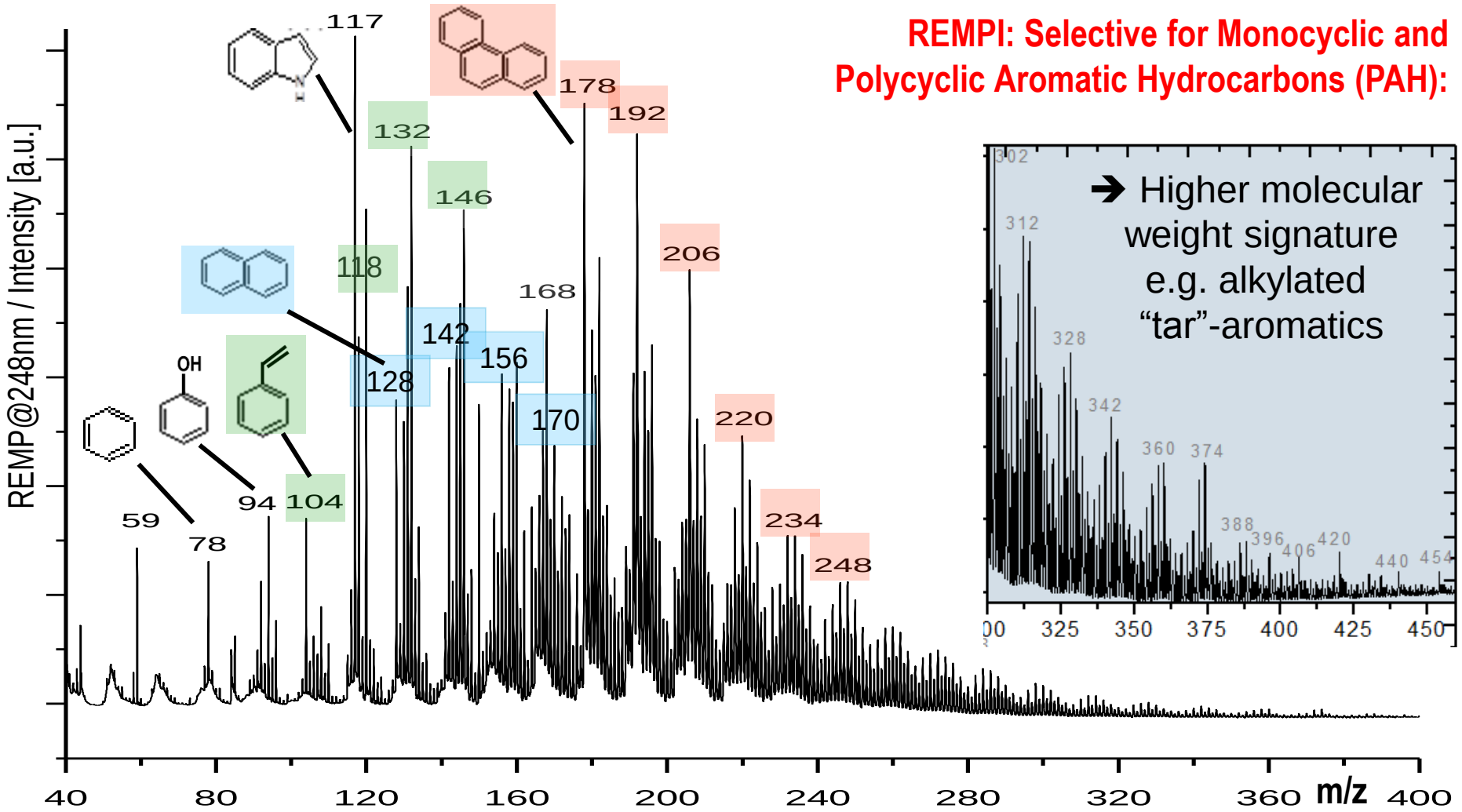


Application of PI-MS for analysis of pyrolysis & combustion products within the cigarette

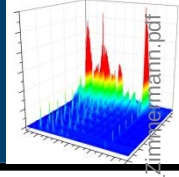


Rich pyrolysis/combustion product spectrum: Aromatics and Polycyclic Aromatic Hydrocarbons (PAH) with masses up to 500 m/z detectable

REMPI: Selective for Monocyclic and Polycyclic Aromatic Hydrocarbons (PAH):

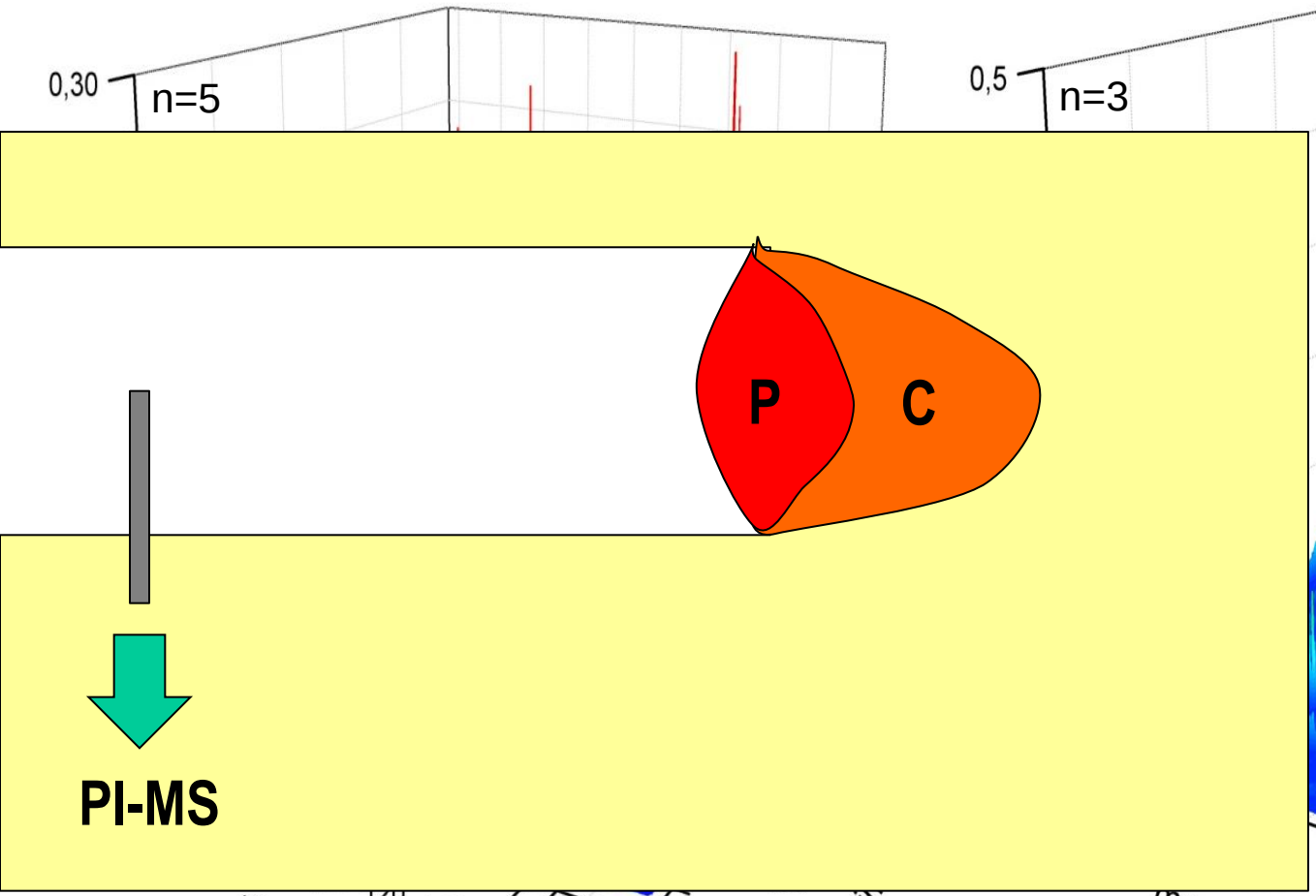


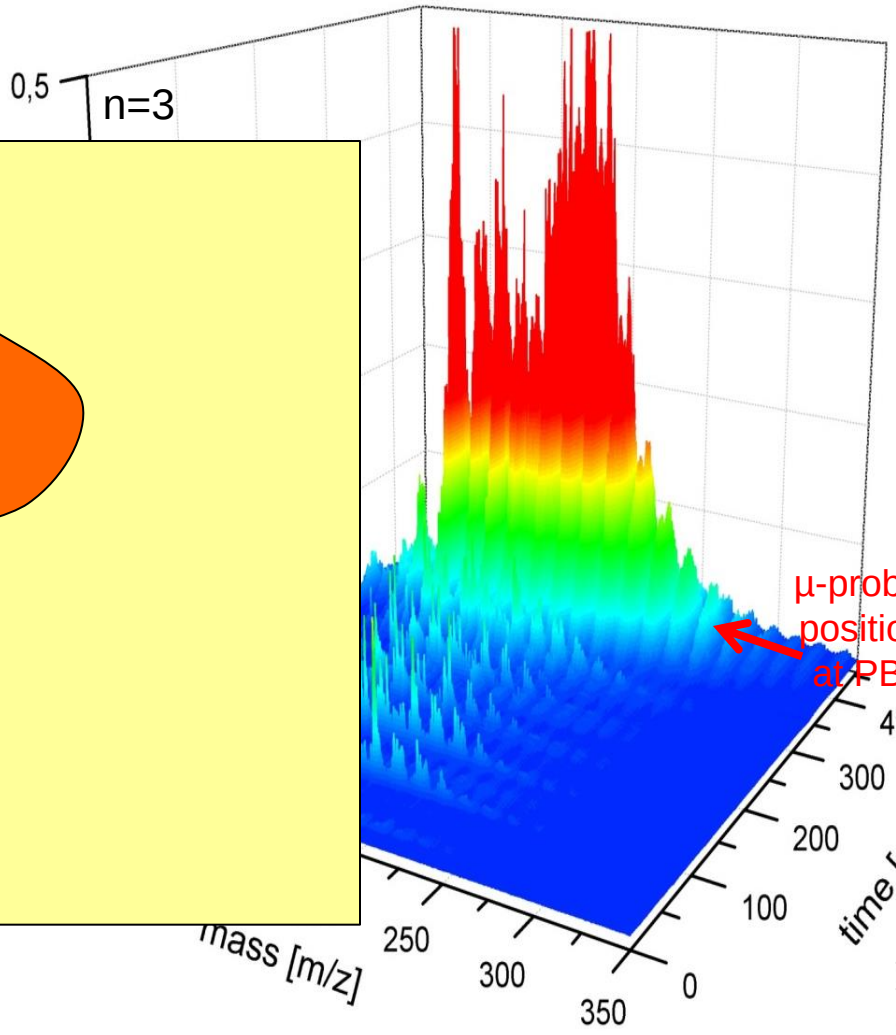
Application of PI-MS for analysis of pyrolysis & combustion products within the cigarette



SPI-TOFMS

REMPI-TOFMS





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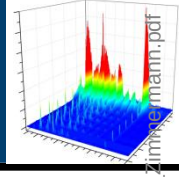
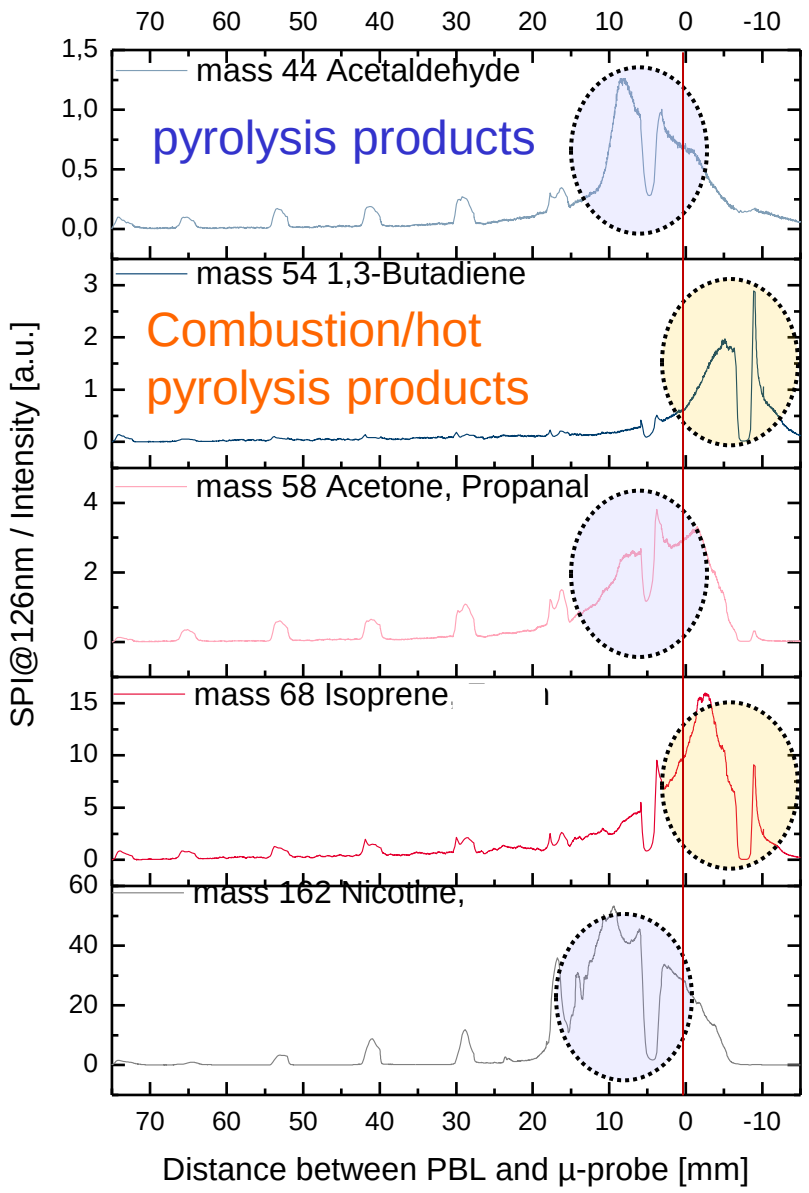
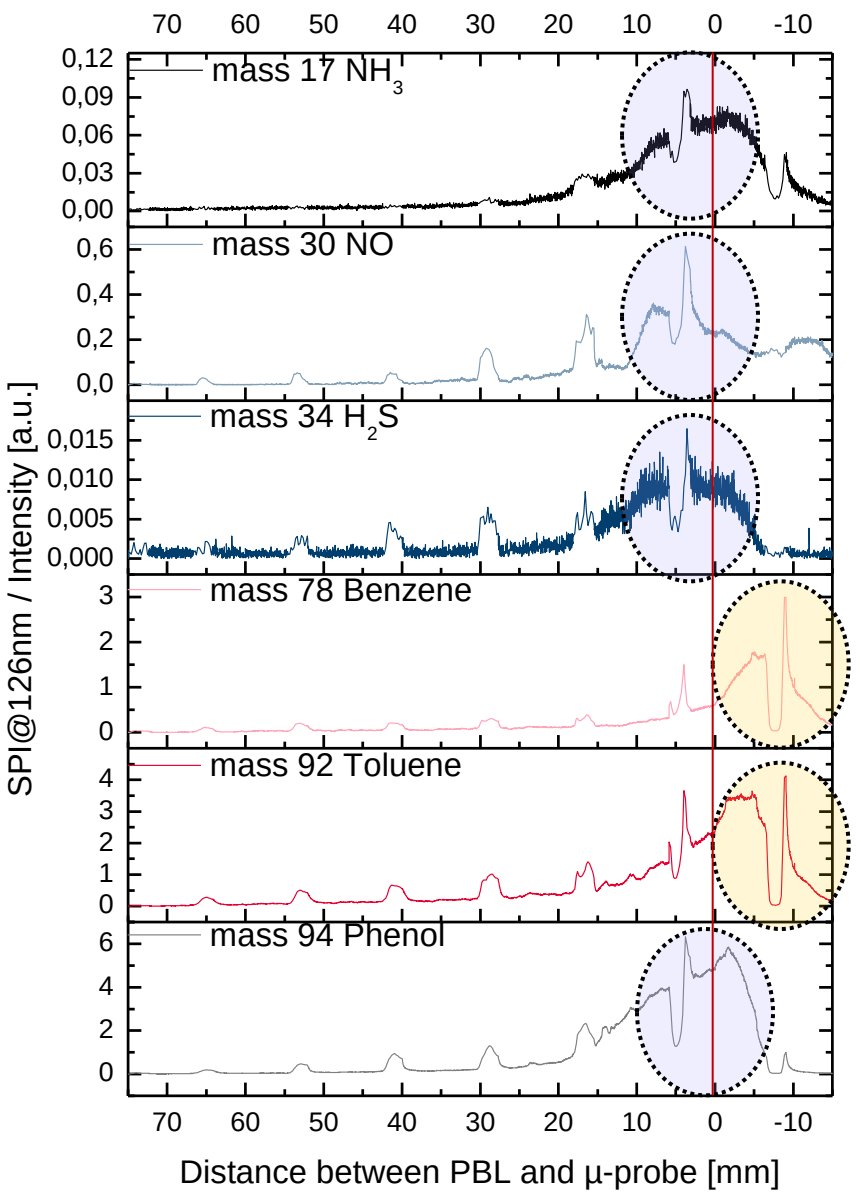
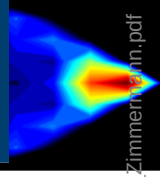


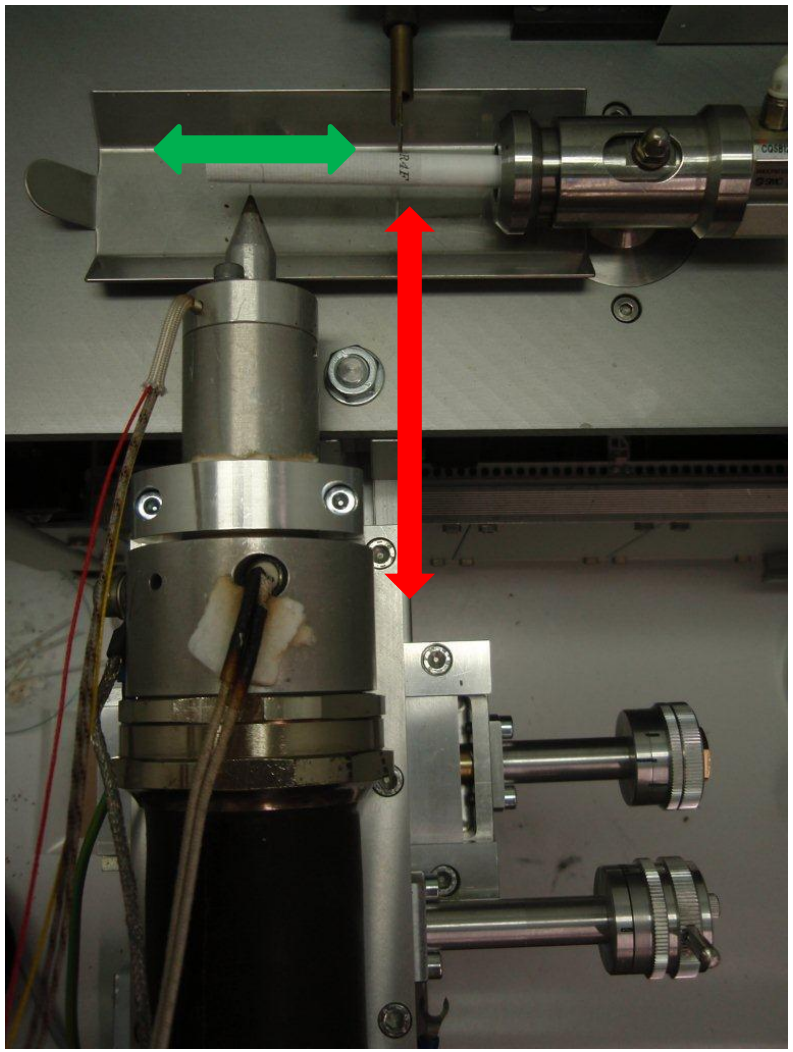


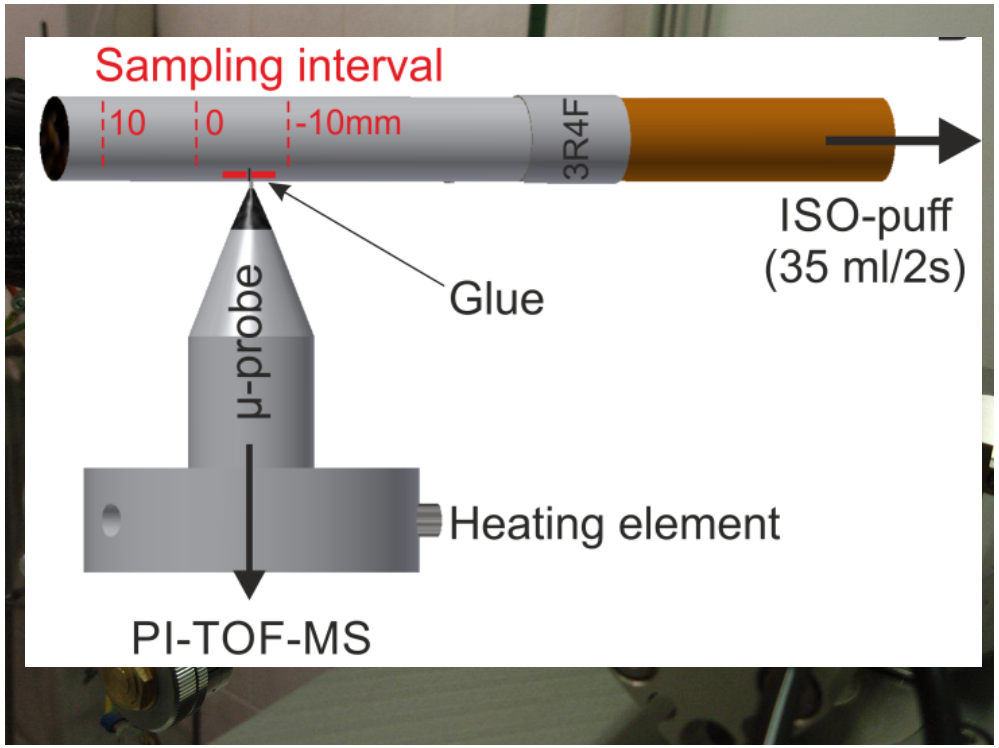


PI-MS for time- and space-resolved chemical mapping of the pyrolysis/combustion zone



Mapping: Addressing multiple position in cigarette during a puff

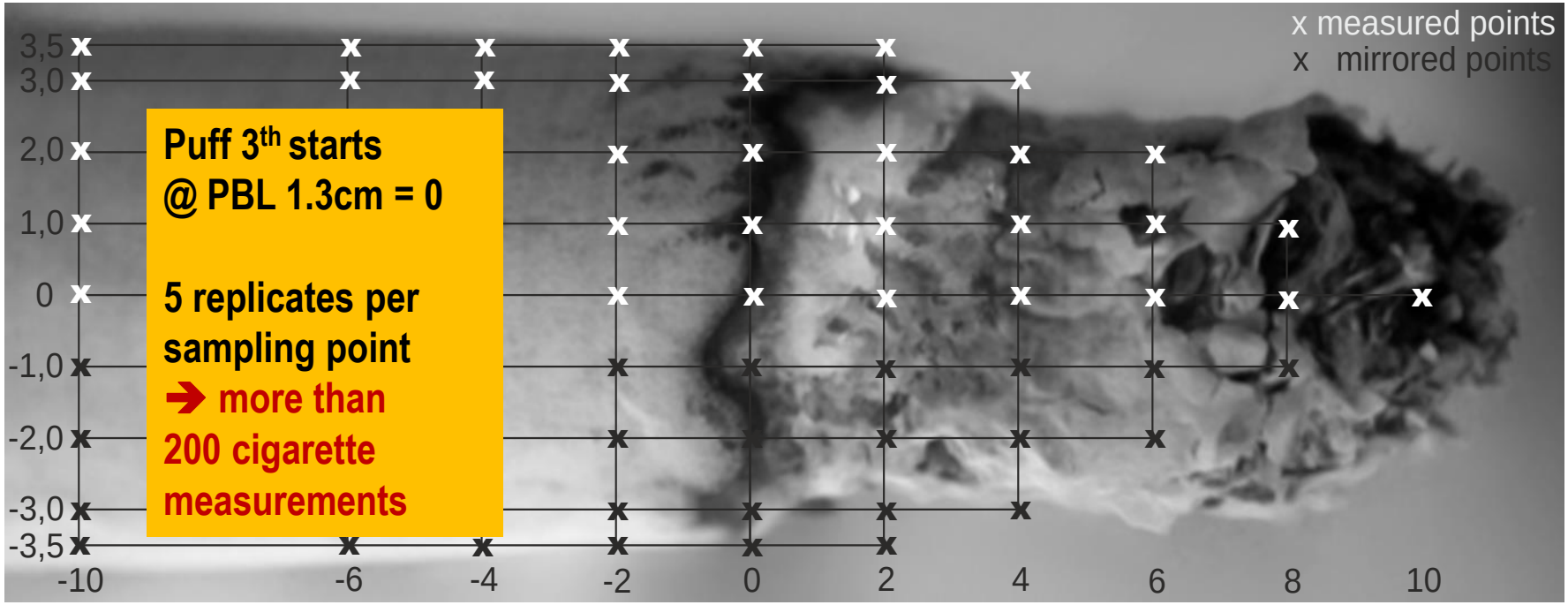




Pressure and temperature changes during the measurement

➔SPI Signals are normalized with respect to the nitrogen LEI signals

PI-MS for time- and space-resolved chemical mapping of the pyrolysis/combustion zone

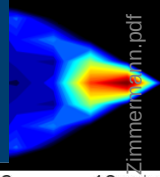


Substance	Quantification
NO	External calibration
Benzene	External calibration
Toluene	External calibration
Acetaldehyde	Cross section: 0.20*
Butadiene	Cross section: 0.60*

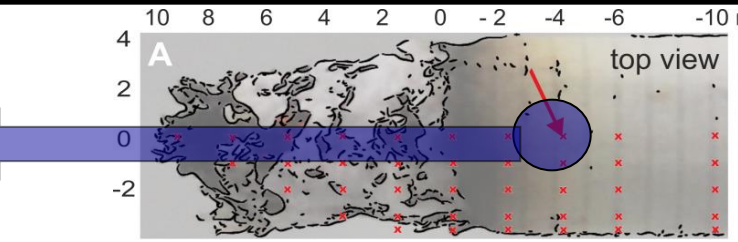
Substance	Relative cross section
Acetone	Cross section: 0.31*
Isoprene	Cross section: 0.59*
Ammonia	-
Phenol	-
Nicotine	-

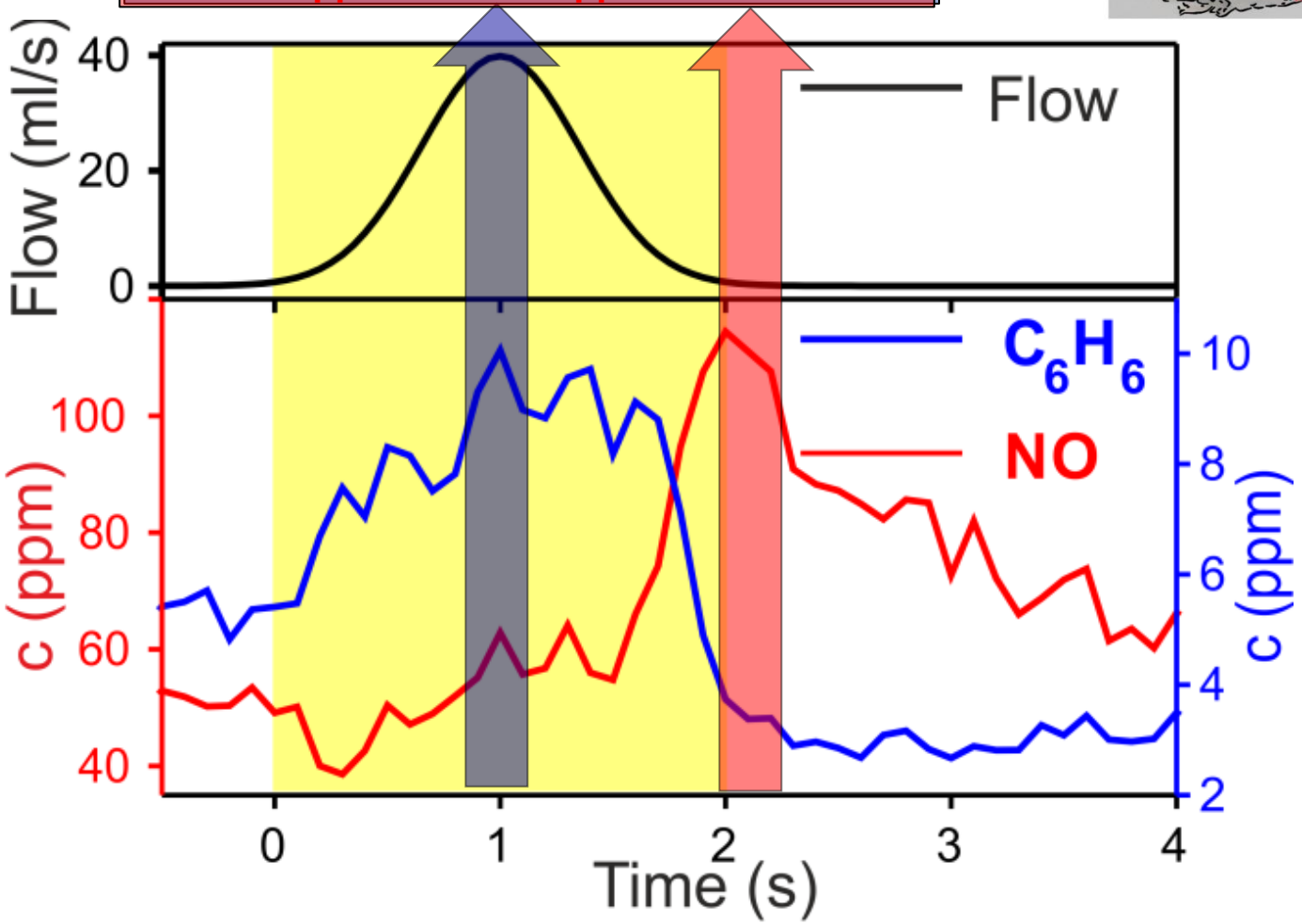
* Relative to benzene,

PI-MS for time- and space-resolved chemical mapping of the pyrolysis/combustion zone

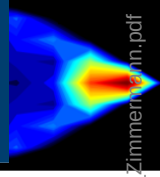


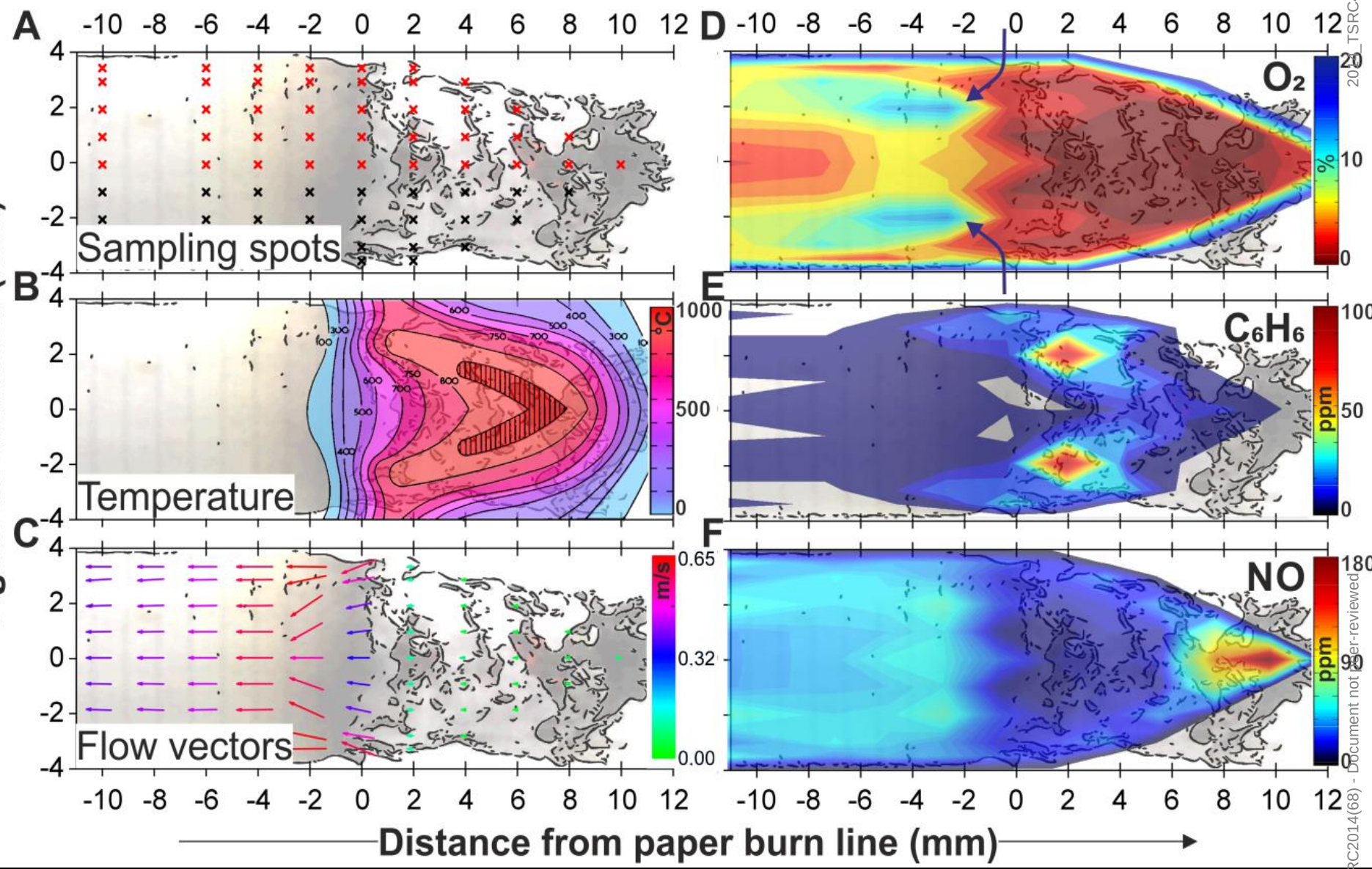
5 measurements averaged value at puff maximum for this sampling point:
~ 110 ppm NO and 1 ppm benzene



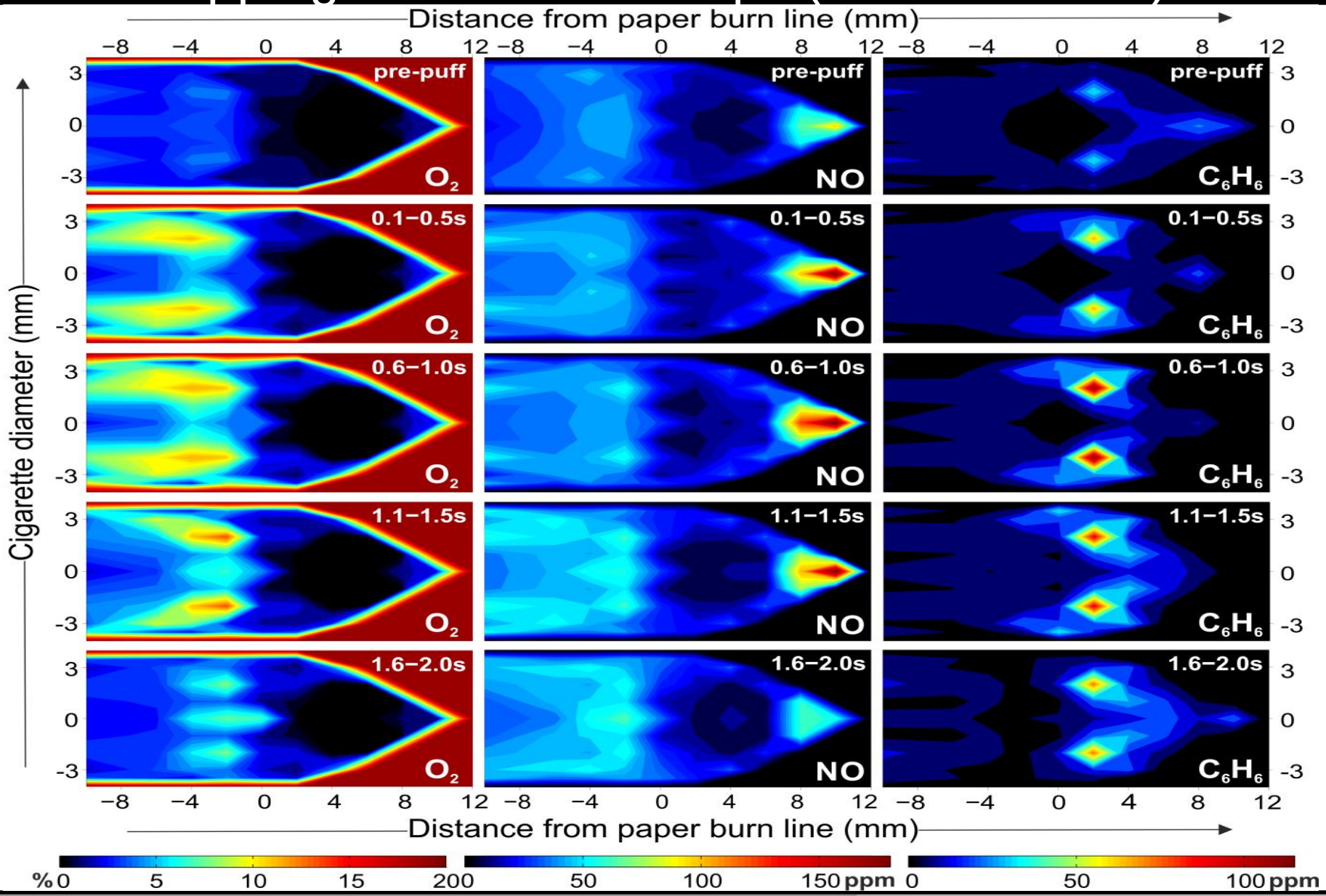


PI-MS for time- and space-resolved chemical mapping: Distribution maps (middle of puff)

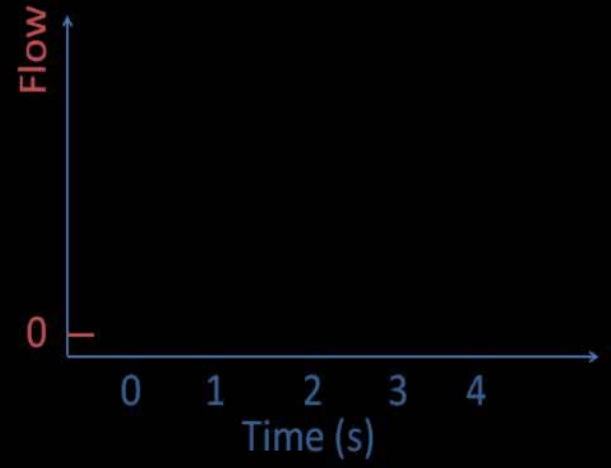


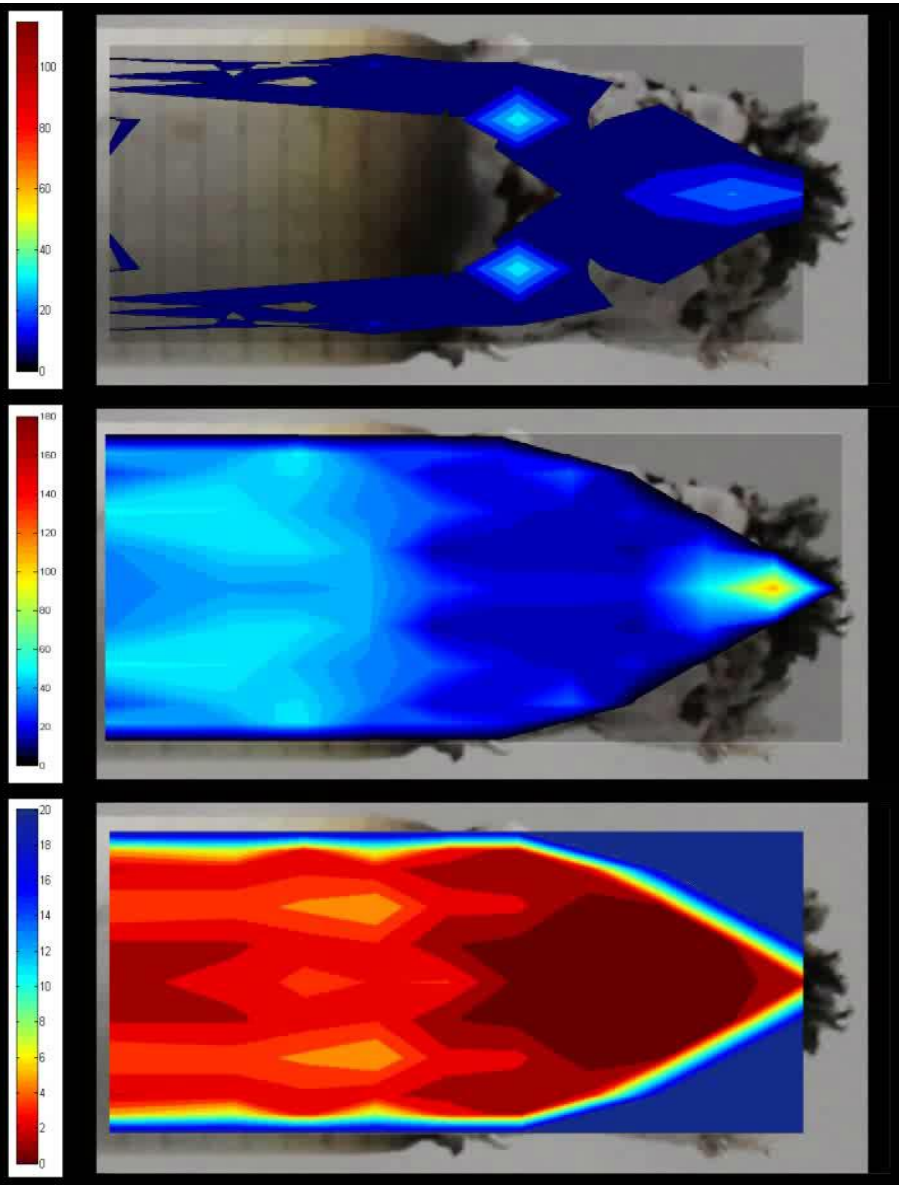


PI-MS for time- and space-resolved chemical mapping: Distribution maps (time-resolved)



PI-MS for time- and space-resolved chemical mapping: Distribution map “movie”



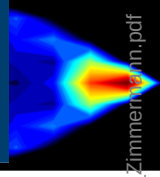


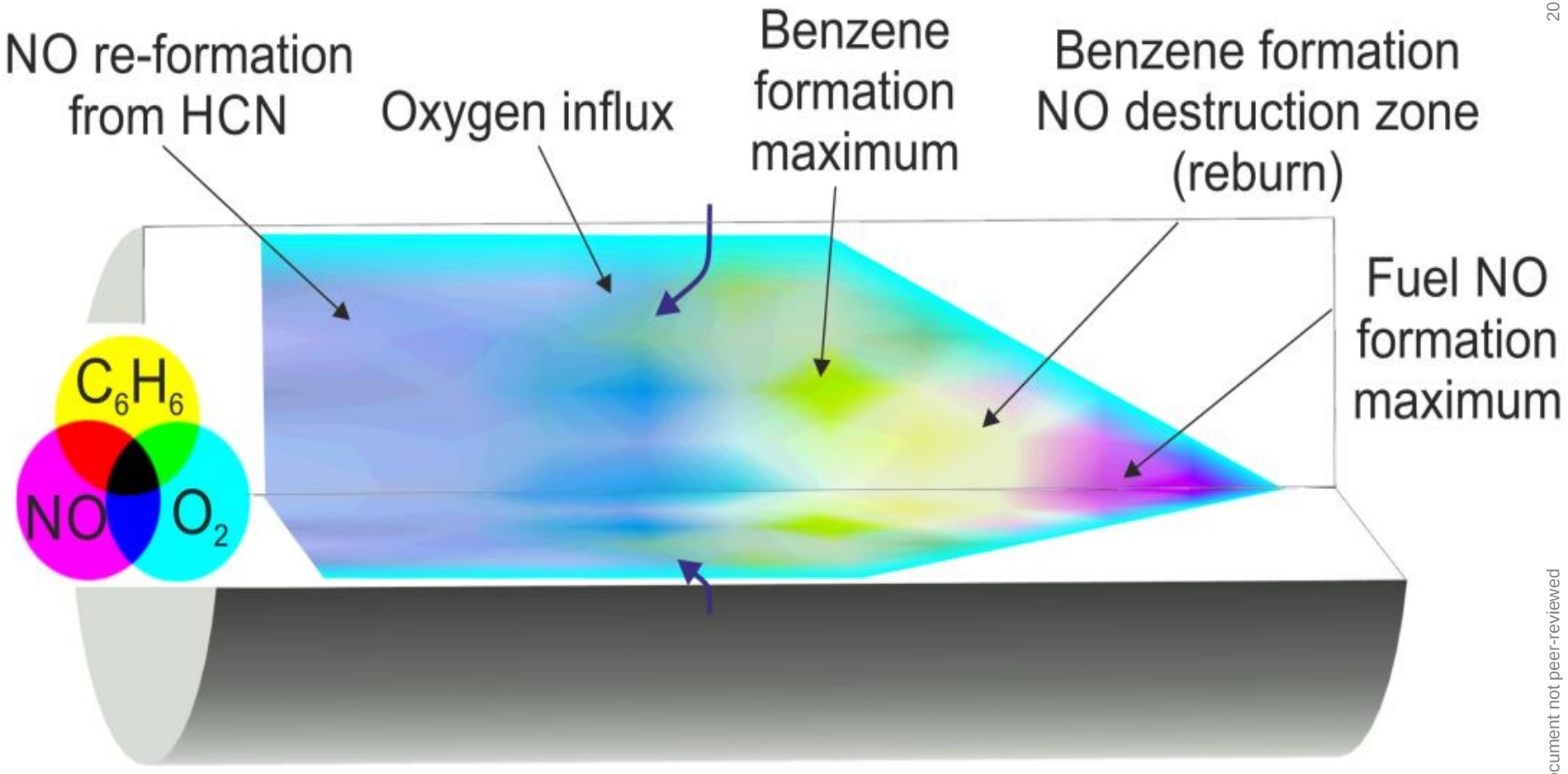
PI-MS for time- and space-resolved chemical mapping: NOx formation and destruction

NOx-Formation in bio mass (tobacco) combustion:

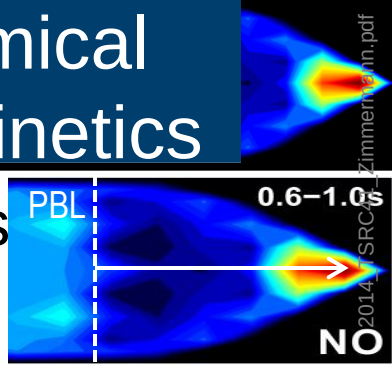
- ⊗ Temperature not sufficient for **Thermal** NOx-formation (*Zeldovich*-mech.)
- ⊗ Rate of **Prompt** NOx-formation (*Fenimore*-mech.) small
- ✓ **Fuel NOx-Formation** is dominating: Heterogeneous (from N-containing char) and Homogeneous (via N-volatiles as HCN etc.) fuel NOx-Formation

PI-MS for time- and space-resolved chemical mapping: 3D-Distribution maps (middle of puff)

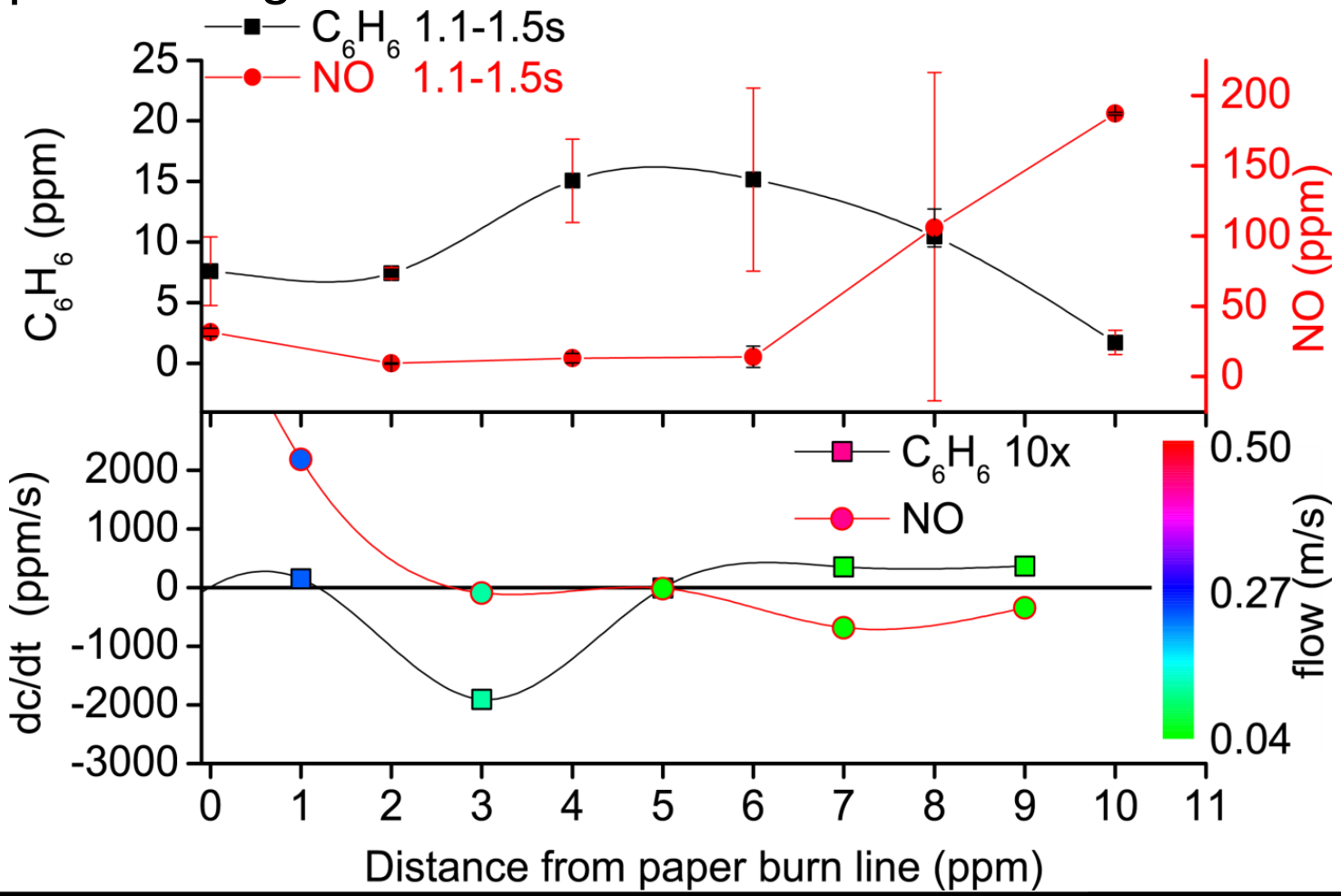




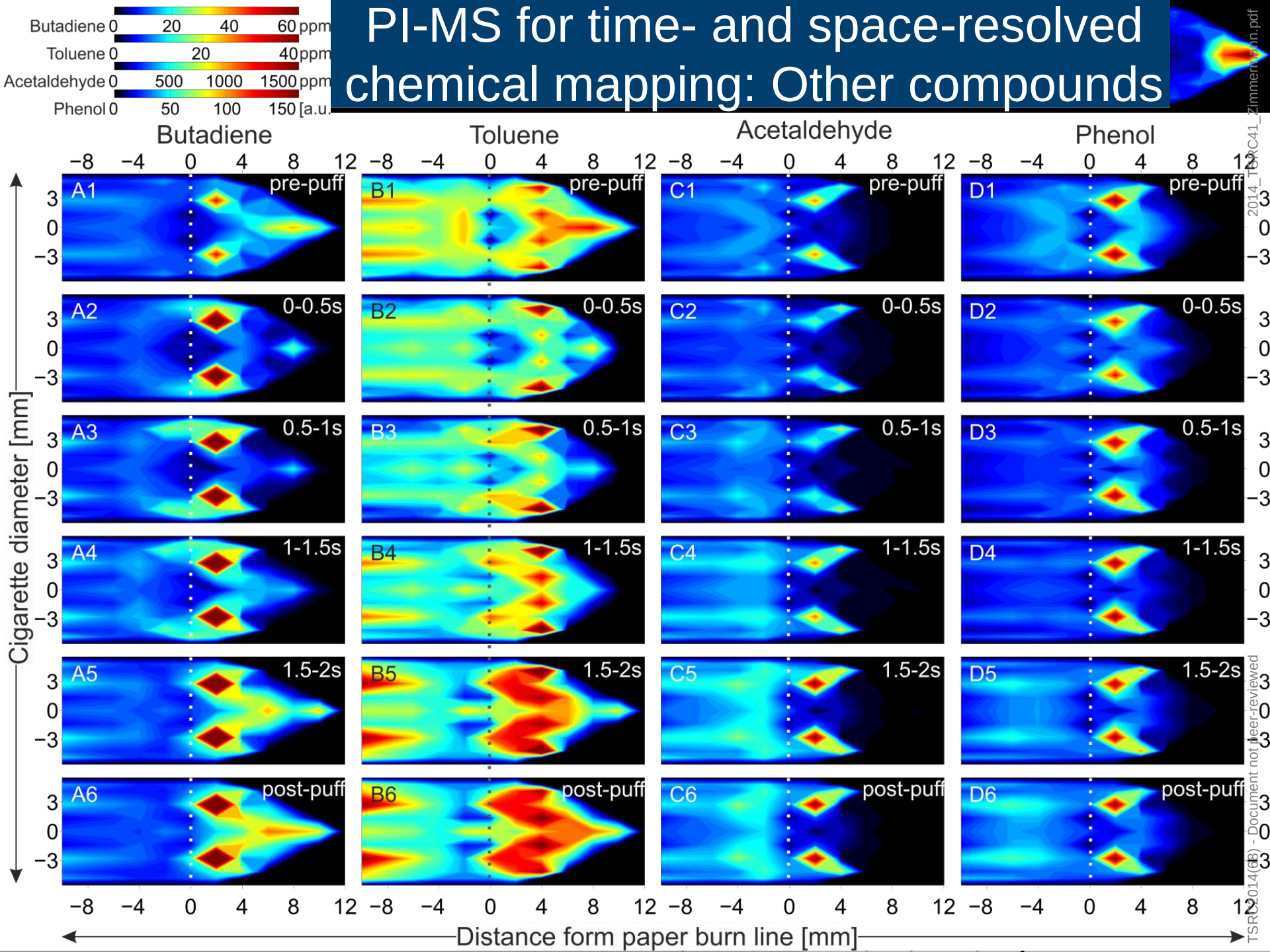
PI-MS for time- and space-resolved chemical mapping: Effective formation/destruction kinetics



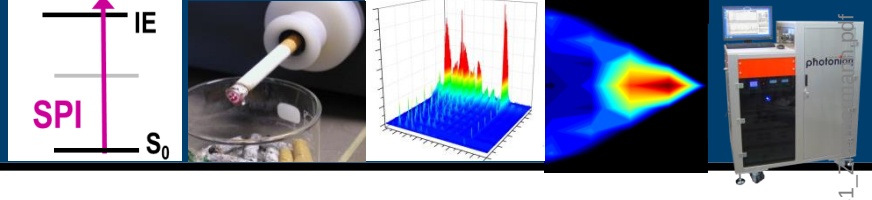
Effective homogeneous formation/destruction kinetics of NO and benzene in a volume increment at puff peak along center line

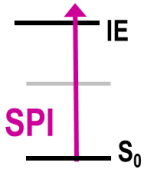


PI-MS for time- and space-resolved chemical mapping: Other compounds



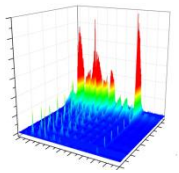
Summary



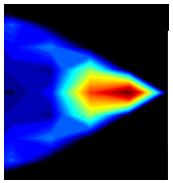


- PI-MS (REMPI, SPI): Soft ionization method for analysis of trace gases and combustion effluents

- Puff-resolved monitoring of gaseous cigarette smoke compounds (health risk estimation tobacco research)



- PI-MS with µ-probe sampling: Analyzing the composition of the pyrolysis and combustion zones: Cigarette as “solid fuel combustion model”



- “Machine smoking” allows repetitive highly dynamic PI-MS measurements: Mapping approach➔ NOx-formation

- Spin-off company Photonion GmbH: Custom-build and standard PI-MS Systems for Industry and Research

Multi-component trace gas analysers

photonion

On-line photoionisation mass spectrometry


Dr. S.Ehlert


Dr. M. Bente


Dr. M. Saraji

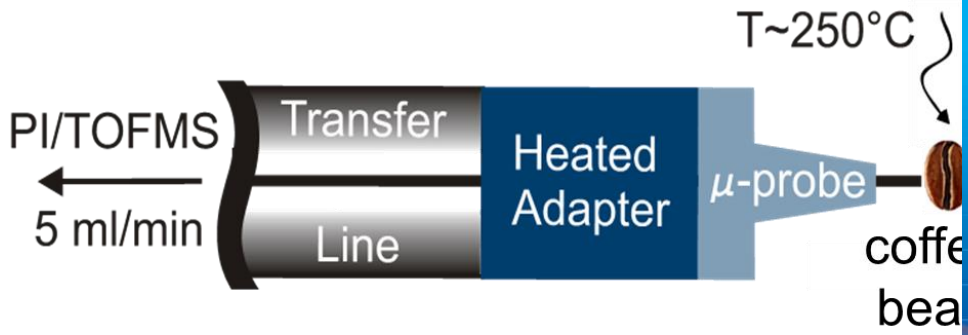
Instrumental Solutions and Applications

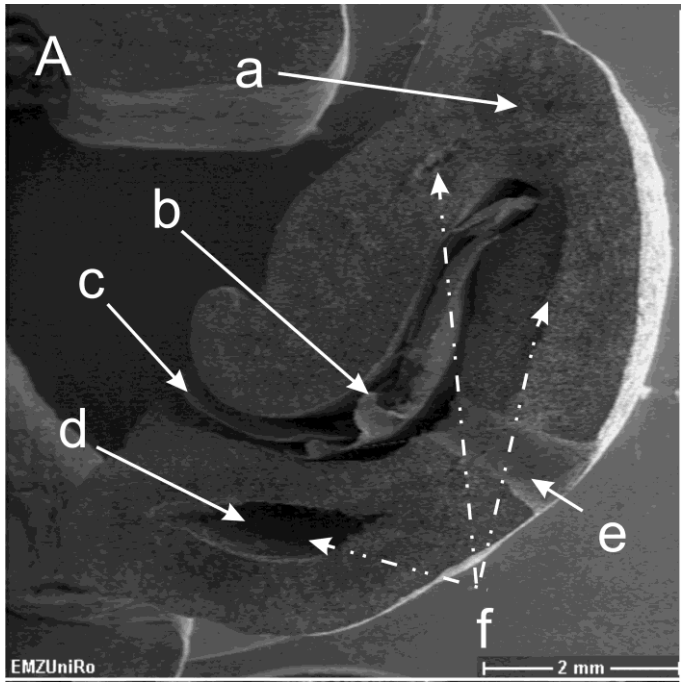
- Flexible Systems for Research and Industry: Photo-TOF (SPI/REMPI/EI)
- On-line Analysis of Cigarette Smoke (OEM for Borgwaldt KC)
- Evolved Gas Analysis in TA (OEM for Netzsch GmbH)

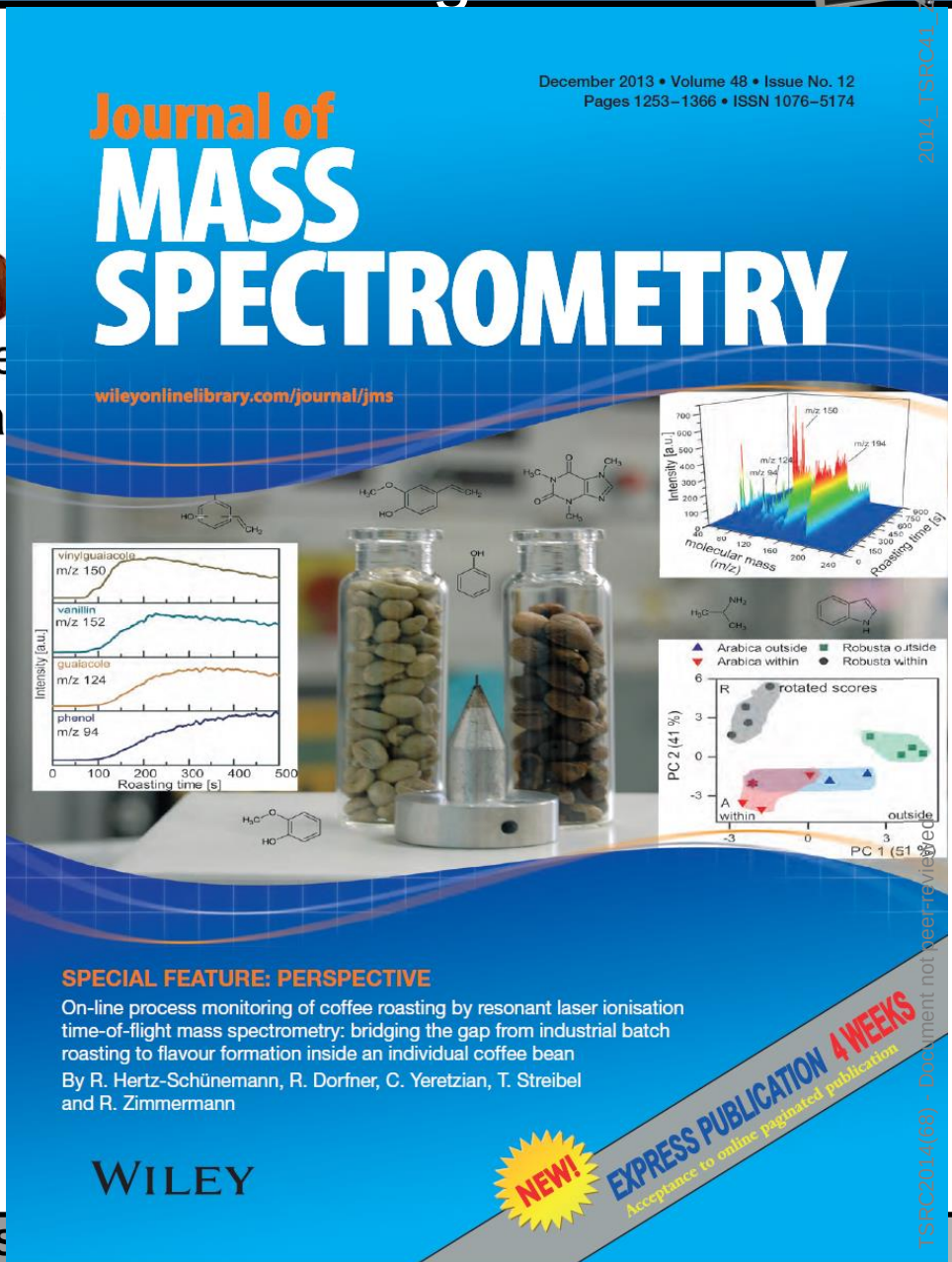
Contact: walte@photonion.de

Outlook – Further microprobe-PI-MS applications: Flavor formation in coffee roasting

Sampling within coffee-bean during







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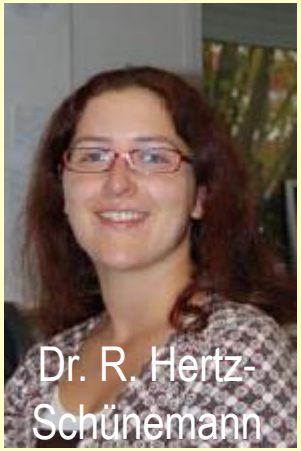
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