On-line puff resolved analysis of cigarette smoke, e-cigarette vapor and vapor of tobacco heating products

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CORESTA 2018

Outline

- **Soft Photoionization Mass Spectrometry**
  - Basic idea
  - Introduction: photoionization - SPI and REMPI
- **Applications & developments**
  - Dynamical cigarette mapping
  - Puff resolved investigation of smoking products
  - Puff resolved fast GC-MS
  - Single aerosol particle analysis
- **Summary**

Basic idea of
Photo Ionization Mass Spectrometry

PIMS - Soft photo ionization in vacuum (no/less fragmentation than in EI-MS and no matrix effects as in CI-MS)

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

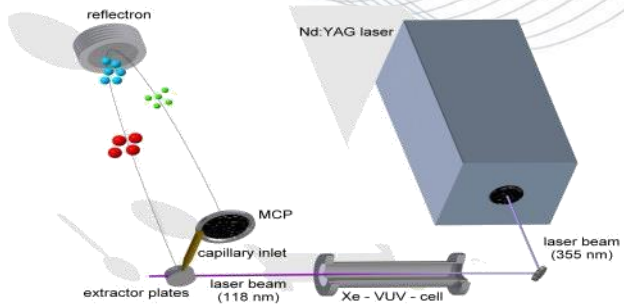
Introduction:
Photo ionization - SPI and REMPI

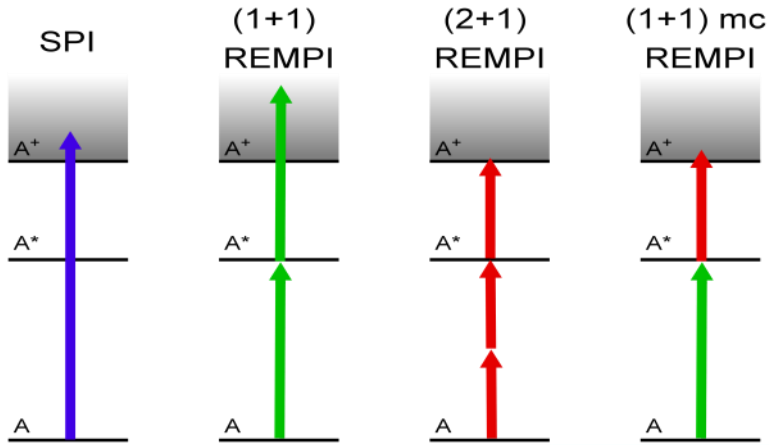
Vacuum UV Single Photon Ionization (SPI)

- ionization with 118 nm laser photons (10.5 eV) or
- incoherent VUV radiation (excimer lamp, e.g. 9.8 eV [126nm] or Kr discharge lamp at 10.6 eV)
- soft ionization of most organic compounds
- ppb on-line concentration range
- suppression of oxygen (IE = 12.06 eV), nitrogen (IE = 15.58 eV), carbon dioxide (IE = 13.77 eV), and especially water vapor (IE = 12.62 eV)

Resonance-Enhanced Multiphoton Ionization (REMPI)

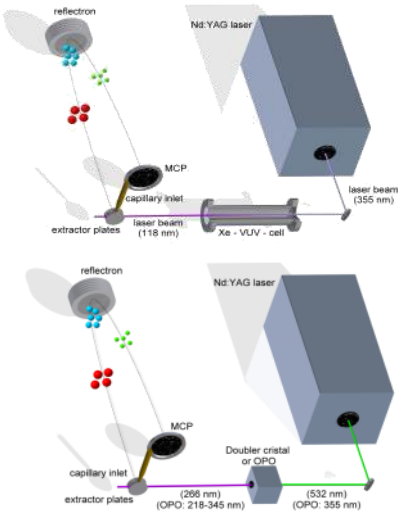
- ionization by UV laser pulses (210-270 nm, ~10^7 W/cm²)
- highly efficient soft two-photon ionization of aromatics
- ppb/ppt on-line concentration range



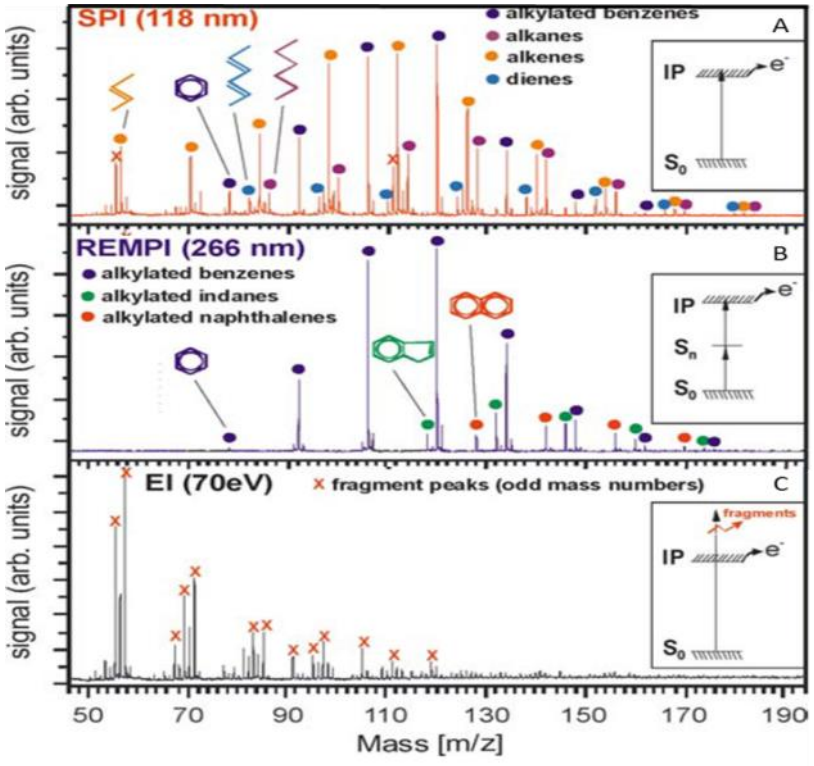


Introduction:

Photo ionization - SPI and REMPI



Mass spectra of Diesel



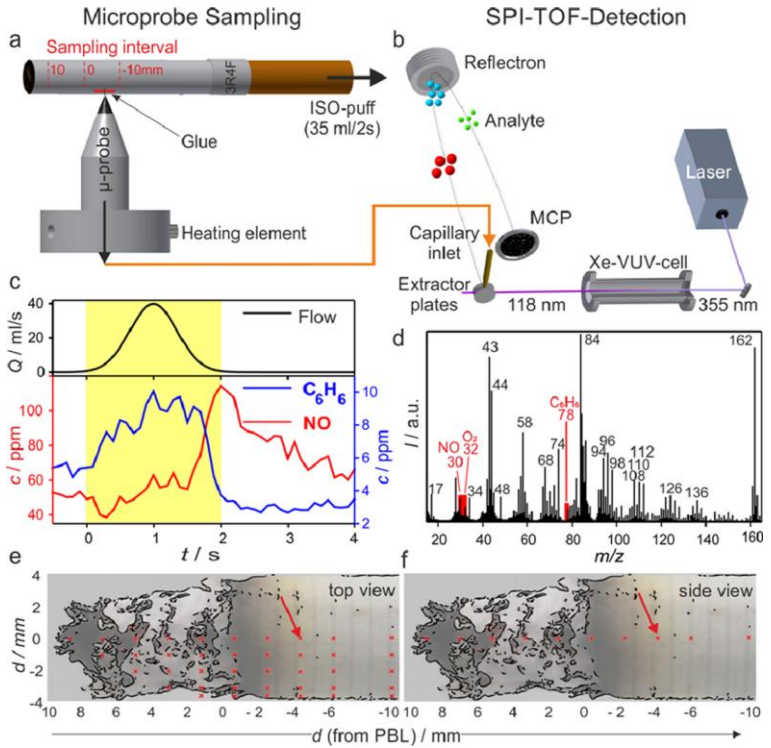
fragment-free/less overview

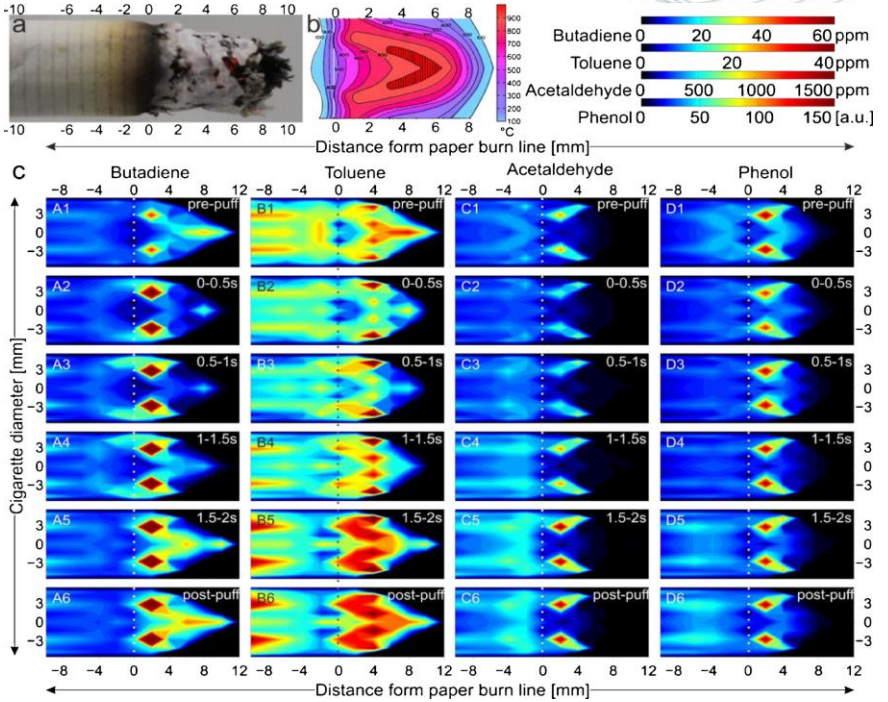
especially selective for aromatic compounds

heavy fragmentation

Applications I

Dynamic chemical cigarette mapping



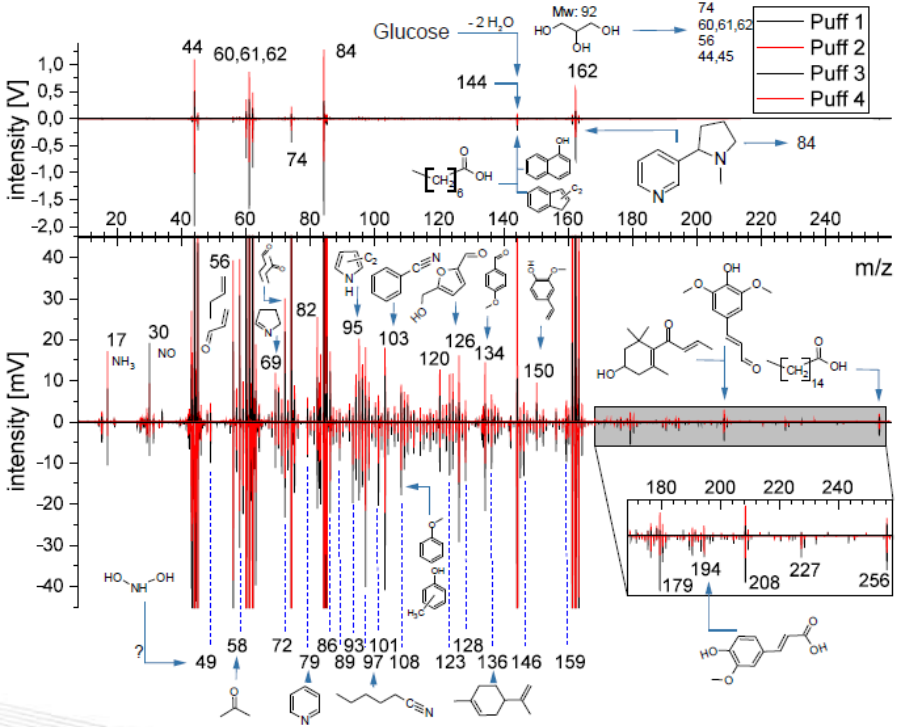


Hertz-Schünemann, R., et al., *High-resolution time and spatial imaging of tobacco and its pyrolysis products during a cigarette puff by microprobe sampling photoionisation mass spectrometry.* Analytical and Bioanalytical Chemistry, 2015. **407**(8): p. 2293-2299.

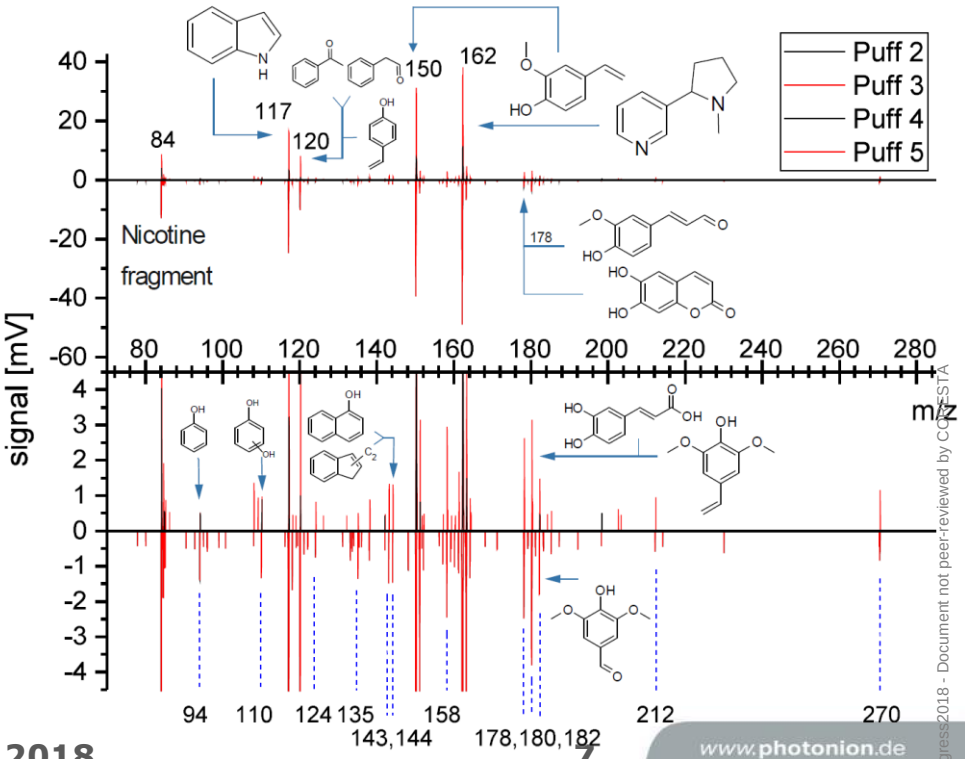
Applications II

Puff by puff analysis of THPs

SPI @ 10.5eV

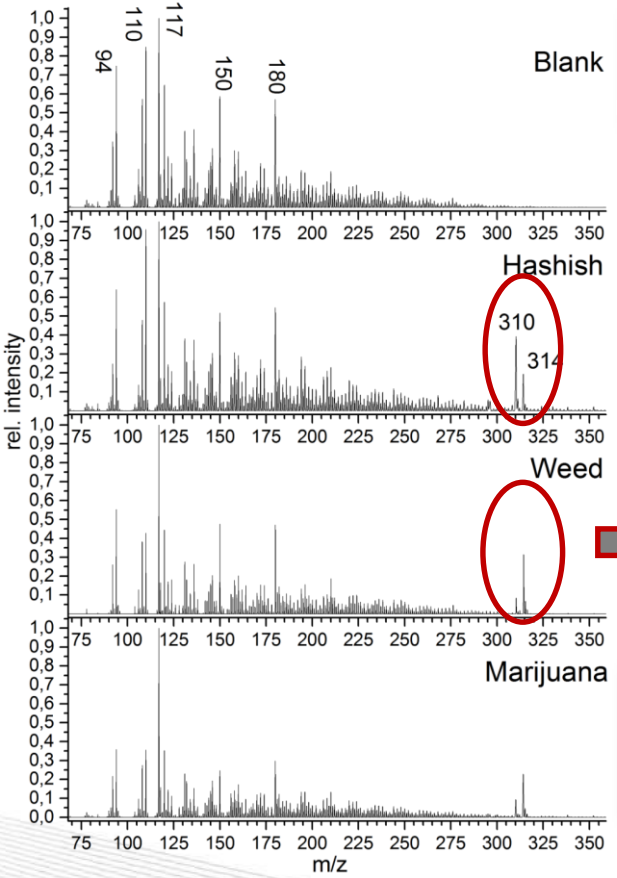


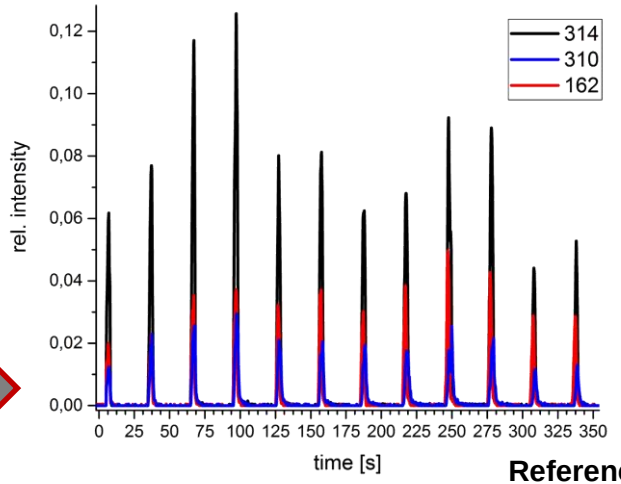
REMPI @ 266nm



Applications III

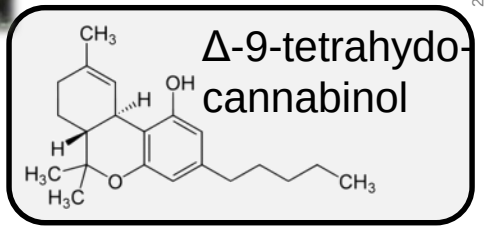
CNB and THC ratio in cannabis smoke

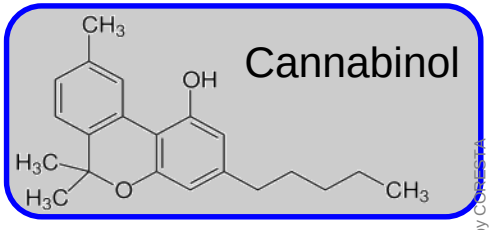




Reference analytics

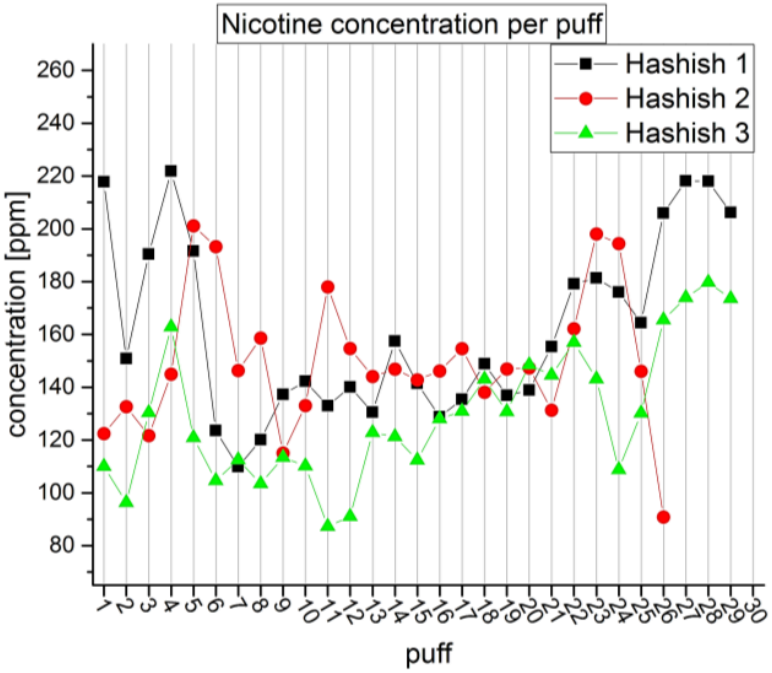
Product	CNB	THC
Weed	0.17%	18.48%
Hashish	2.05%	16.71%

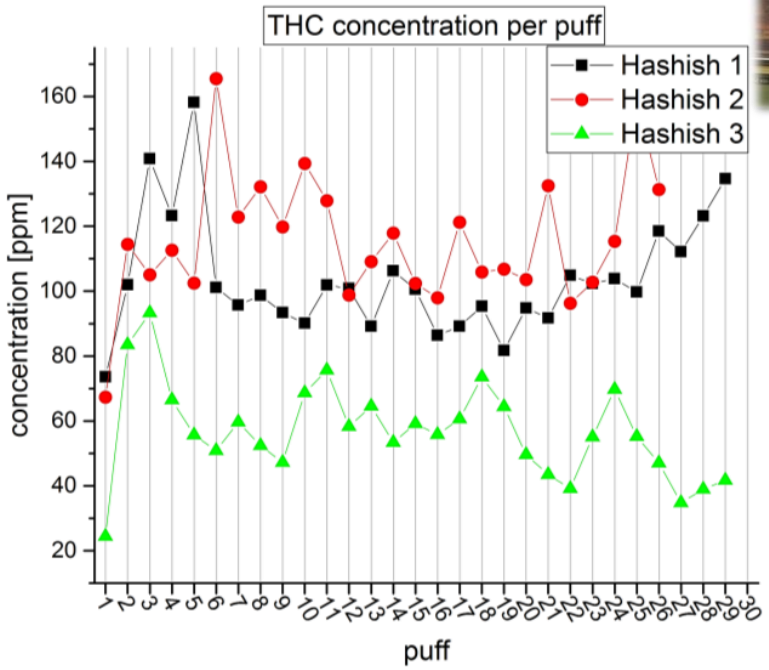




Applications III

Nicotine and THC **quantification** in cannabis smoke



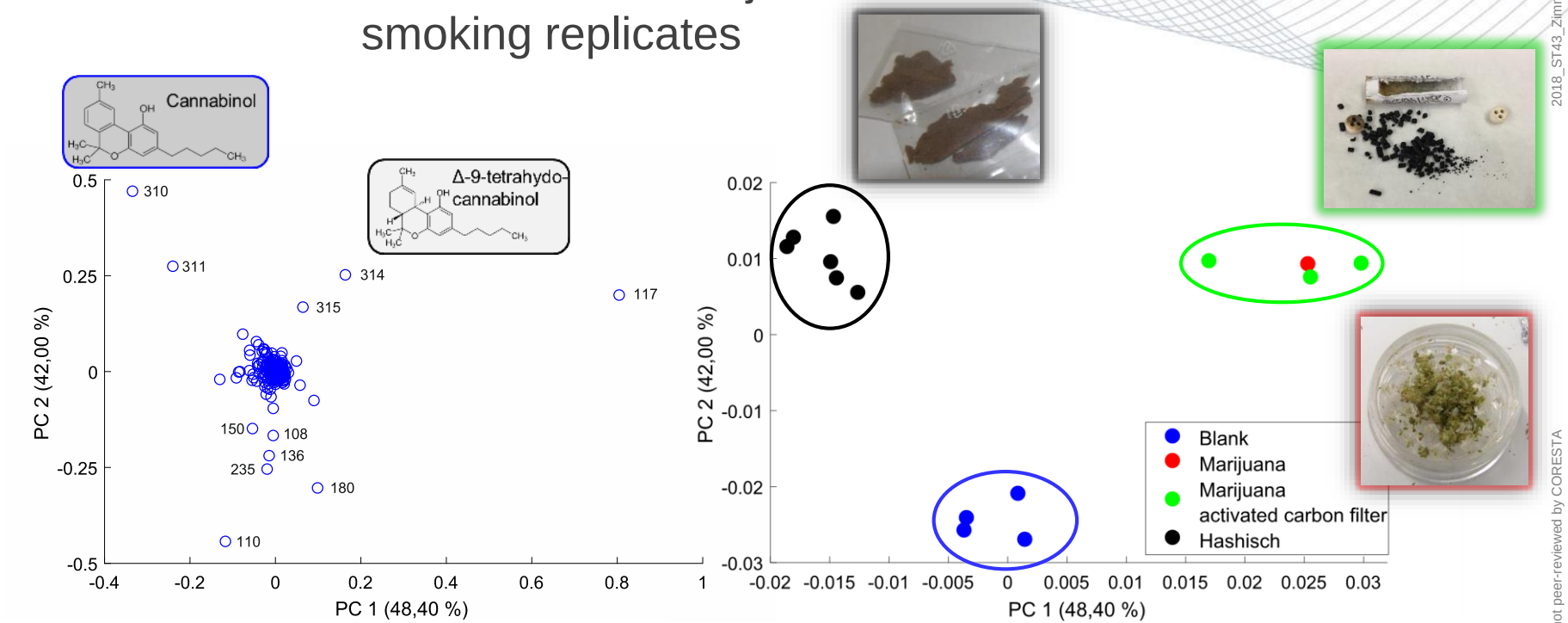


Reference analytics

Type	THC
Hash 1	16.7%
Hash 2	17.3%
Hash 3	10.4%

Applications III

statistical evaluation of joint smoking replicates



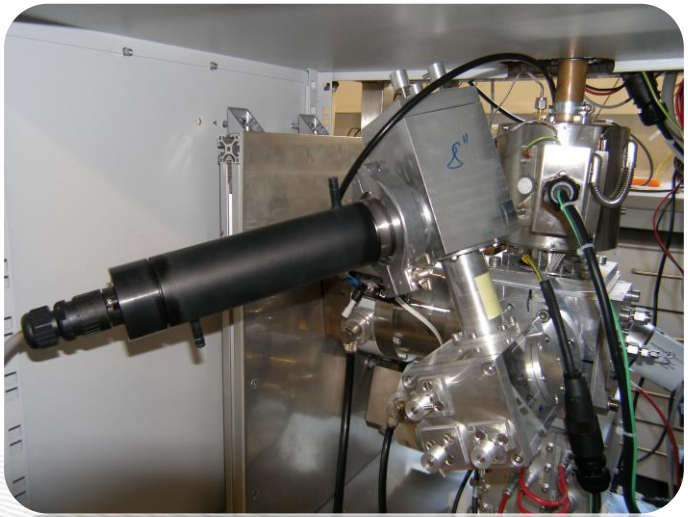
PCA – Principal components analysis

Applications IV

Puff resolved pipe smoking

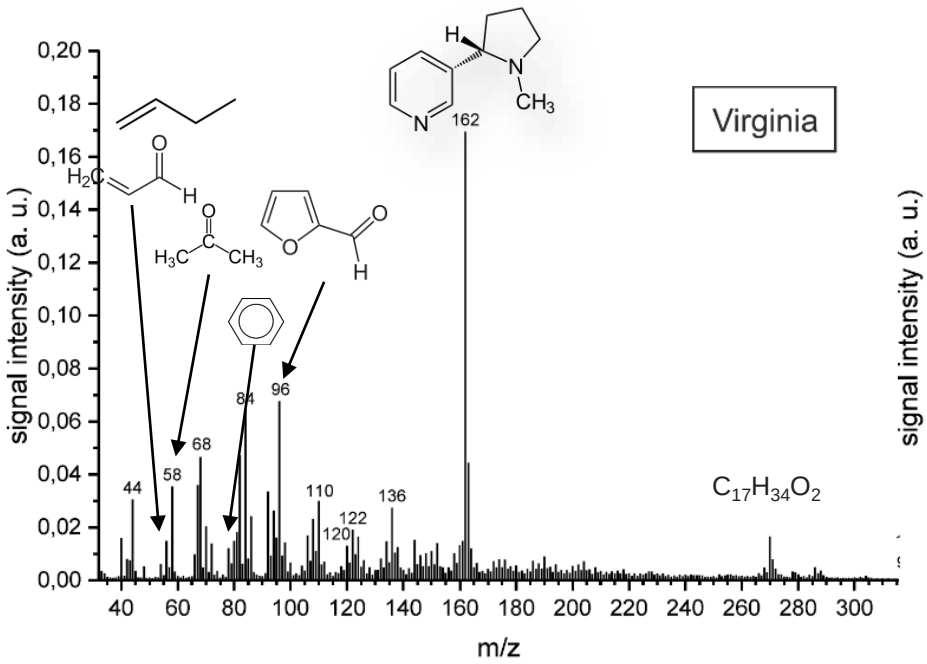
puff profile
- 55 ml
- 3 puffs per minute
- 3 s puff duration
- first 20 puffs used

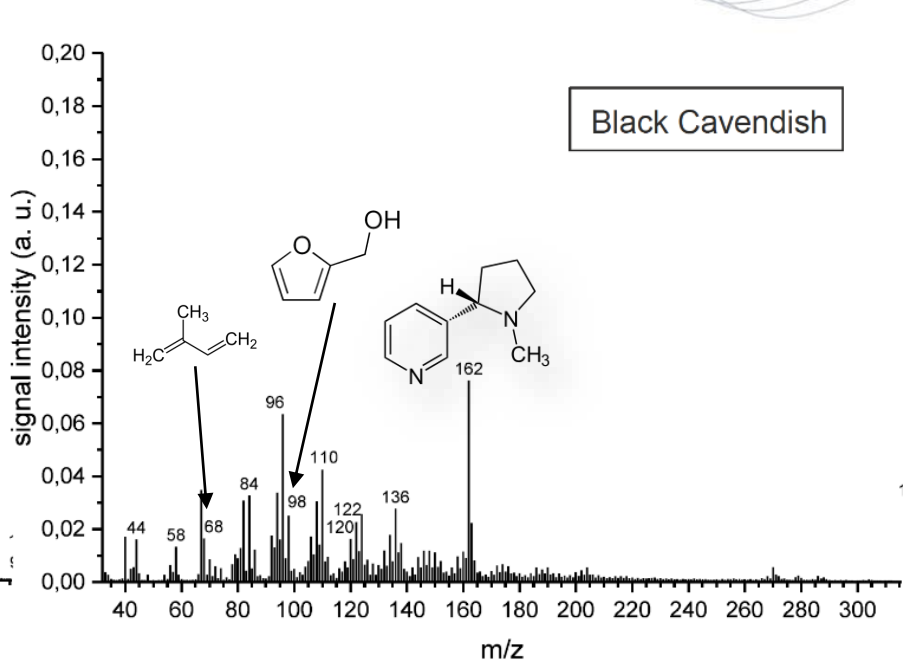
MS setup
- for ionization cw - deuterium lamp max IE of 10.2 eV
- Orthogonal ToF system



Applications IV

Puff resolved pipe smoking





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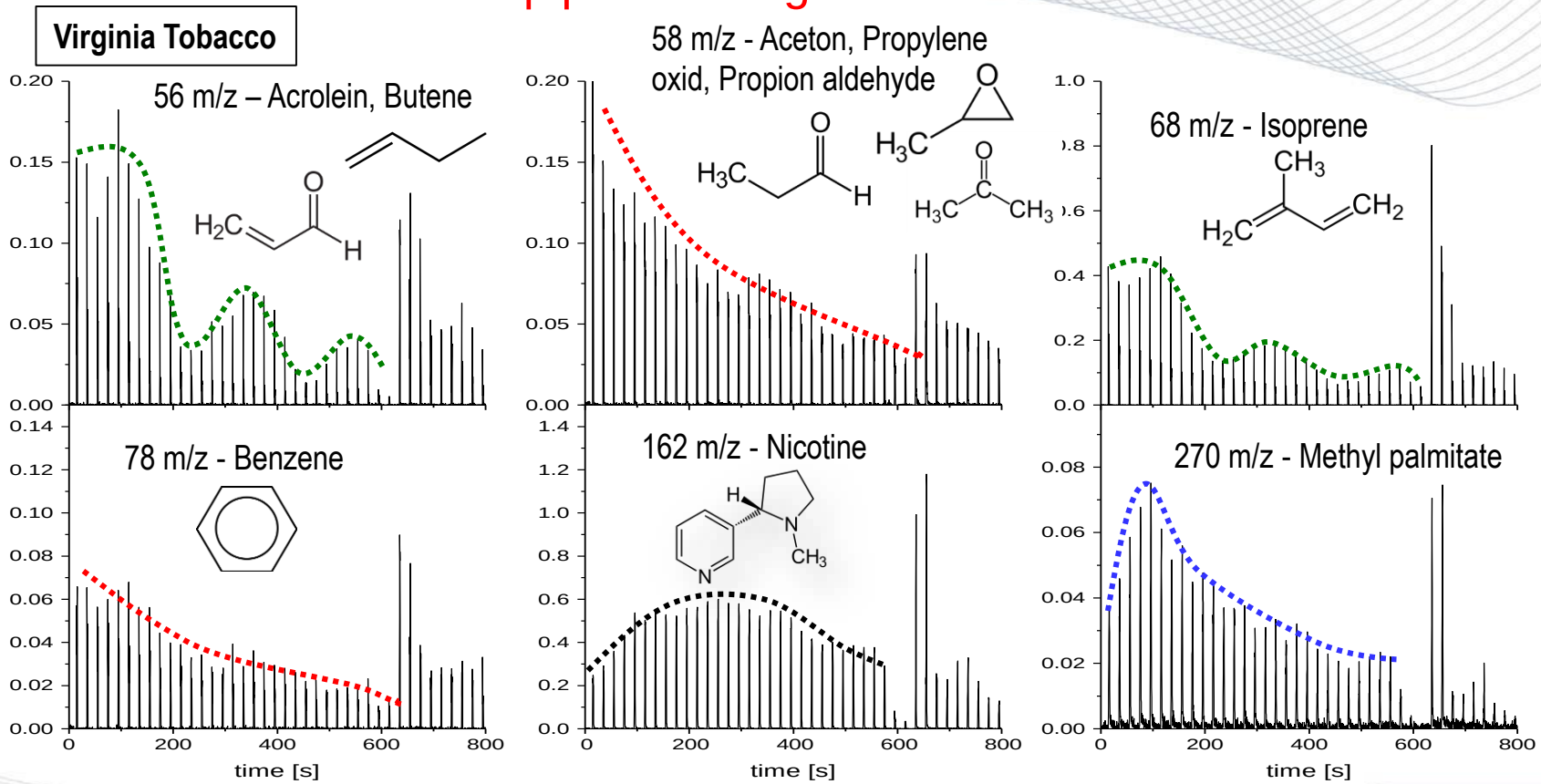
Puff resolved pipe smoking



Applications V

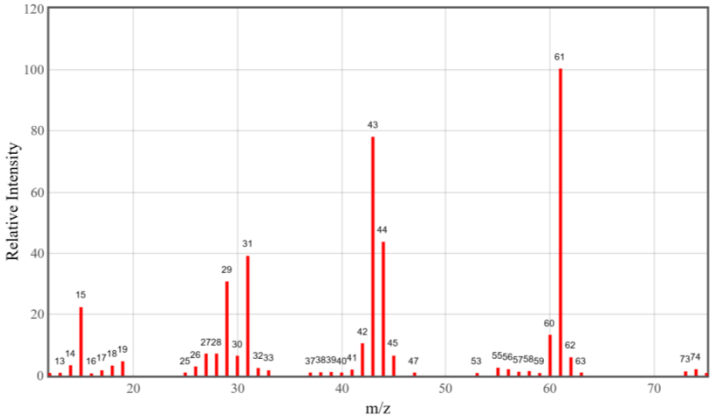
Puff resolved e-cigarette vapor

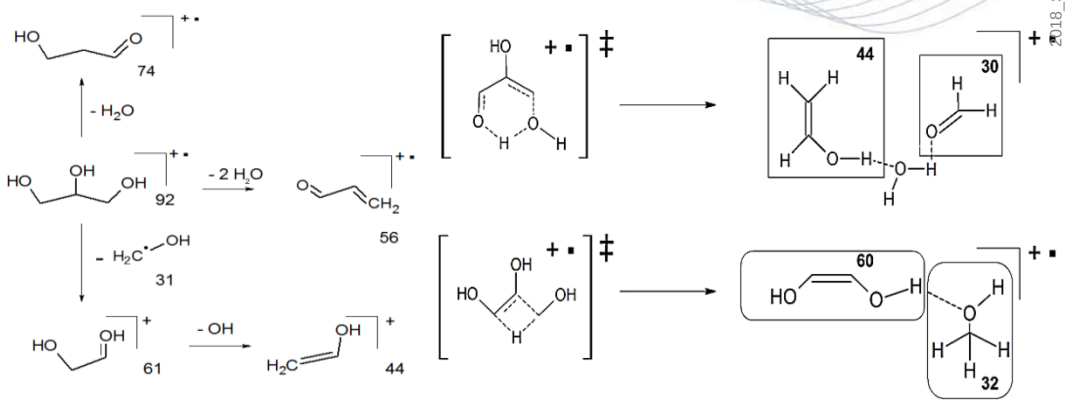
Glycerin is main issue in online puff by puff MS analysis

Applications V

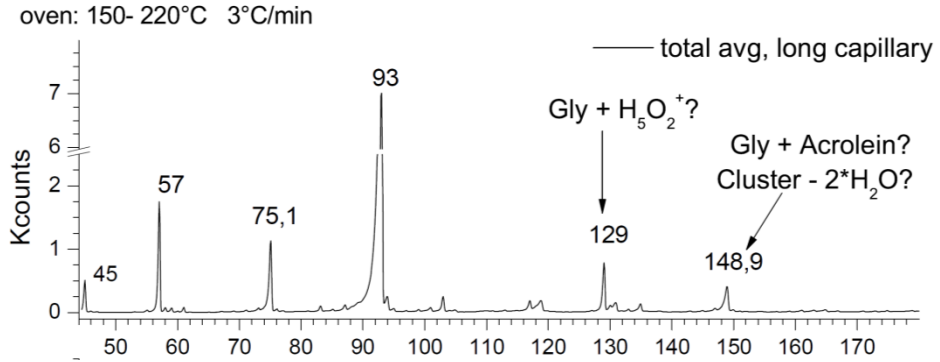
Puff resolved e-cigarette vapor

EI (NIST)

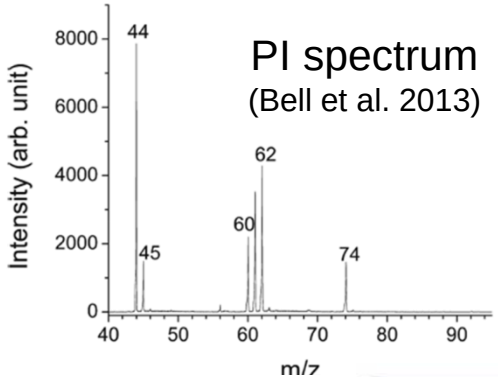




CI (pos. Methane)

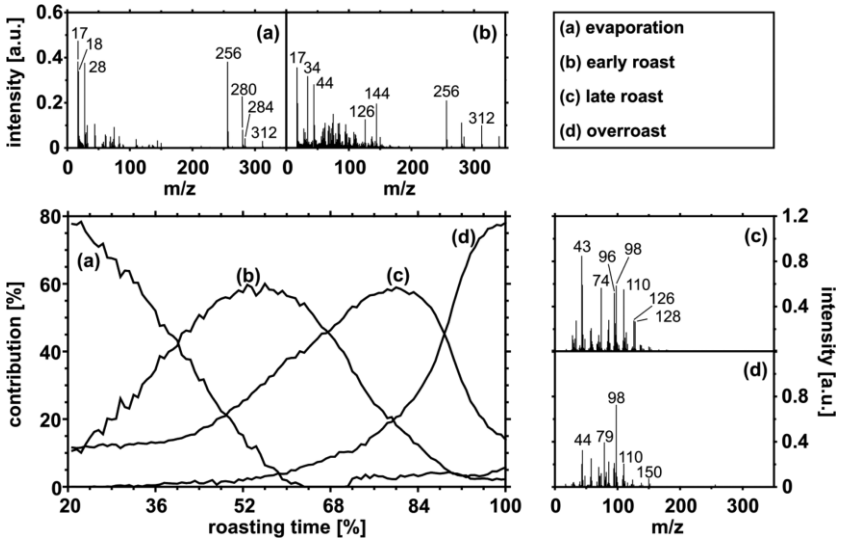


PI spectrum
(Bell et al. 2013)

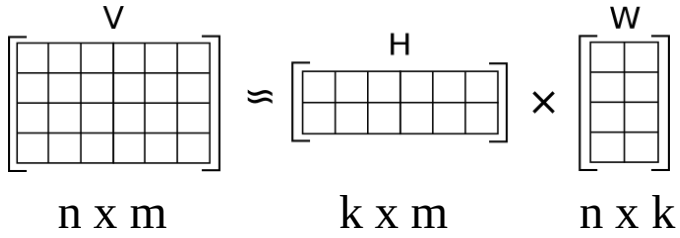


Introduction PMF

Non-negative/**P**ositive **M**atrix **F**actorization applied to coffee roasting gasses for roast phase determination



Idea:
Separating matrix of mass spectra over time into single sources/spectra (loadings) and their contribution (scores)

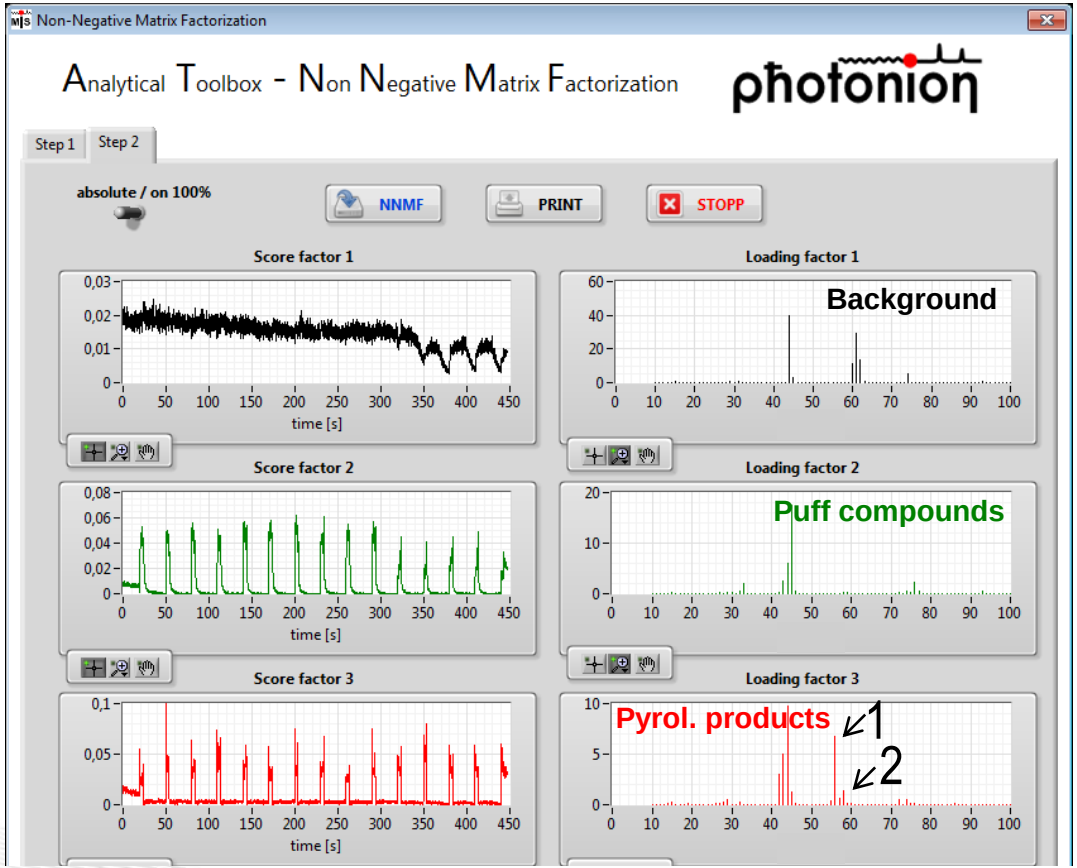


$$F(W,H) = \|V - WH\|_F^2$$

Czech, H., et al., *Resolving Coffee Roasting-Degree Phases Based on the Analysis of Volatile Compounds in the Roasting Off-Gas by Photoionization Time-of-Flight Mass Spectrometry (PI-TOFMS) and Statistical Data Analysis: Toward a PI-TOFMS Roasting Model.* J Agric Food Chem, 2016. **64**(25): p. 5223-31.

Applications V

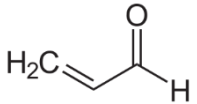
Puff resolved e-cigarette vapor



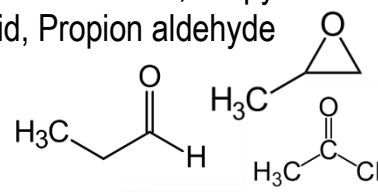
Three factor NMF applied to puff resolved online e-cig measurement

Separation of formation behaviour of different vapor compounds within the factors

1 56 m/z - Acrolein

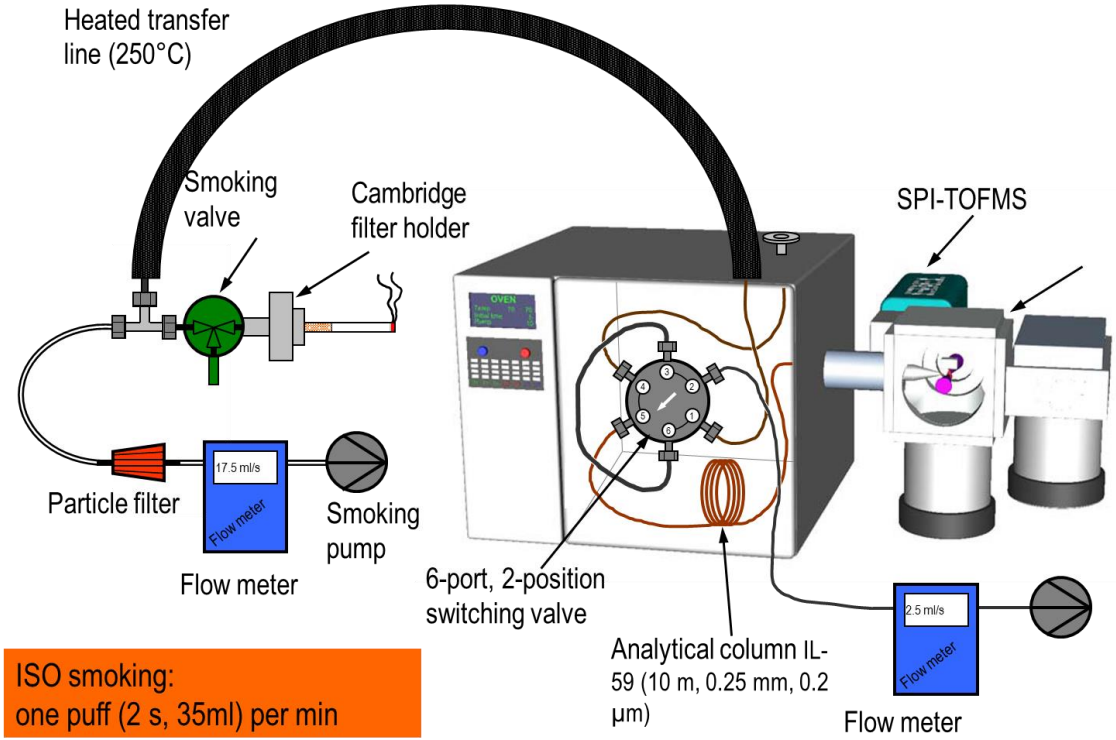


2 58 m/z - Aceton, Propylene oxid, Propion aldehyde

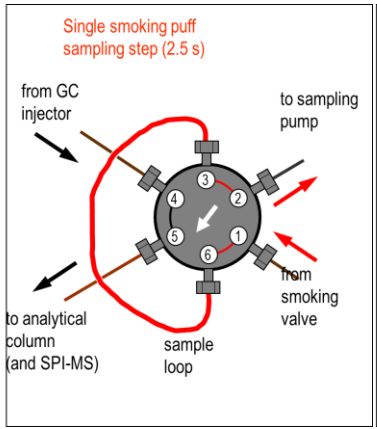


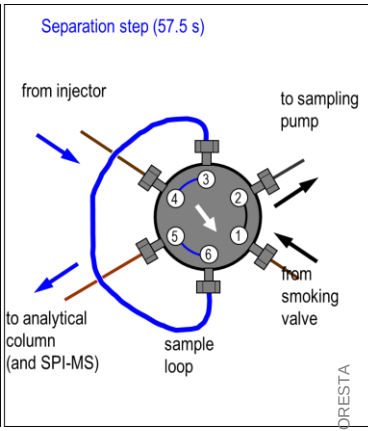
Outlook

On-line, puff-resolved GCxSPI-MS analysis



ISO smoking:
one puff (2 s, 35ml) per min





Eschner et al.
Anal. Chem., **2011**, *83* (17), pp 6619–6627
DOI: 10.1021/ac201070j

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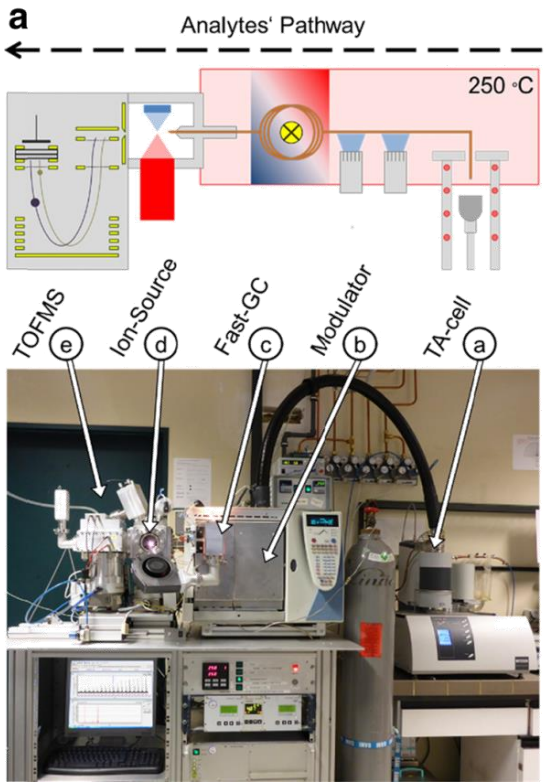
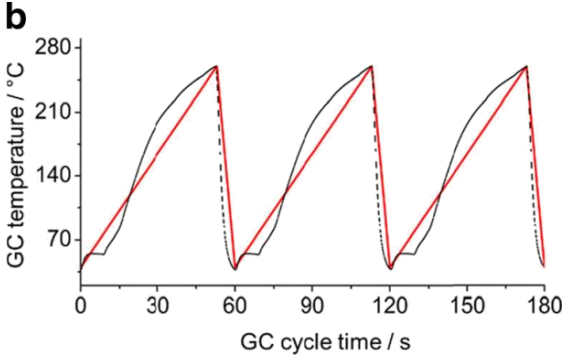
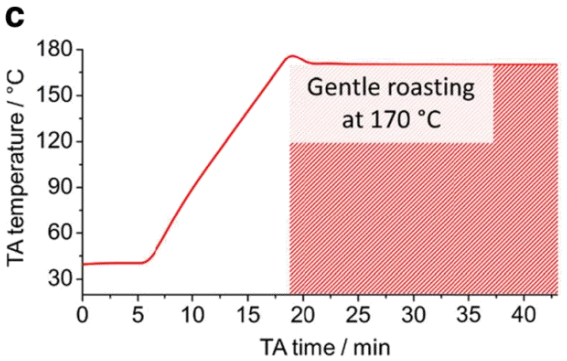
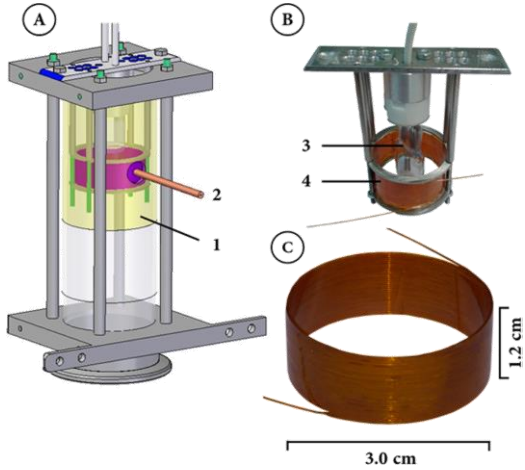
On-line, puff-resolved GCxSPI-MS analysis





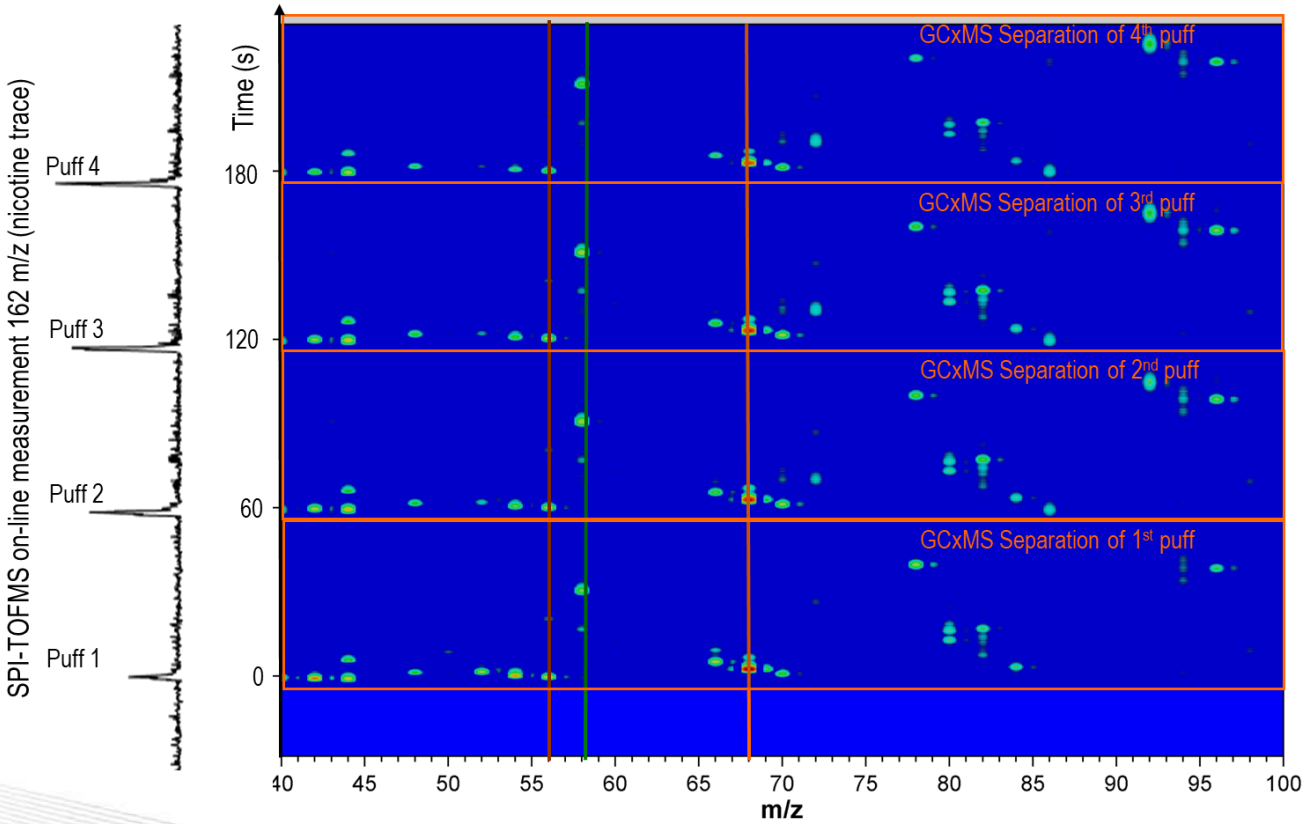




Fischer, M., Wohlfahrt, S., Varga, J. et al. Food Anal. Methods (2017) 10: 49. doi:10.1007/s12161-016-0549-8

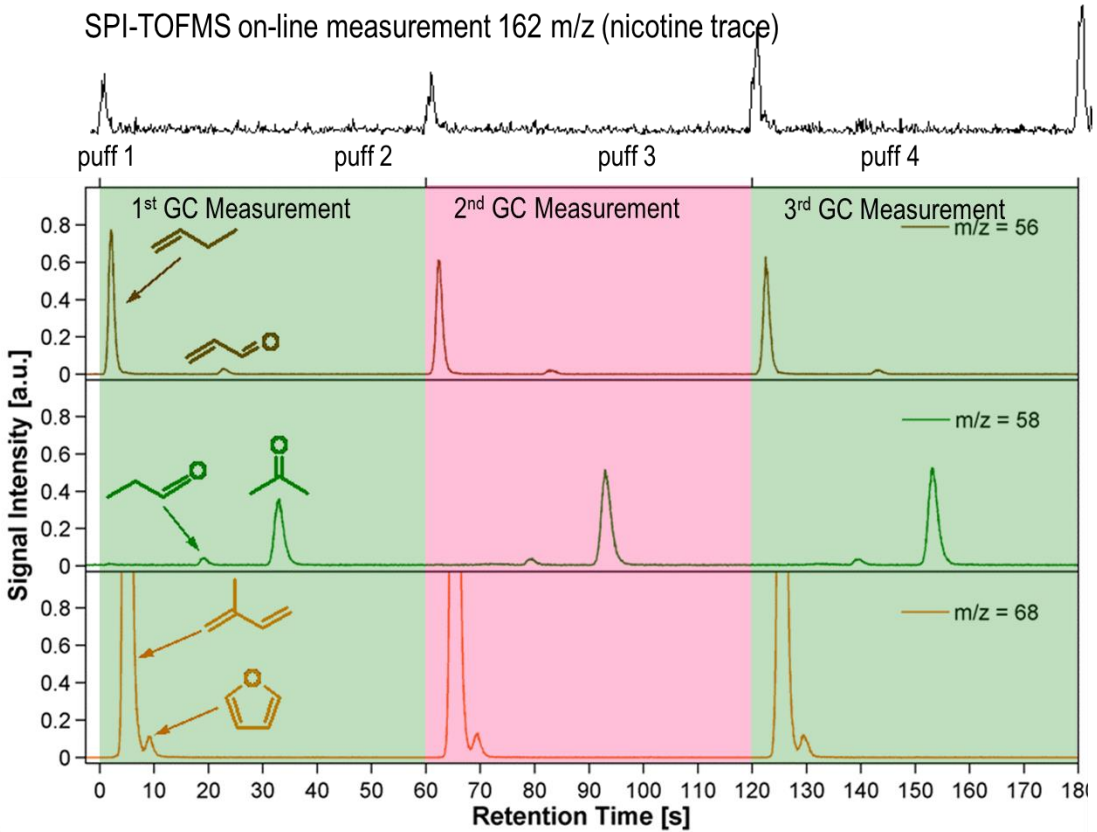
Outlook

On-line, puff-resolved GCxSPI-MS analysis



Outlook

On-line, puff-resolved GCxSPI-MS analysis



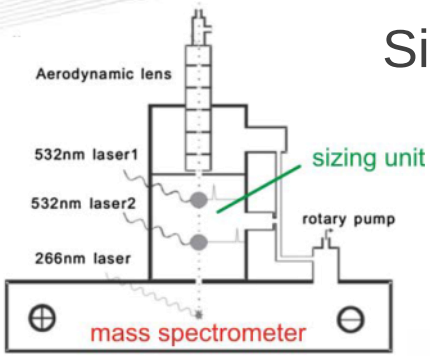
Acrolein vs. Butene

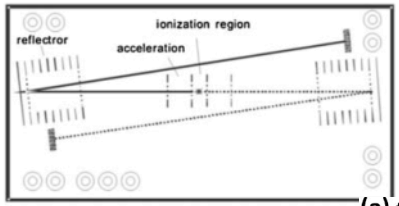
Aceton vs. Propionaldehyde

Isoprene vs. Furan

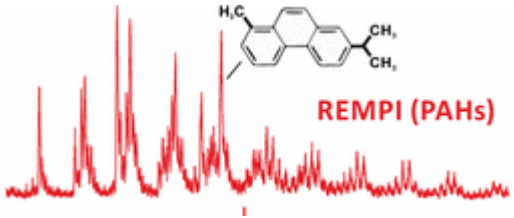
New Technique

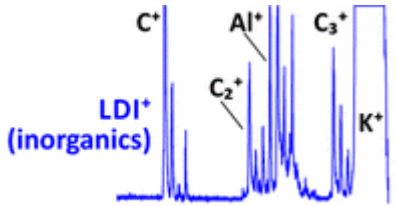
Single Particle MS (ATOF)

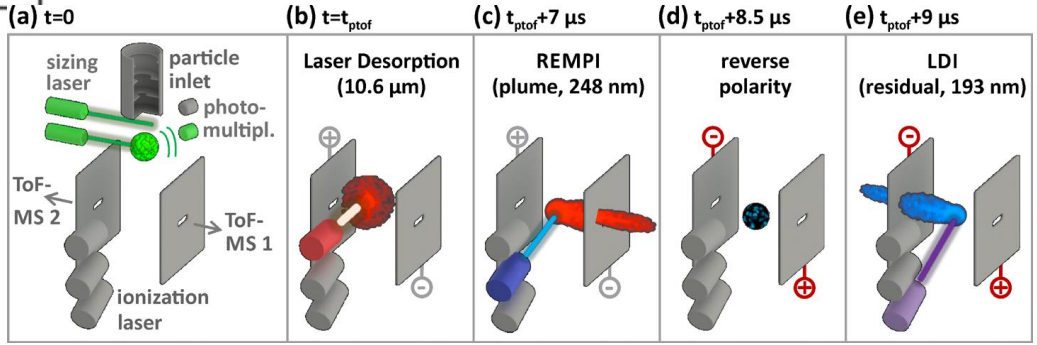




- Typically environmental aerosol analysis







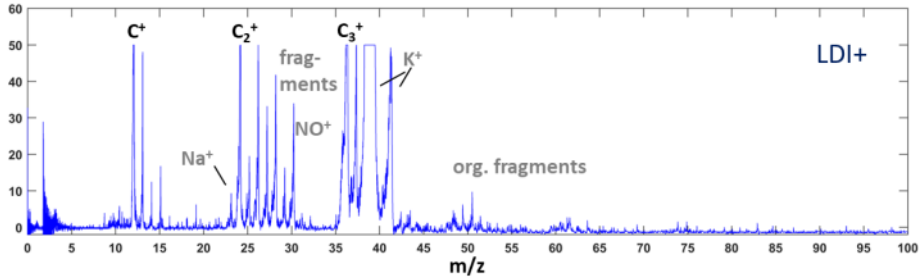
2017 Passig *et al.* Anal Chem

PHOTO-**ATOF-MS**
SINGLE PARTICLE ANALYZER

New Technique

Single Particle MS (ATOF)

Cigarette
soot dominated particle (size~0.7µm)



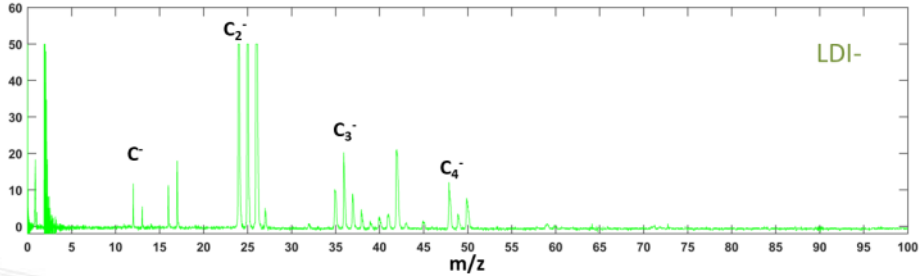
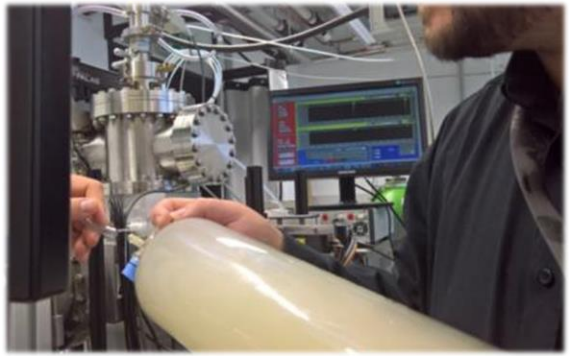


PHOTO-**ATOF-MS**
SINGLE PARTICLE ANALYZER



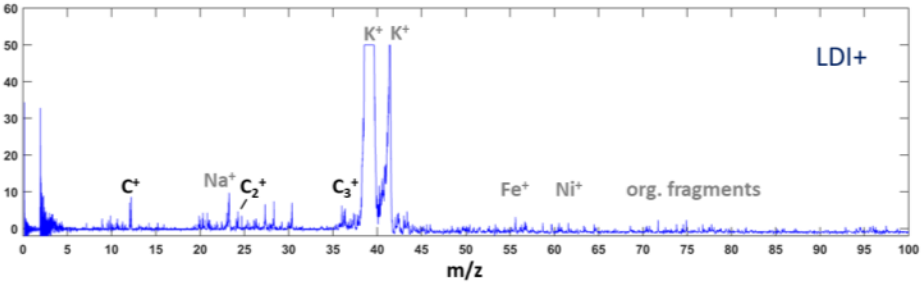
www.photonion.de

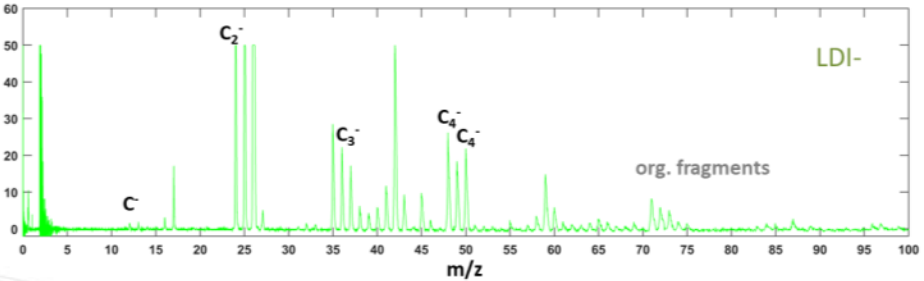
New Technique

Single Particle MS (ATOF)

Cigarette

Soot/organic particle (size~0.6µm)





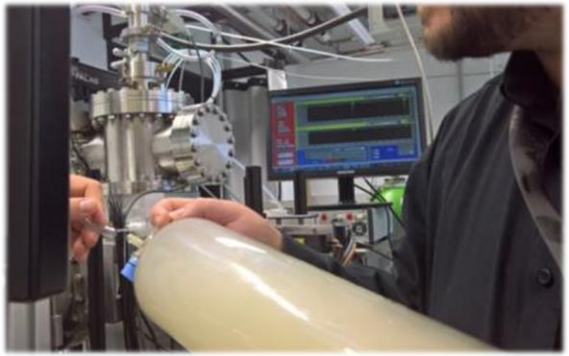


PHOTO-**ATOF-MS**

SINGLE PARTICLE ANALYZER

www.photonion.de

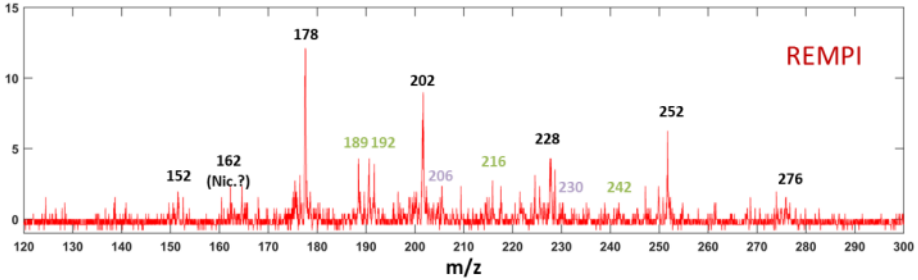
New Technique

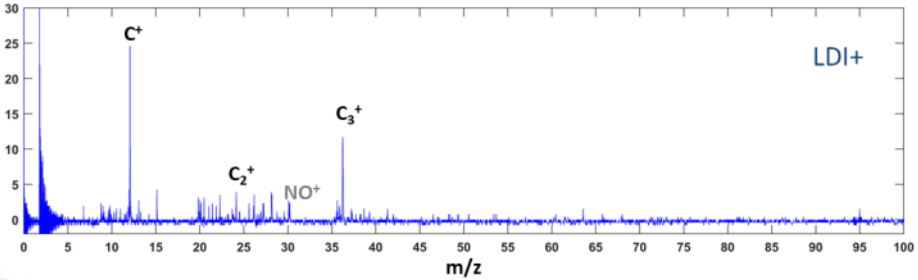
Single Particle MS (ATOF)

photonion

Cigarette

Soot/PAH particle (size~1.5µm)





number of aliphatic carbons	n = 0	n = 1	n = 2	n = 3	n = 4
PAHs	m/z				
naphthalene	128	142	156	170	184
acenaphthylene	152				
phenanthrene; anthracene	178	192	206	220	234, e.g., retene
pyrene; fluoranthene	202	216	230		
benzanthracene(s); benzphenanthrene(s)	228	242			
benzpyrene(s); benzfluoranthene(s)	252	266			
benz[ghi]perylene; indeno(1,2,3)[c,d]pyrene	276				
dibenzphenanthrene(s); dibenzanthracene(s)	278				

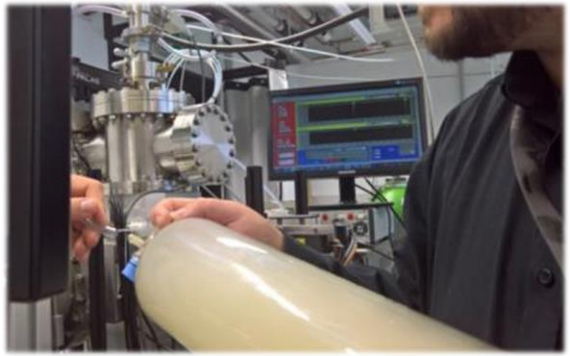


PHOTO-**ATOF-MS**

SINGLE PARTICLE ANALYZER

Summary

Online puff resolved PIMS

- Soft Photoionization (SPI/REMPI) Mass Spectrometry enables a puff by puff resolved investigation of smoking products legal/illegal ones
- Release of active or target compounds e.g. nicotine, THC can be identified and quantified
- PIMS is a technique for a fast and reliable analysis of complex gas mixtures

TG-PIMS
THERMOGRAVIMETRY- PHOTOIONIZATION MS

PHOTO-**TOF-MS**
EXPOSURE SYSTEM GAS ANALYZER

VITROCELL SYSTEMS

Unique flexible heated transfer line and customized sampling solution for the VITROCELL exposure module.

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

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

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Acknowledgement

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TG-PIMS
THERMOGRAVIMETRY- PHOTOIONIZATION MS

Thank you for you attention!

Universität Rostock Traditio et Innovatio
HelmholtzZentrum münchen
Deutsches Forschungszentrum für Gesundheit und Umwelt
JOINT MASS SPECTROMETRY CENTRE

PHOTO-TOF-MS
CUSTOMIZED GAS ANALYZER

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EXPOSURE SYSTEM GAS ANALYZER

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SMOKE ANALYZER

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