Puff-resolved on-line real-time analysis and quantification of tobacco smoke components by a commercial smoke profiler (Smoking machine - Photo Ionisation TOF-Mass Spectrometer system)

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Puff-resolved on-line analysis of cigarette smoke by photo ionization TOFMS

Total Yields of Smoke Constituents of the 2R4F Research Cigarette of Three Different Studies (ISO Smoking Machine Conditions)

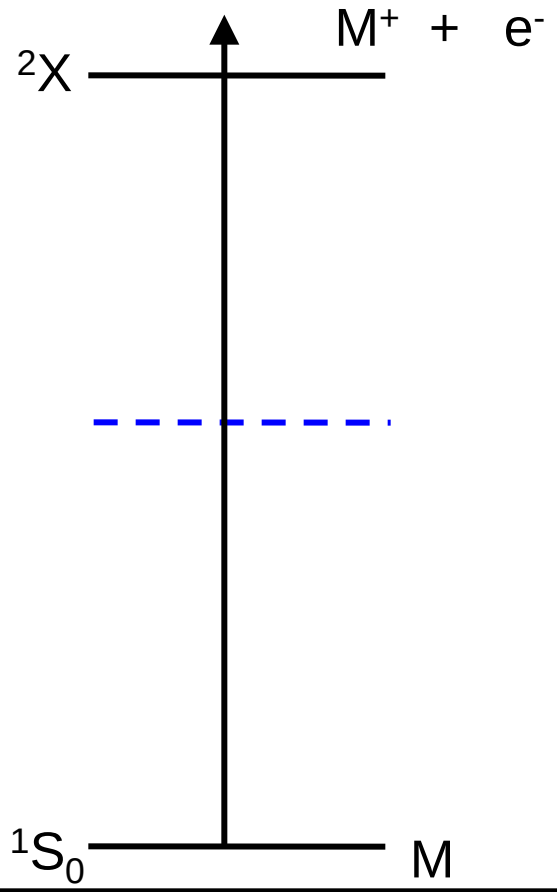
Laser SPI 118 nm

compound	SPI-TOFMS this work (1)	Chen et al. (2)	Wagner et al. (3)
	Whole Smoke		
NO [μg/cig]	309.6 ± 13.9	223.41	-
Acetaldehyde [μg/cig]	527.1 ± 26.7	560.48; 583.74 ± 13.18[a]	562
Butadiene [μg/cig]	38.5 ± 2.2	29.94	37.1
Acetone [μg/cig]	265.1 ± 15.1	264.74; 261.62 ± 7.35[a]	248
Isoprene [μg/cig]	397.2 ± 15.3	297.68	391
Benzene [μg/cig]	48.2 ± 3.6	43.39	51.8
Toluene [μg/cig]	84.5 ± 4.3	64.91	88.0
	"Gas Phase"		
Acetaldehyde [μg/cig]	310.7 ± 17.6	396.78 ± 71.02	–
Acetone [μg/cig]	148.1 ± 9.6	205.52 ± 8.35	–

1) Adam, T., Mitschke, S., Streibel, T., Baker R.R., and Zimmermann R. ; Chem. Res. Toxicol. 2006, 19, 511-520
2) Chen, P. X., and Moldoveanu, S. C. (2003) Beitr.Tabakforsch. Int. 20 (7), 448-458.
3) Wagner, K. A., Higby, R., and Stutt, K. (2005) Beitr.Tabakforsch. Int. 21 (5), 273-279.

Single photon ionisation (SPI)

Mass spectrometry with soft photo ionisation: SPI-MS

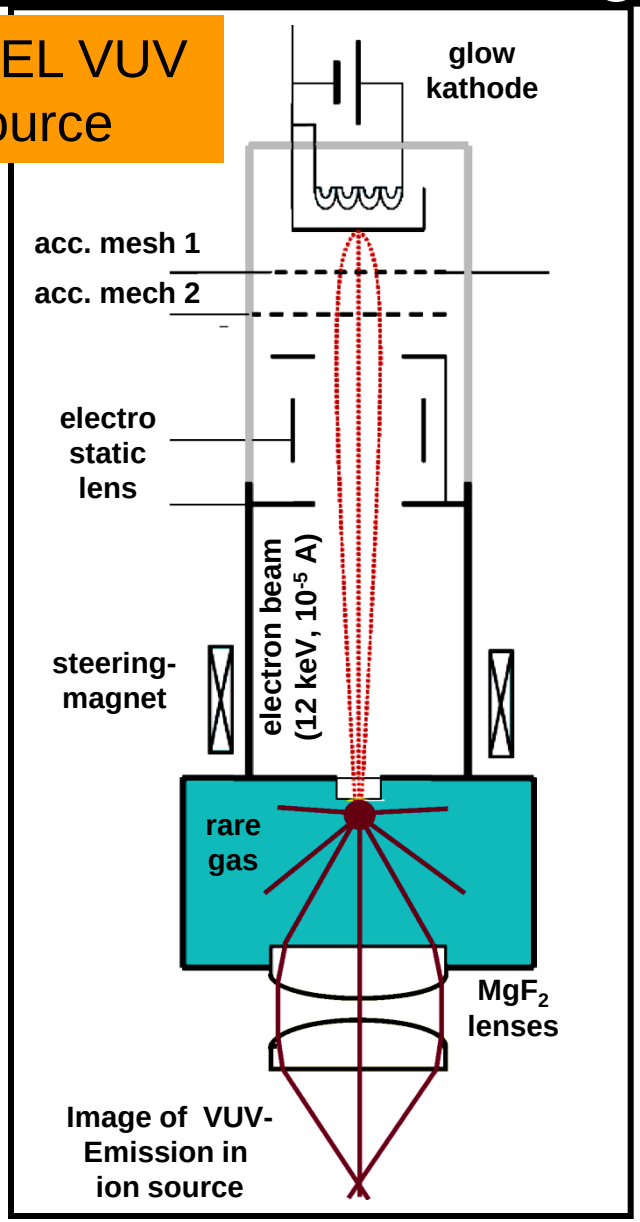


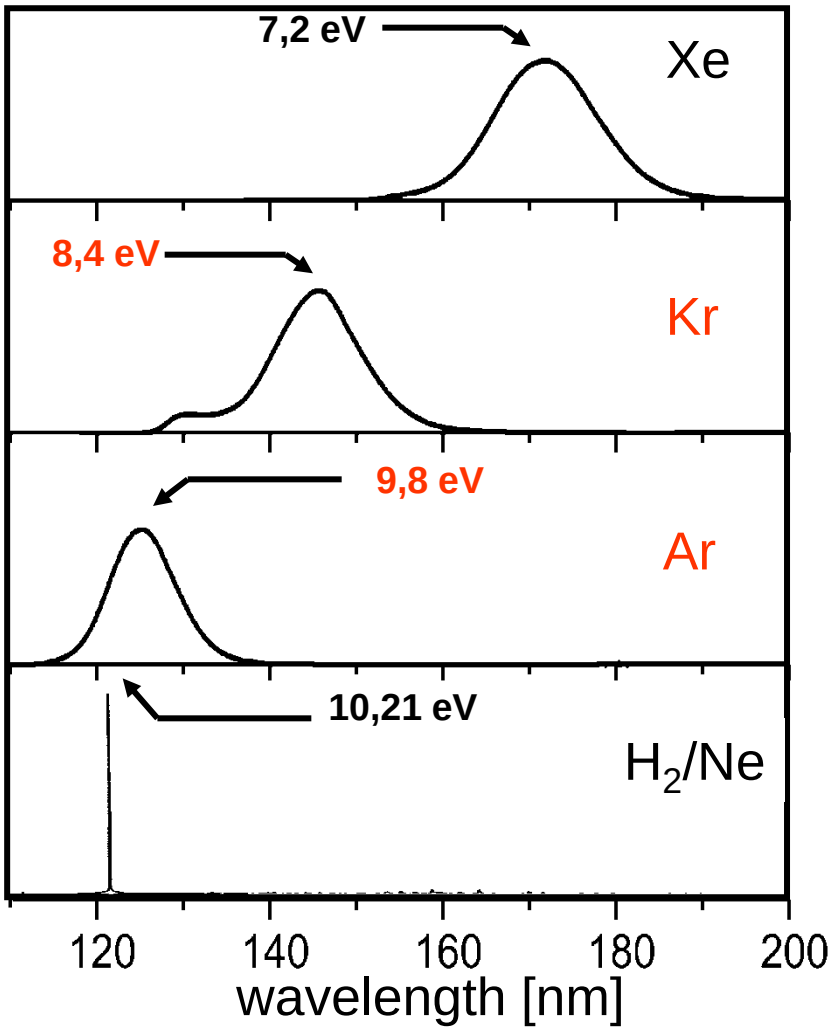
Single Photon Ionisation (SPI):

- photon energies 8 - 12 eV (VUV range)
- **soft ionisation** (molecular ions, no fragments)
- matrix supression (small molecules/carrier gas)
- universal ionisation of organic compounds
- VUV photon generation:
  - novel incoherent VUV light sources (EBEL)
  - third harmonic generation with UV laser pulses (Nd:YAG 355 nm → 118 nm)

On-Line SPI-TOFMS Smoke Analysis with high power VUV light source

The EBEL VUV light -source





Different rare gases – different wavelengths

photonion

On-Line SPI-TOFMS Smoke Analysis: Special valve, transfer line and inlet MS set-up

Special Coupling of SPI-TOFMS Analyser and Smoking Machine

Clean air

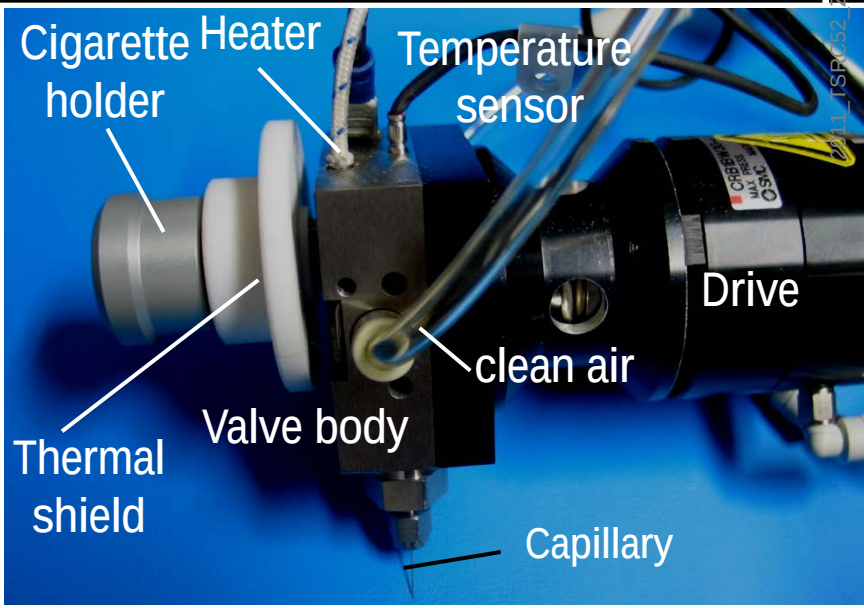
Heated valve

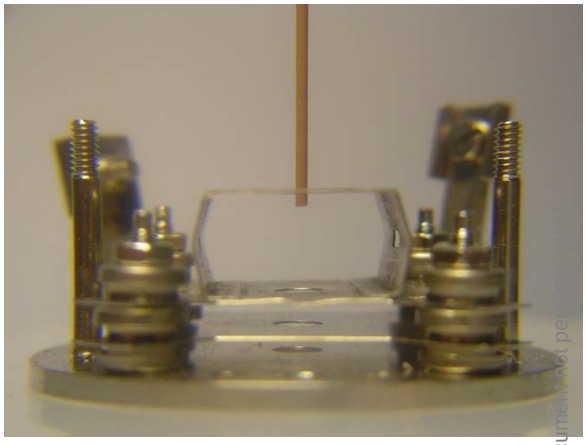
TOF Analyser

Heat protectection

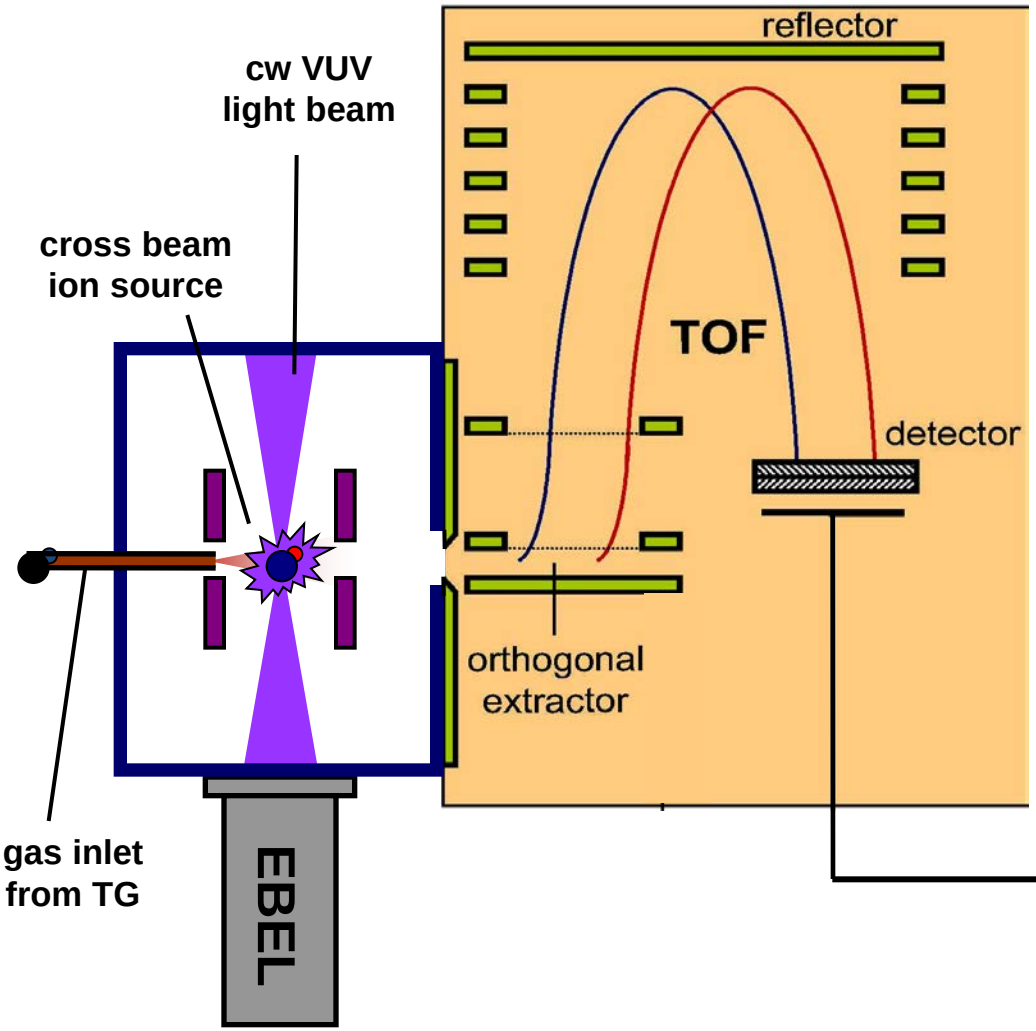
Exhaust

Syringe



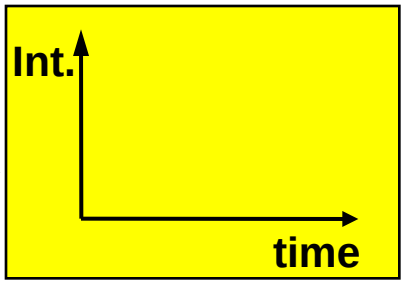


On-Line SPI-TOFMS Smoke Analysis: Fast – oaTOF mass analyzer



Compact orthogonal acceleration TOF mass analyzer:

- **fast (~50 kHz rep. rate)**
- **scan-free**
- **sensitive**
- **mass resolution m/Δm ~ 700**



Set-up:
LM2x-TOF-MS Smoke Profiler (Borgwaldt KC)

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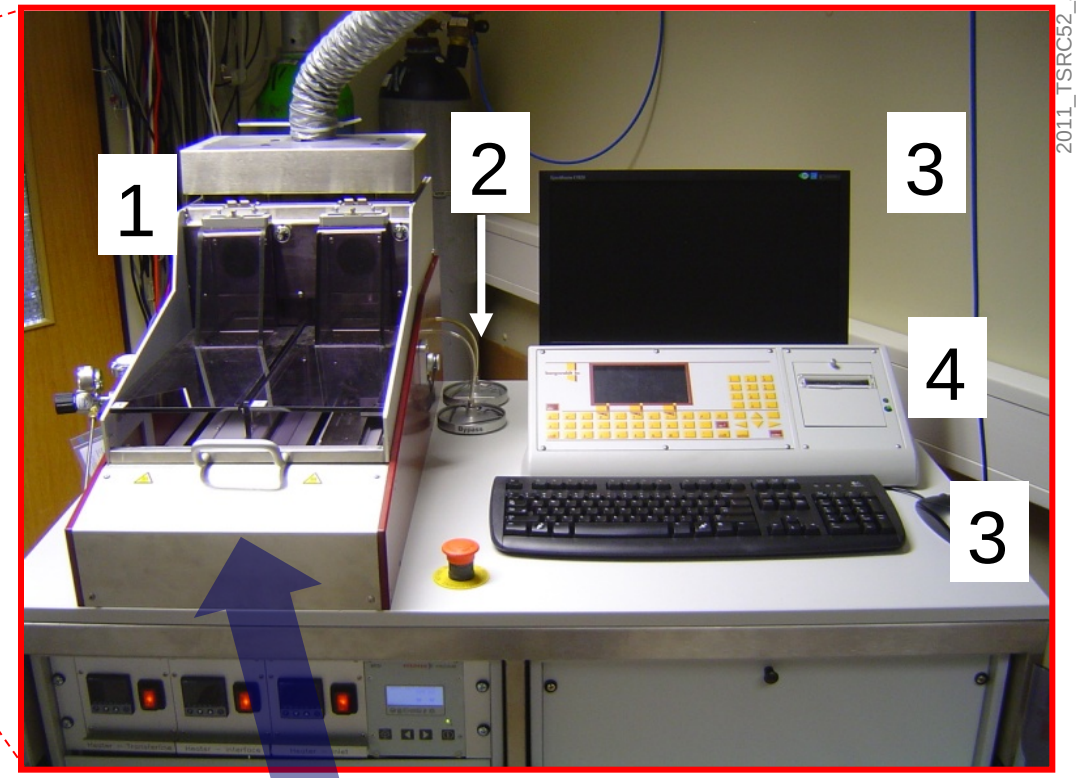
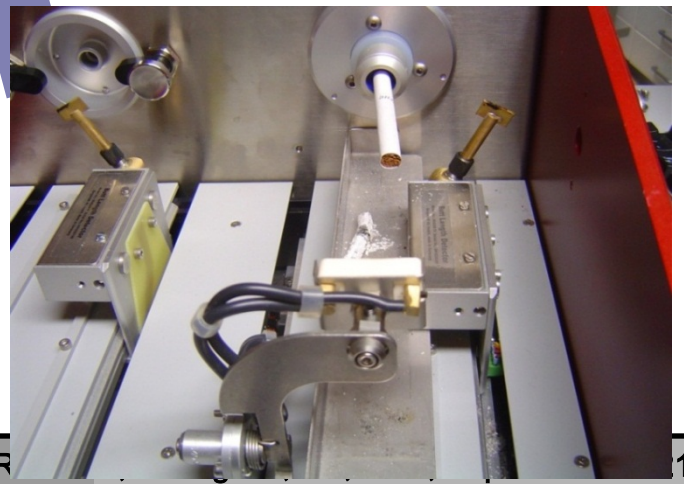
Frontside



1) ISO-Hood
2) Filter holder (Bypass and Pump)
3) Control panel for the MS and the EBEL-VUV-Light Source
4) Control Panel for the smoking machine



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LM2x-TOF-MS Smoke Profiler (Borgwaldt KC)

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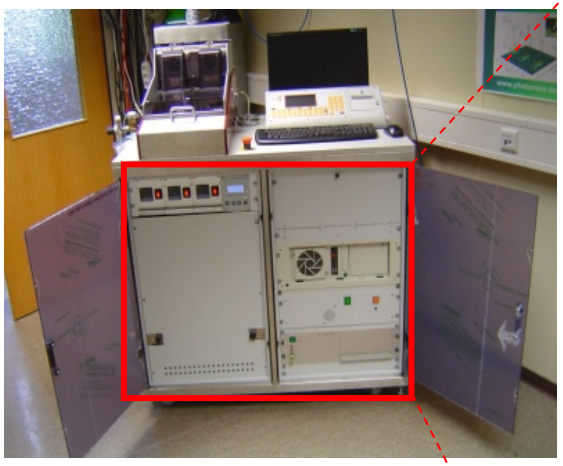
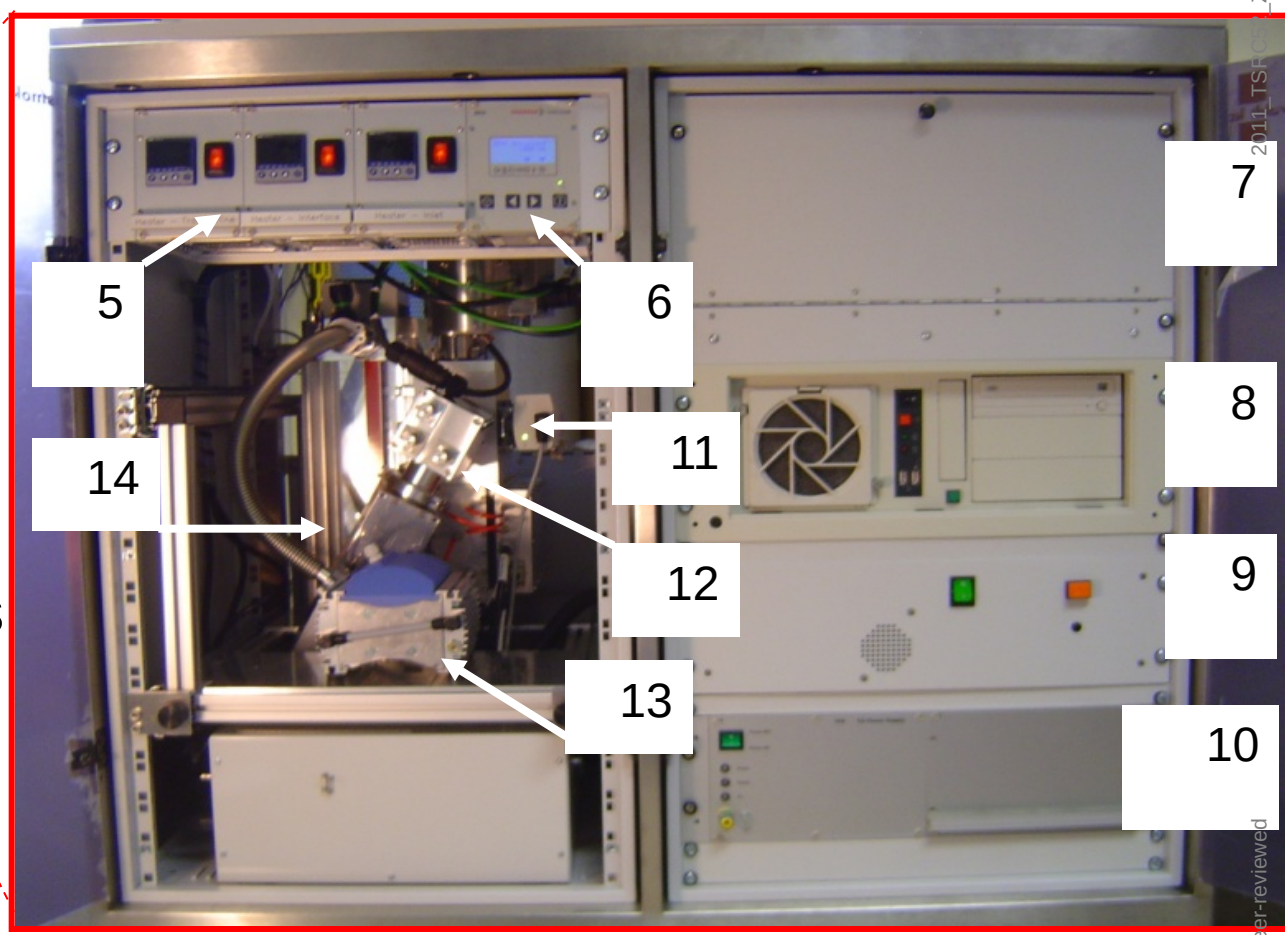


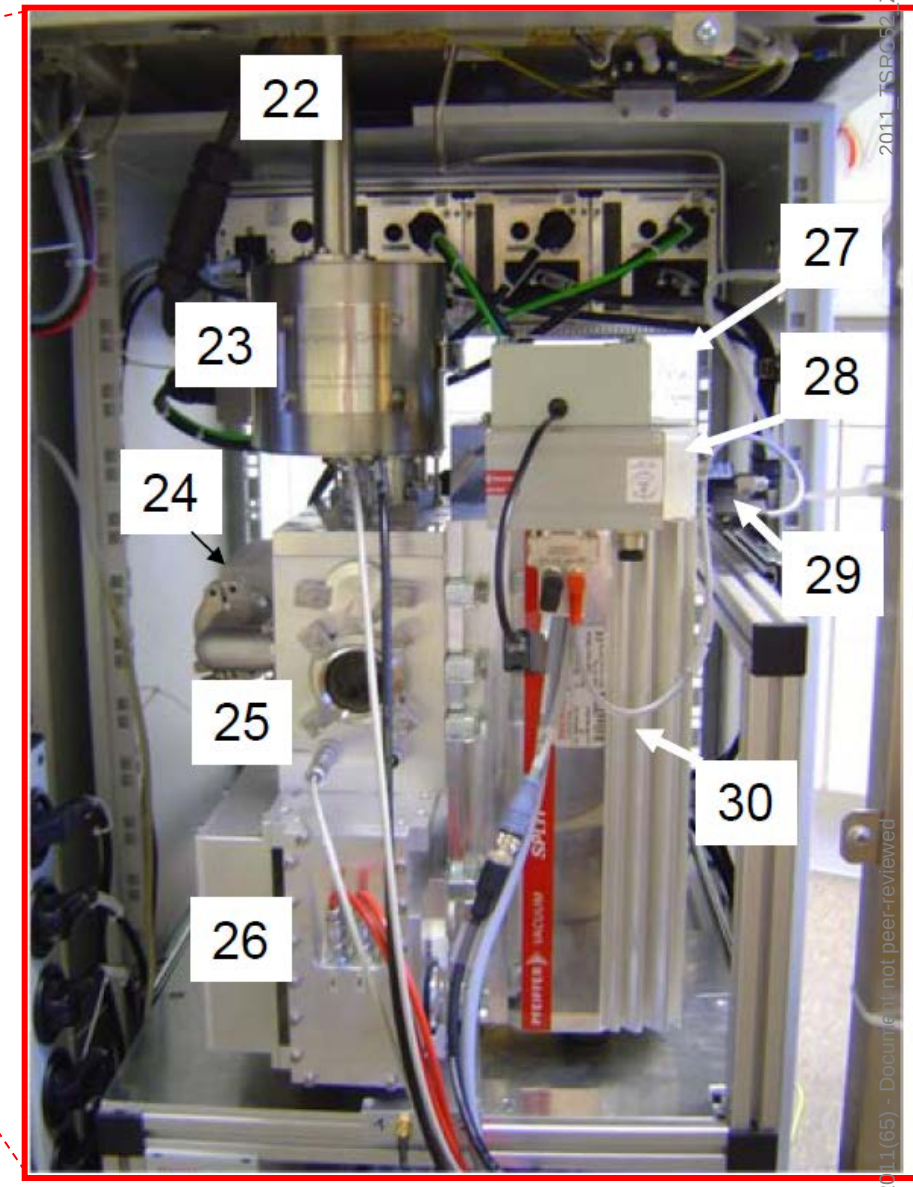


5) Heater control units
6) Turbo pump controler
7) Syringe pump for smoking machine
8) Computer
9) EBEL-power supply
10) Power supply MS
11) Pressure gauge
12) Ellipsoid VUV mirror module
13) Rough pump
14) EBEL VUV-Lightsource

Set-up:
LM2x-TOF-MS Smoke Profiler (Borgwaldt KC)

Back side

22) Transfer line (T up to 250°C
23) Interface (T up to 250°C)
24) Pressure Gauge.
25) Ion source window
26) TOF Mass spectrometer
27) turbo pump cooling fan
28) turbo pump electronics
29) Venting valve.
30) Split flow turbo pump



Technical data: LM2x-TOF-MS Smoke Profiler (Borgwaldt KC)

LM2X Smoking Machine:

Configuration:
19“-module rack, two syringes smoking train, microprocessor/ stepper motor contollrd

Cigarette samples:
60-120 mm

Diameter of cigarette samples:
4.5 to 9 mm

Total dimensions (WxDxH):
1130x800x1250 mm

Power supply:
100-230V, 50/60Hz

Puff volume/duration:
V: 5-100 mL in 1s, 5-150mL in 2s
D: 1-9.9s

Puff shape:
Programmable (ISO, Intense, human smoking profile replication)

Interface:
1xRS232

Photo-TOF Smoke Analyzer:

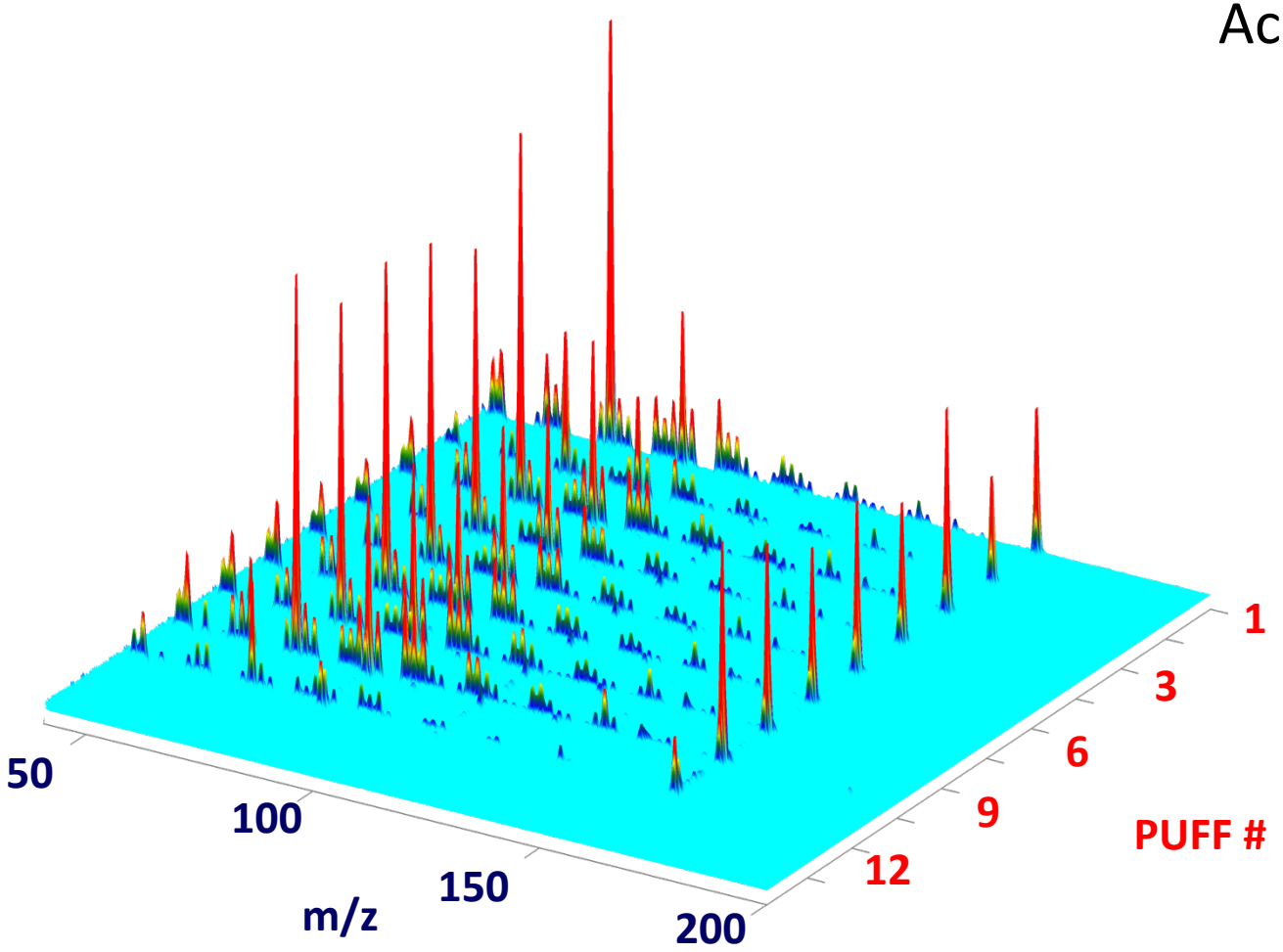
Special Inlet System:
- Deactivated quartz transfer line
- Whole smoke/gas phase analysis
- Interface/inlet system/transfer line heated to 250°C

VUV-photo ionization light source:
- Electron-beam pumped argon excimer vacuum ultraviolet light source (EBEL) with 9.8 eV photon energy (126 nm) & MgF_2 coated ellipsoidal mirror or refractive VUV-optics

oaTOF-Mass analyzer:
- Mass range/resolution: 1-600 m/z m/Δm = 700
- Dynamic range: 10^6
- Detection limit (Benzene): 100 ppb
- Max. prim. DAQ-rate: 100kHz/MS rec. rate: 50 Hz
- Acquisition hardware: On-board mass spectra accumulation
- Soft EBEL SPI ionization mode (standard) and hard electron ionization mode (EI, 70 eV)

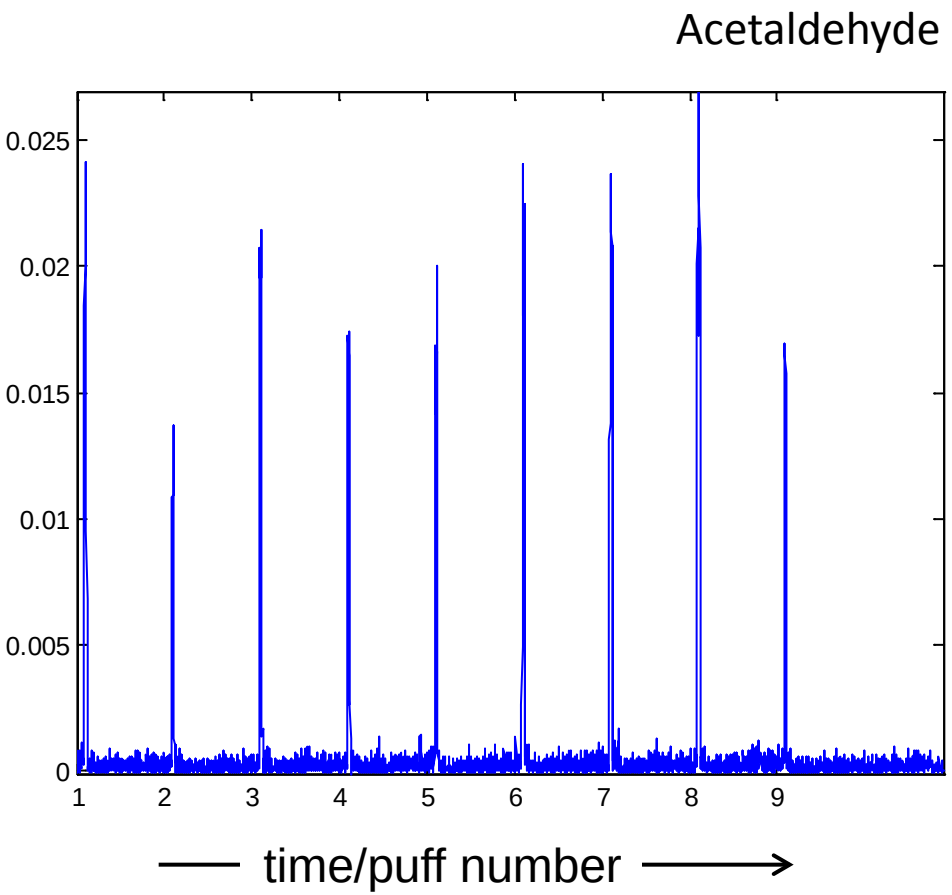
LM2x-TOF-MS Smoke Profiler: 3 D data set of a cigarette measurement

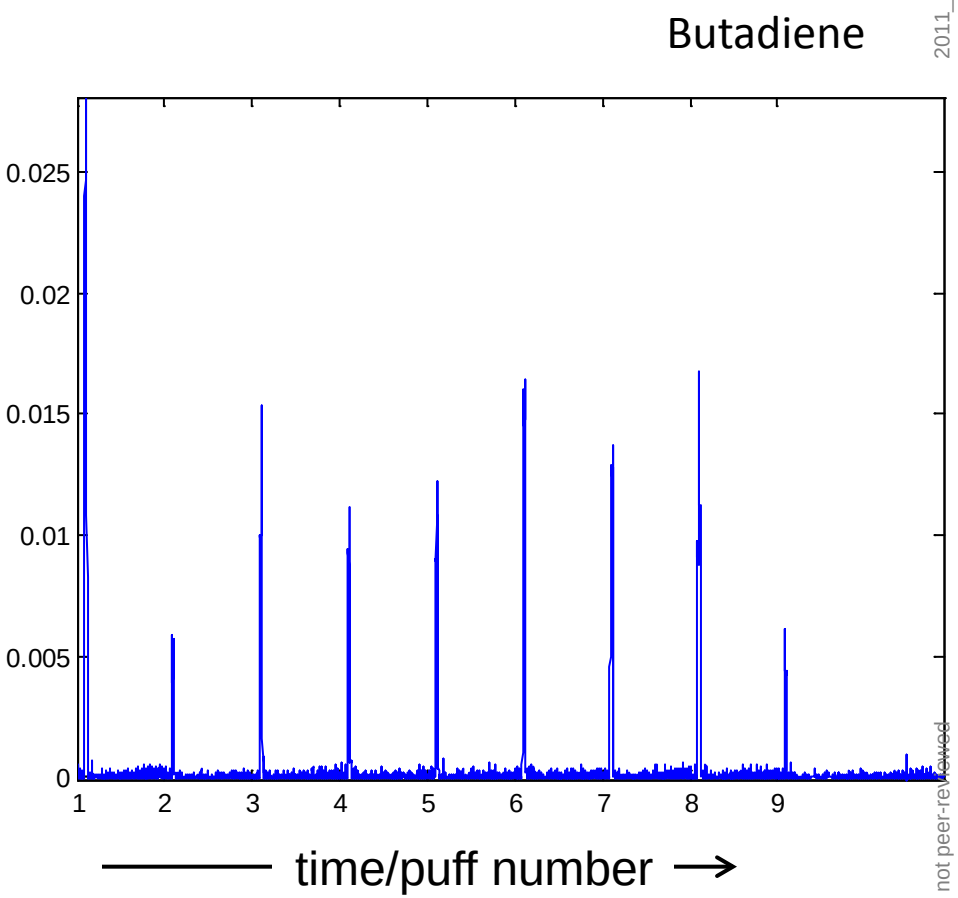
Full smoking profile of cigarette (CM6)



Acetaldehyde = 44 m/z
Butadiene = 54 m/z
Aceton = 58 m/z
Isoprene = 68 m/z
Butanone = 72 m/z
Benzene = 78 m/z
Toluene = 92 m/z
Nicotine = 162 m/z

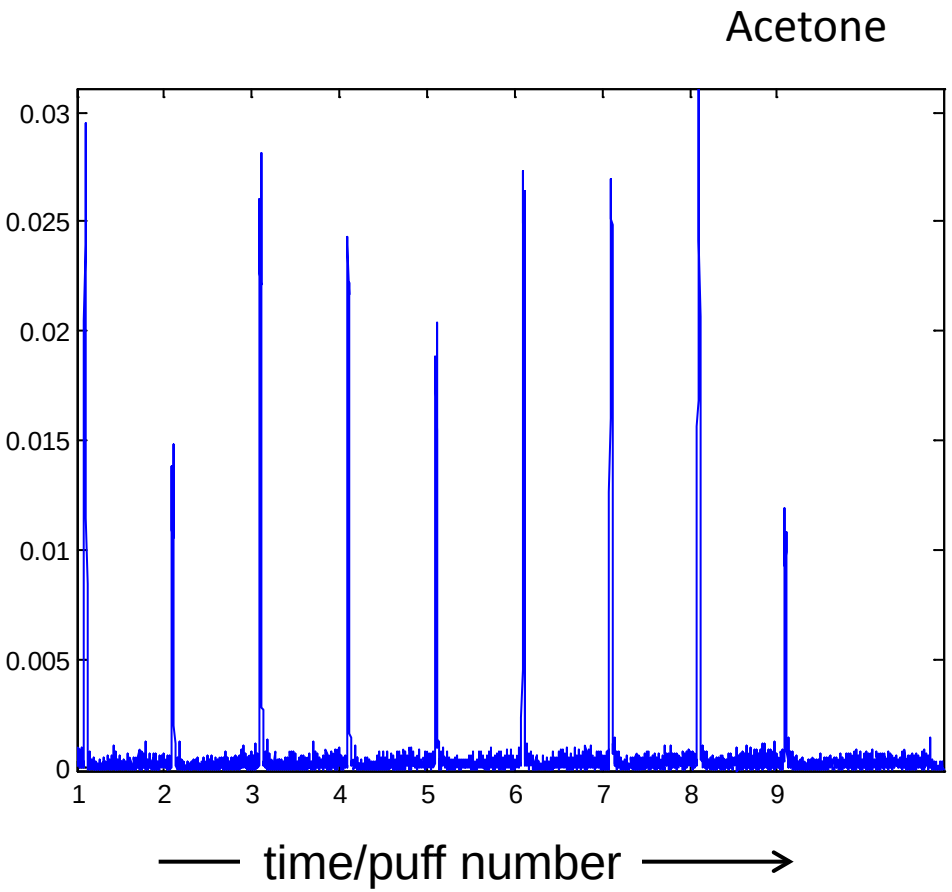
LM2x-TOF-MS Smoke Profiler: 2D puff profiles for selected compounds (m/z)

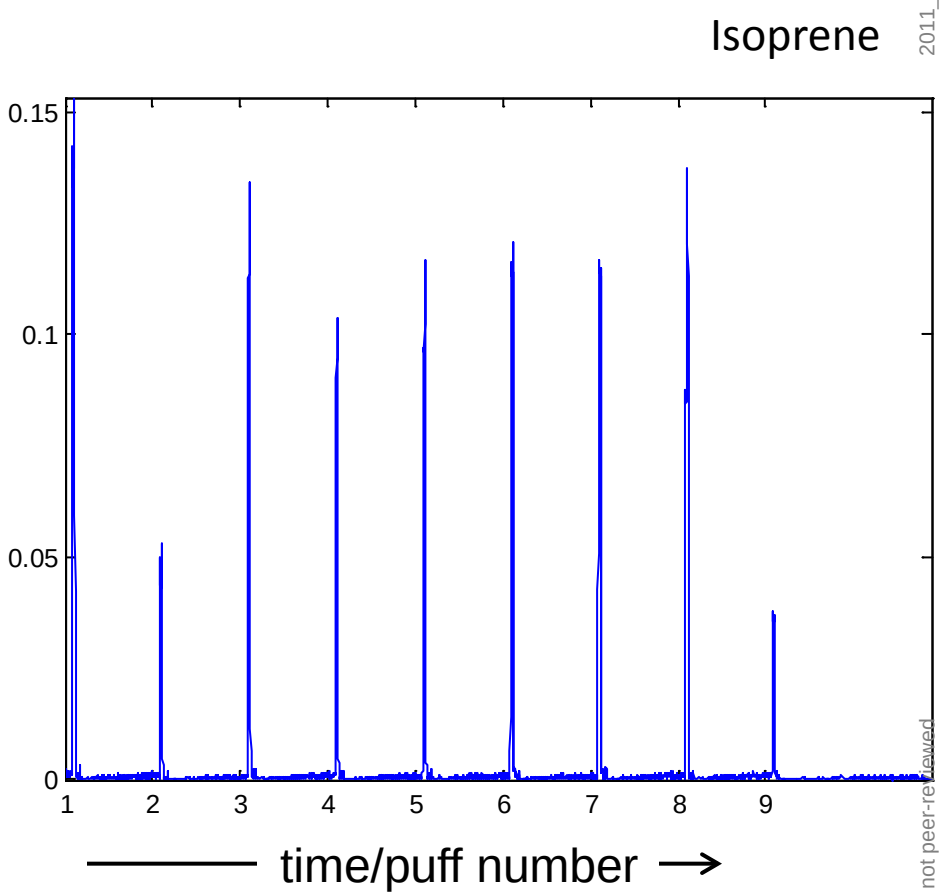




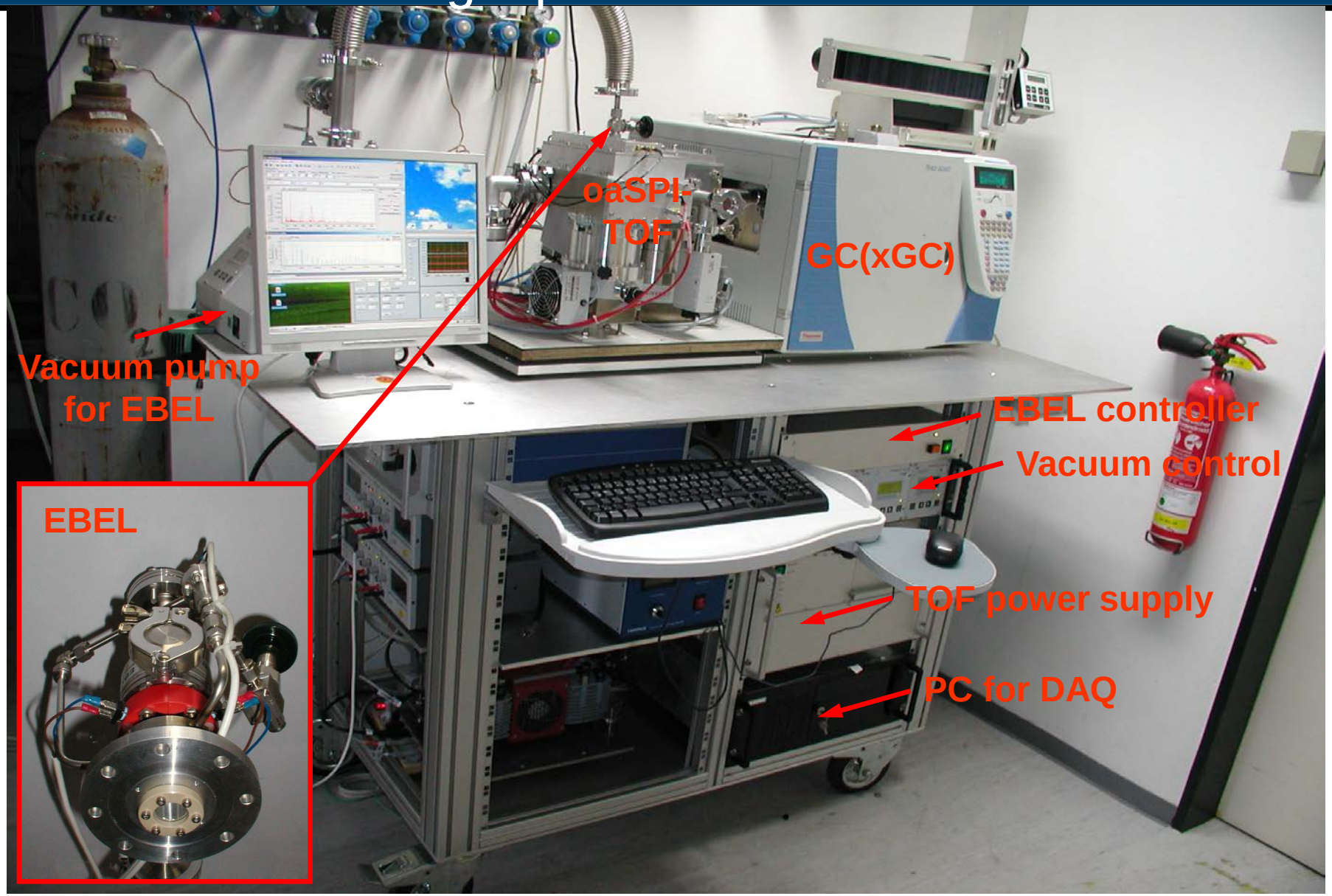
➔ Cleaning puffs not anymore visible in mass spectra

LM2x-TOF-MS Smoke Profiler: 2D puff profiles for selected compounds (m/z)





LM2x-TOF-MS Smoke Profiler: Quantification via single photon ionization cross sections



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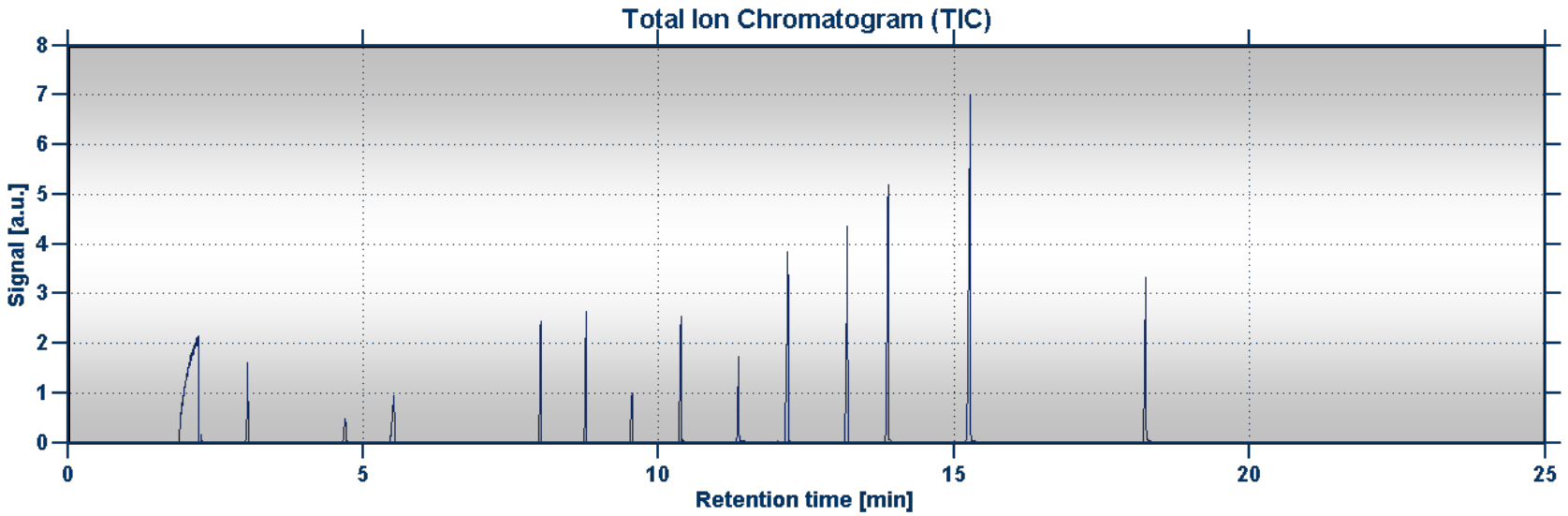

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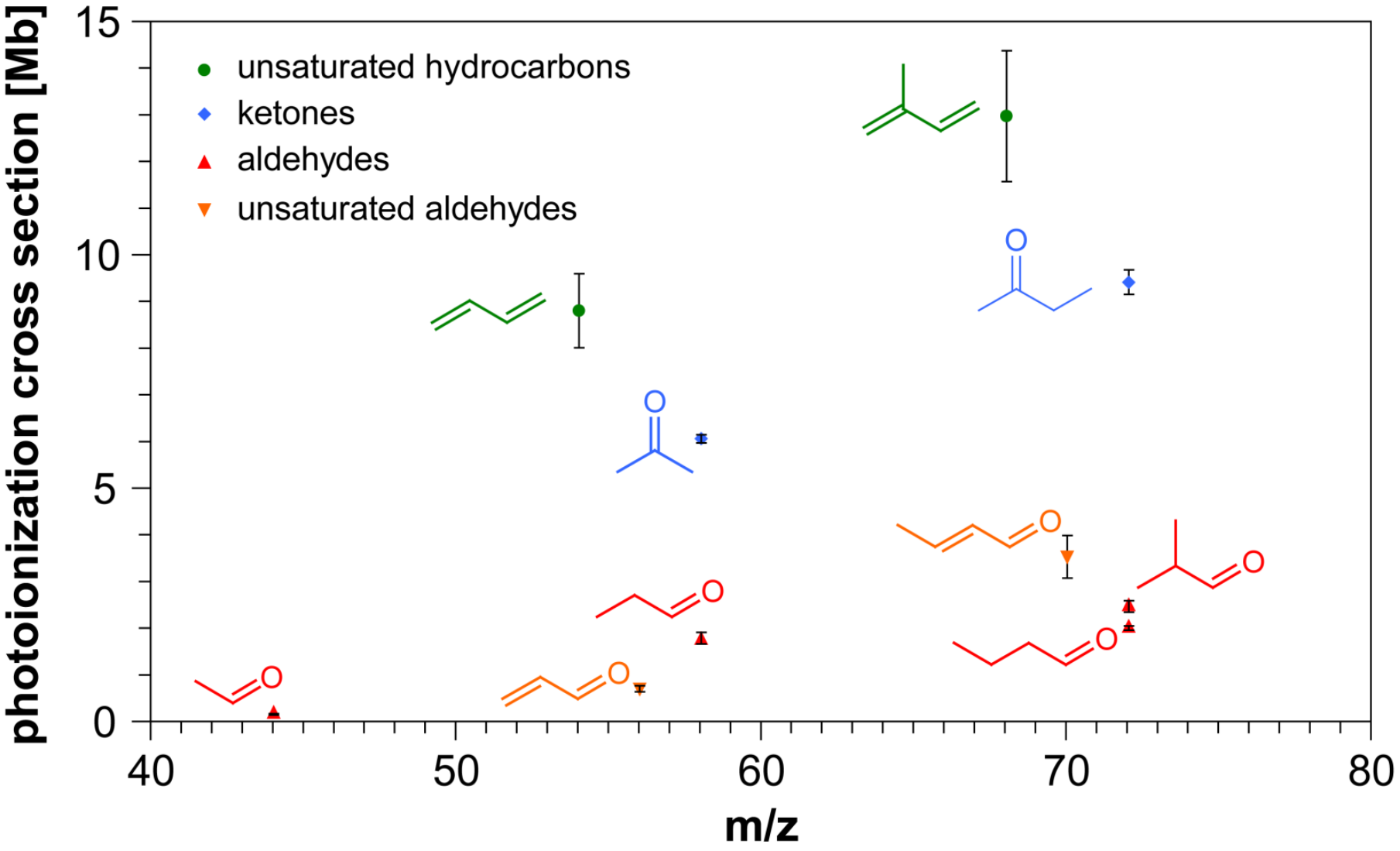
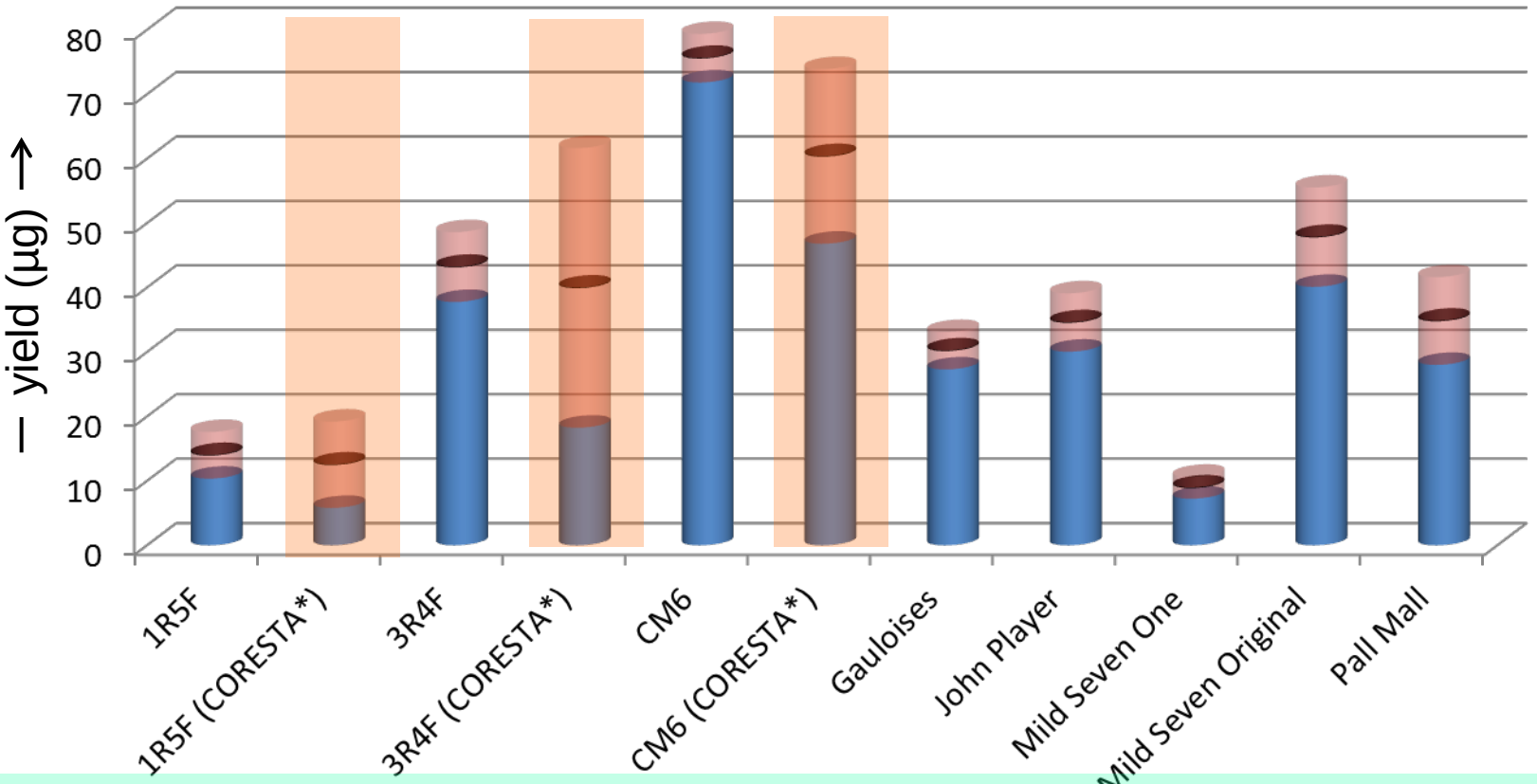


LM2x-TOF-MS Smoke Profiler: Quantification of butadiene



1) Michael Intorp, Steve W. Purkis , and Wendy Wagstaff, Beiträge zur Tabakforschung International/Contributions to Tobacco Research, Volume 24, 2011, 244-251

2) Michael Intorp and Steve Purkis, Beiträge zur Tabakforschung International/Contributions to Tobacco Research,Volume 24 , 2011, 174-168

3) Michael Intorp, Steve Purkis, Martin Whittaker, and Wendy Wright, Beiträge zur Tabakforschung International/Contributions to Tobacco Research, Volume 23, 2009, 161-202

Beiträge zur Tabakforschung International/*Contributions to Tobacco Research* Volume 24 · No. 4 · January 201

Determination of Selected Volatiles in Cigarette Mainstream Smoke. The CORESTA 2008 Joint Experiment*

by

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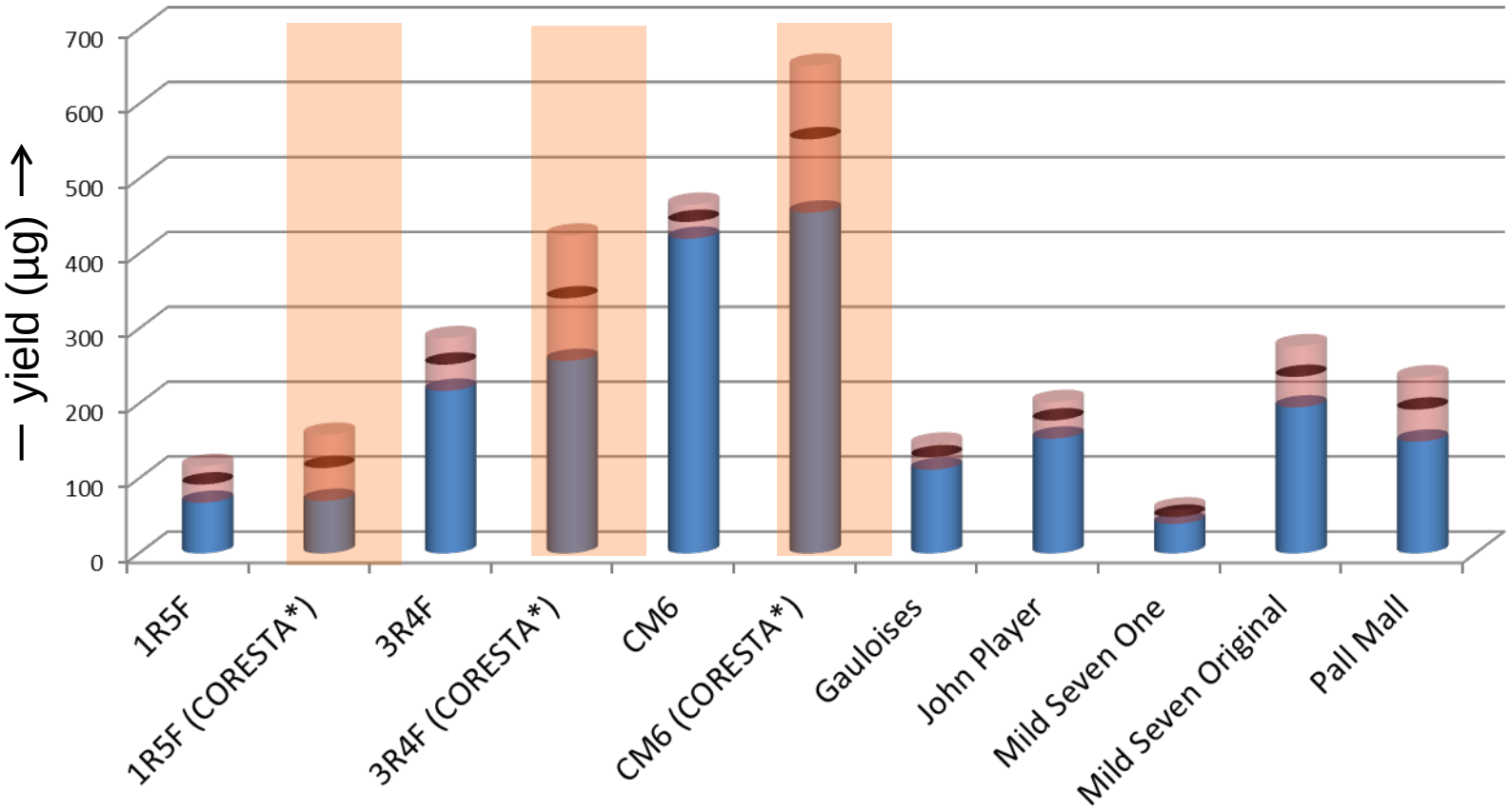
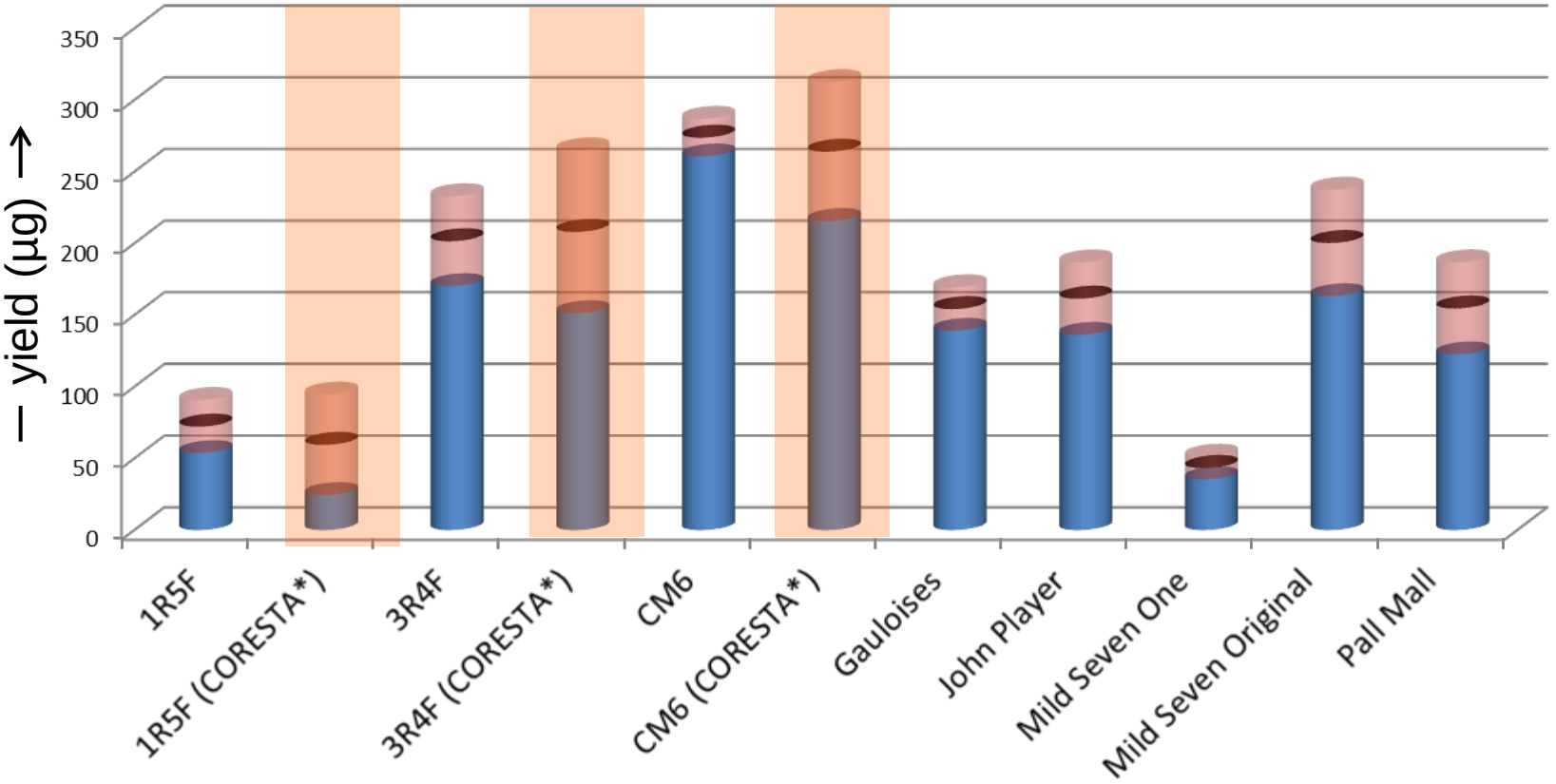
[2] Imperial Tobacco Limited, PO Box 244, Southville, Bristol BS99 7UJ, UK

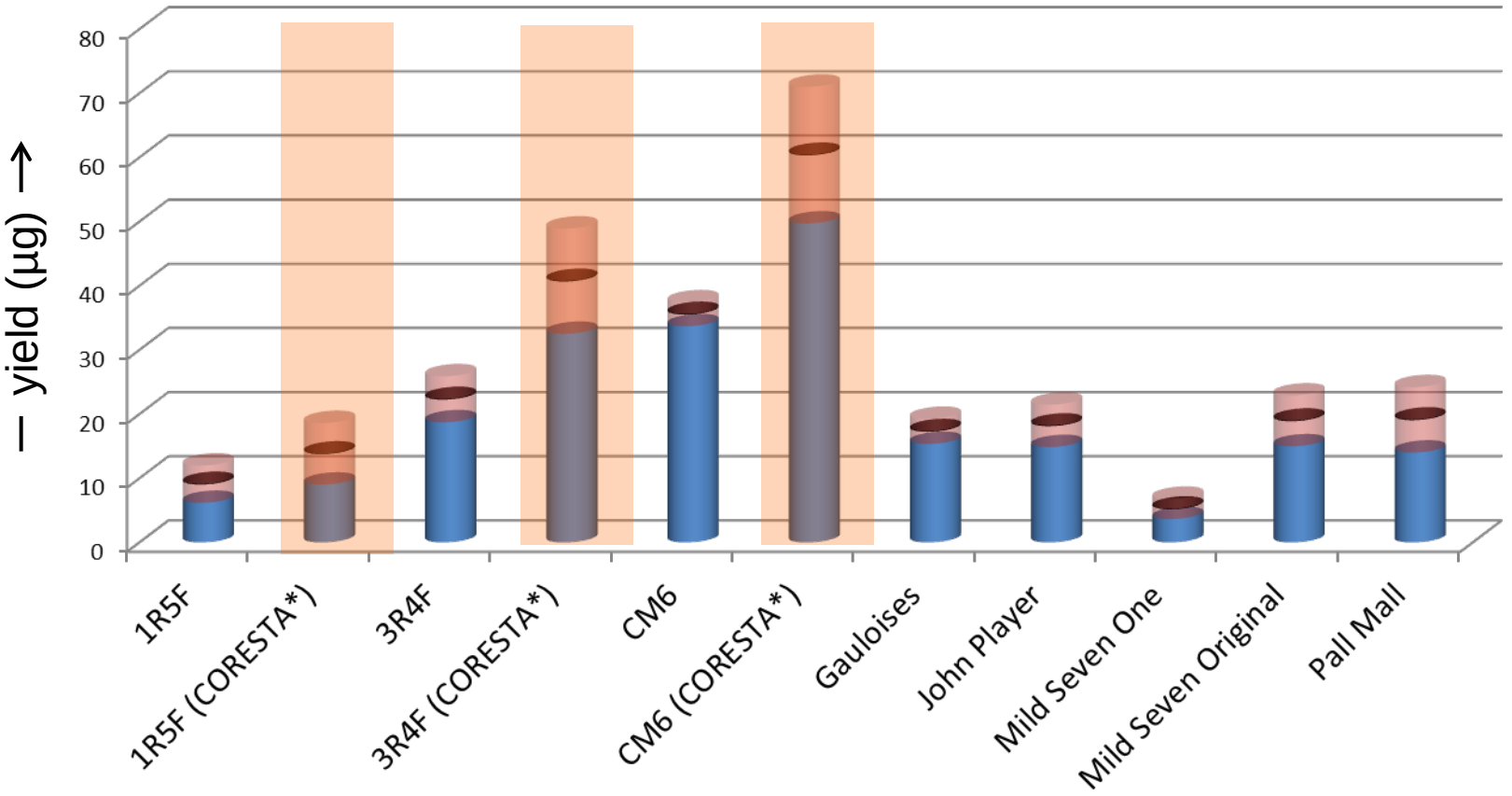
LM2x-TOF-MS Smoke Profiler: Quantification of isoprene



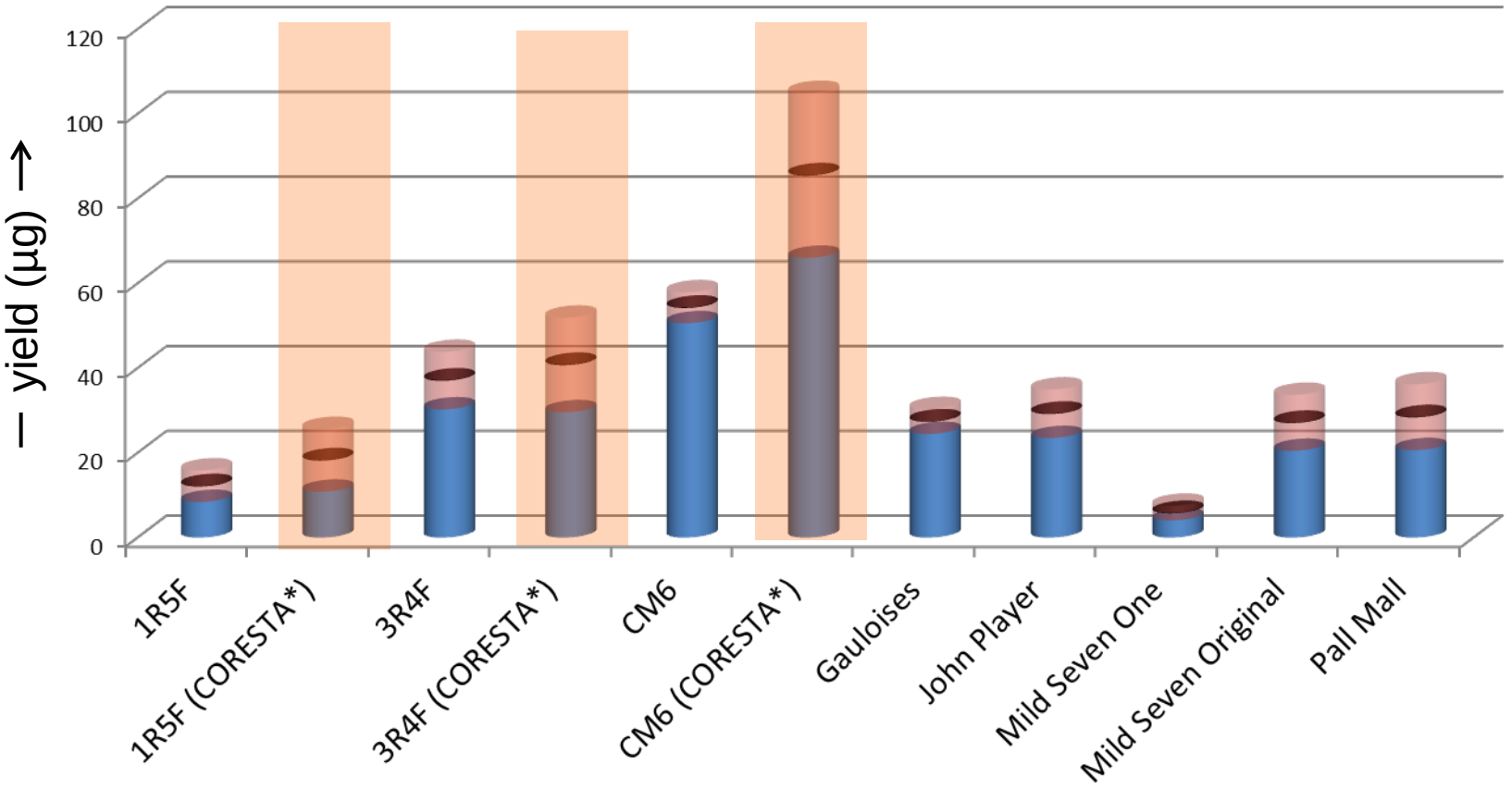
LM2x-TOF-MS Smoke Profiler: Quantification of acetone



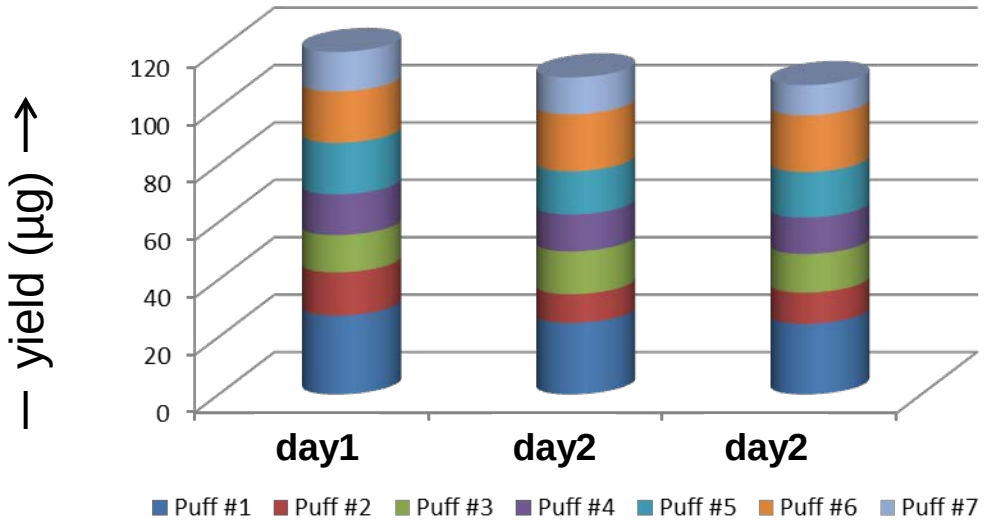
LM2x-TOF-MS Smoke Profiler: Quantification of benzene



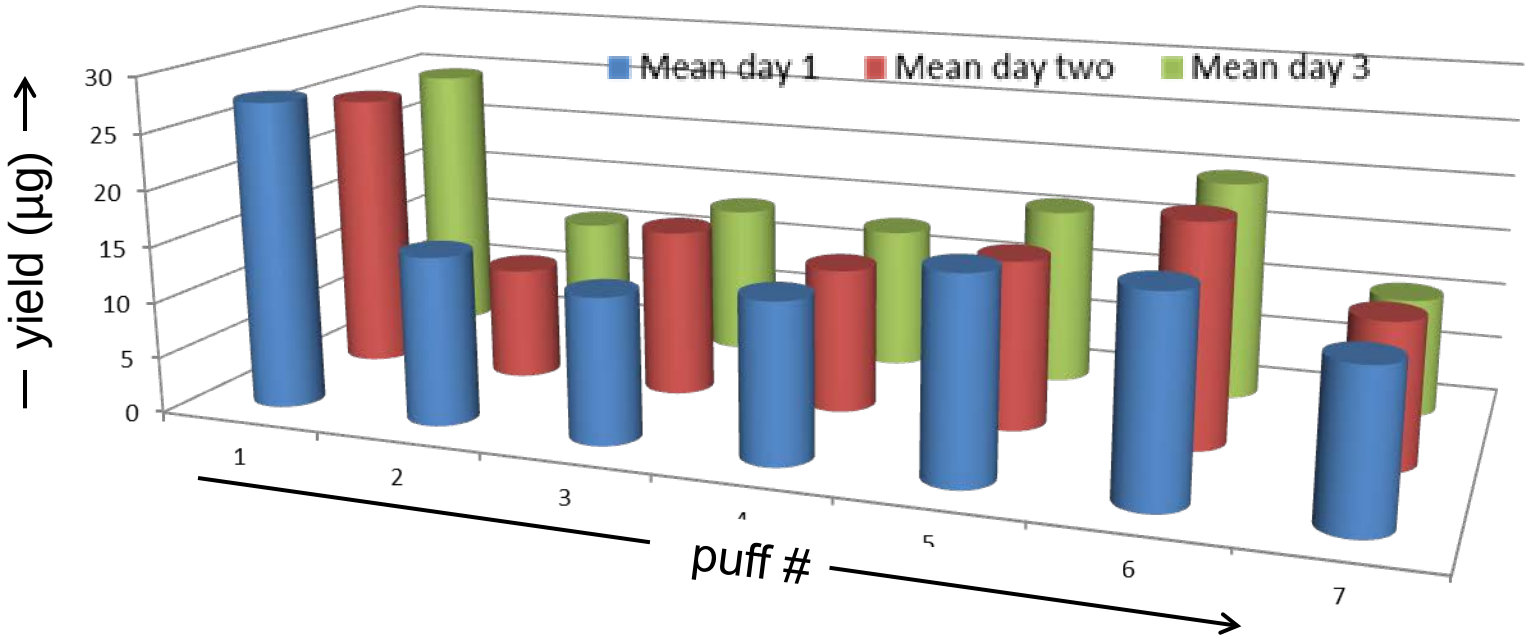
LM2x-TOF-MS Smoke Profiler: Quantification of toluene



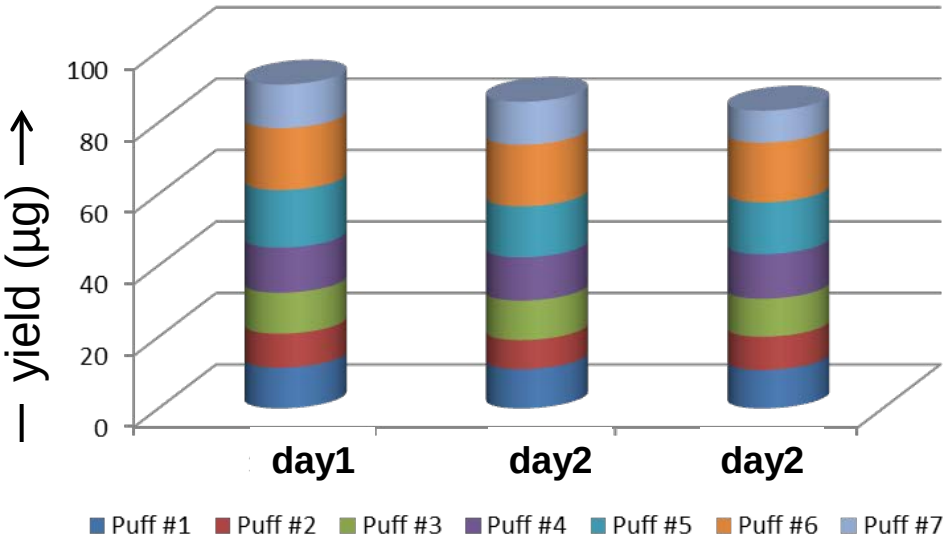
Reproducibility: Quantification of isoprene on consecutive days (1R5F) without recalibration



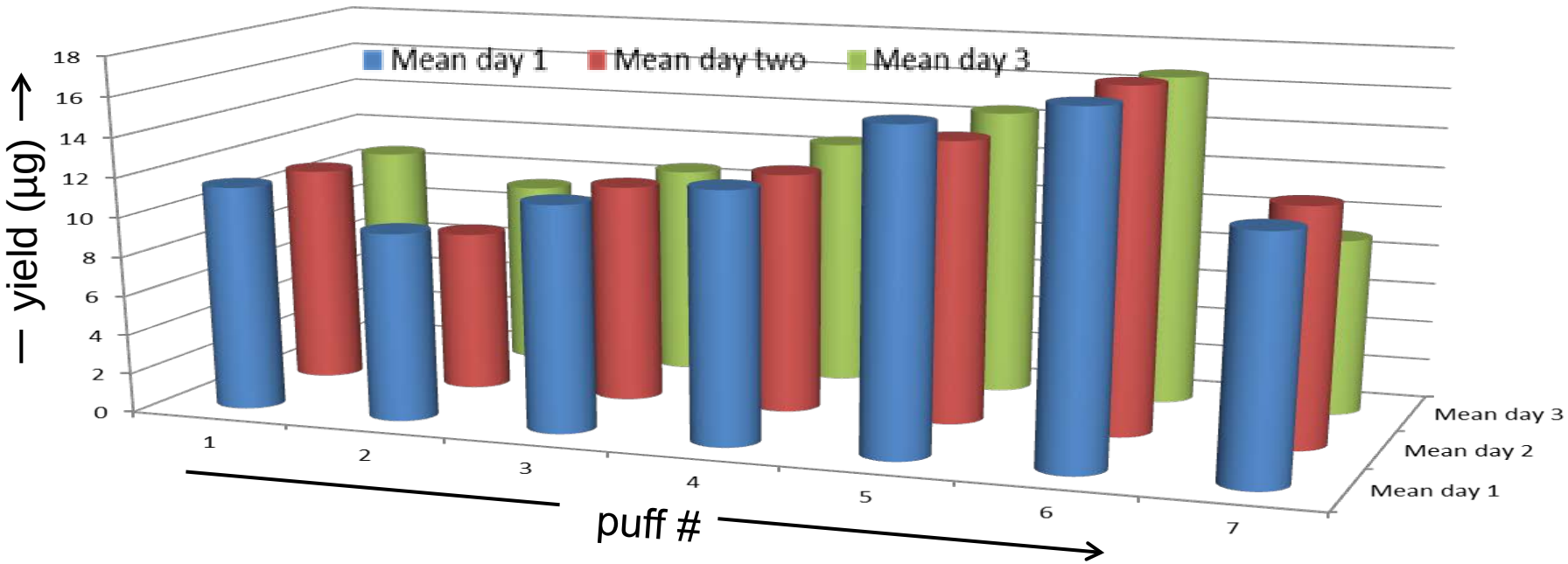
Isoprene 68 m/z



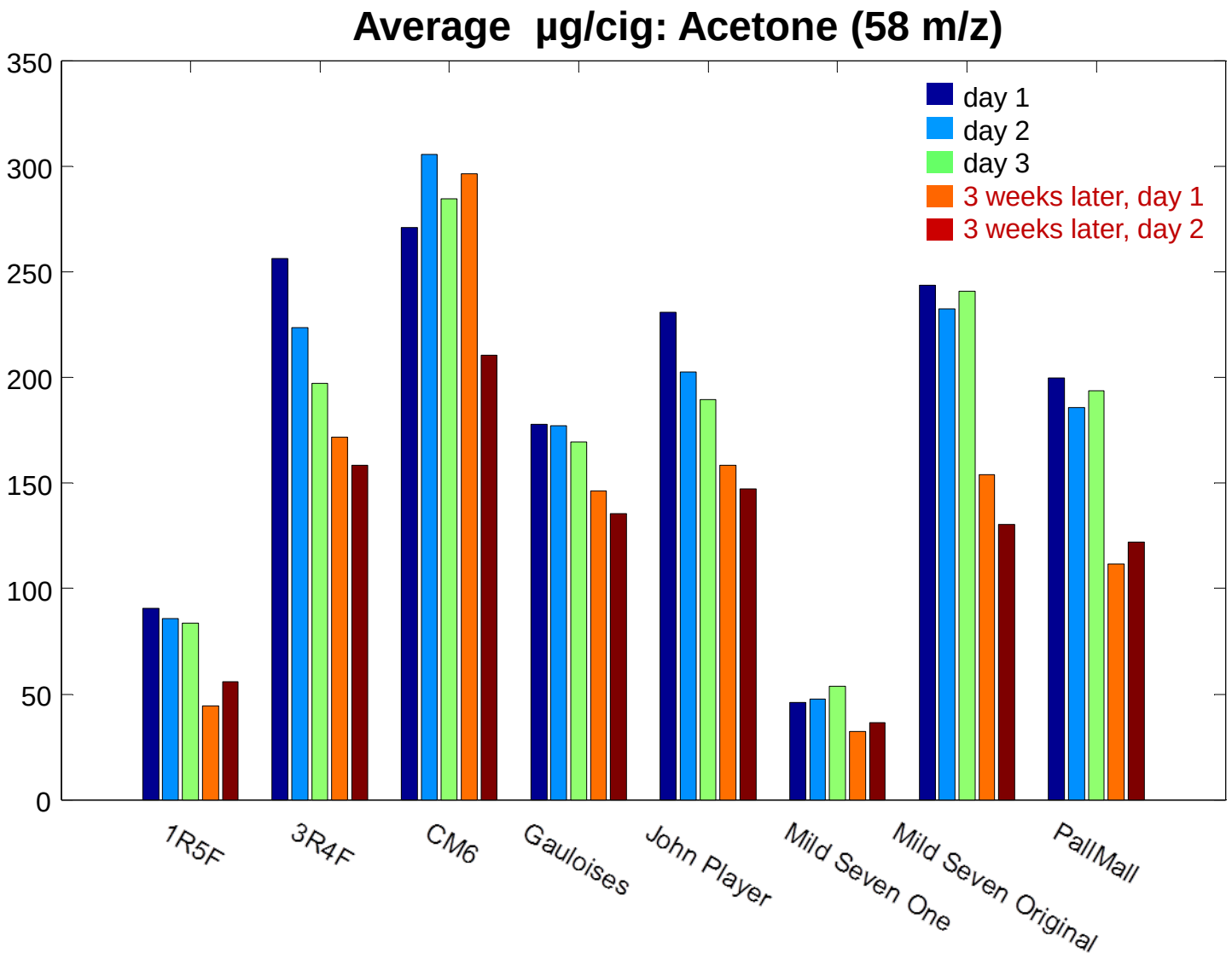
Reproducibility: Quantification of acetone on consecutive days (1R5F) without recalibration



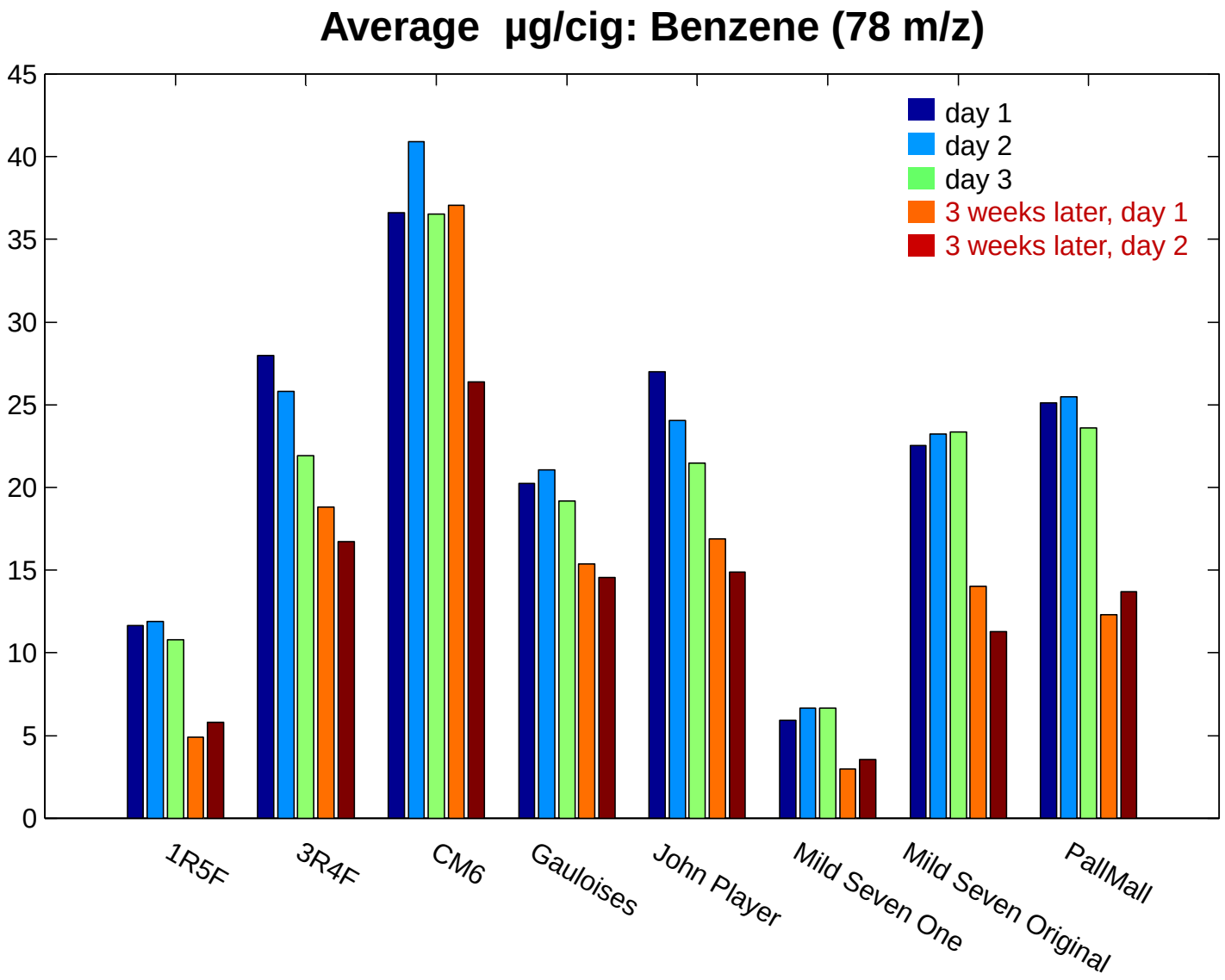
Acetone
58 m/z



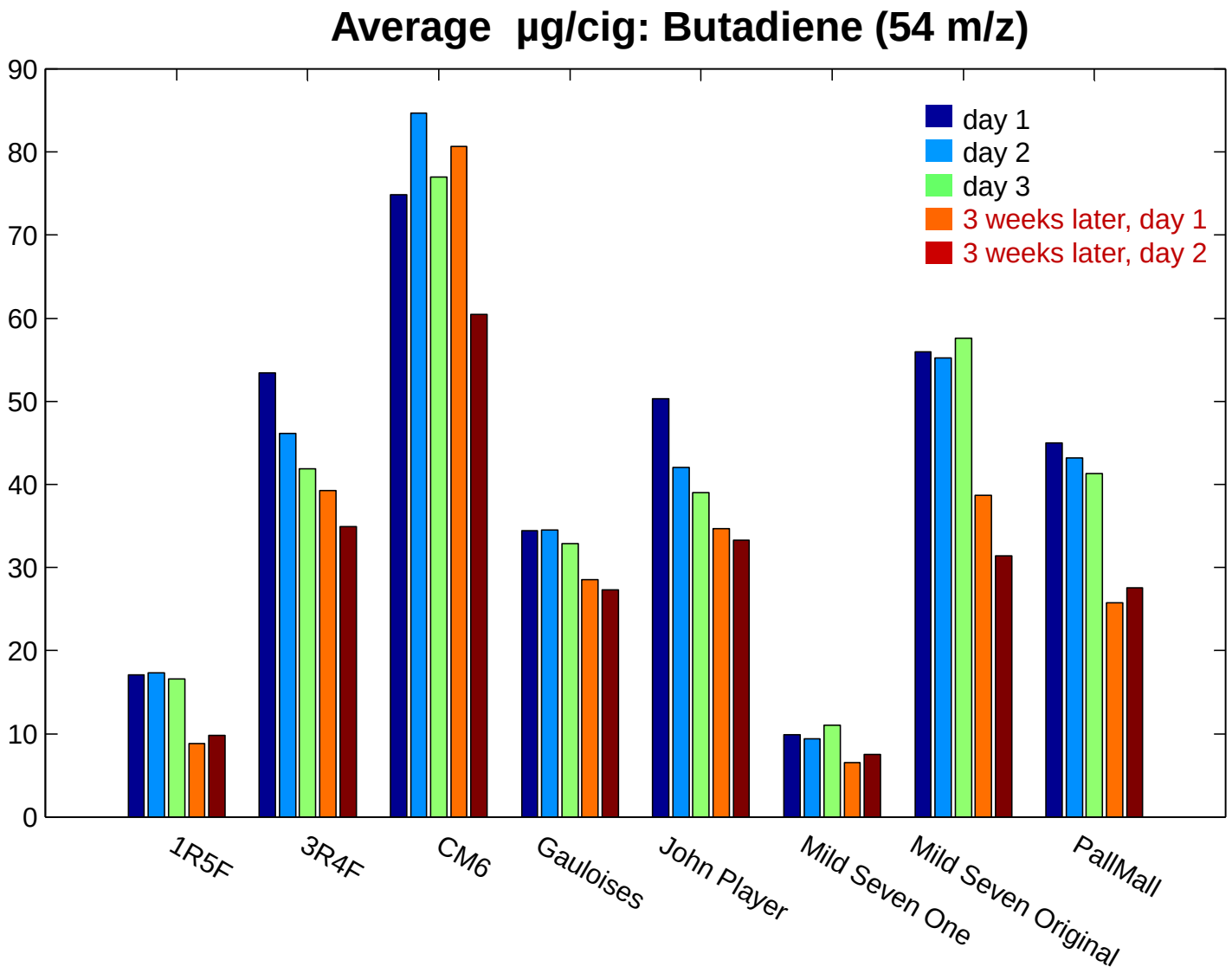
Reproducibility: Quantification of acetone – Long term stability (no recalibration)



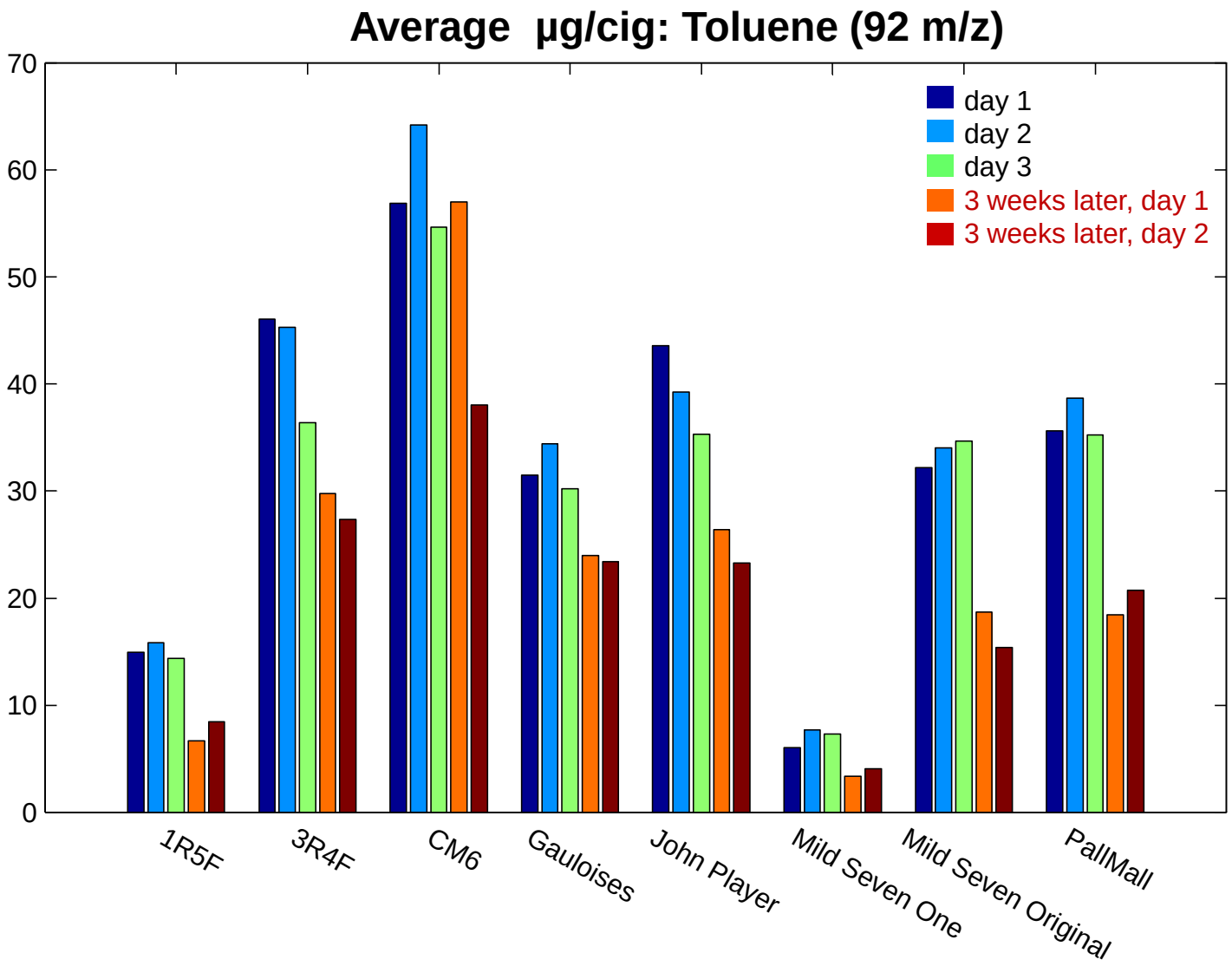
Reproducibility: Quantification of benzene – Long term stability (no recalibration)



Reproducibility: Quantification of butadiene – Long term stability (no recalibration)



Reproducibility: Quantification of toluene – Long term stability (no recalibration)



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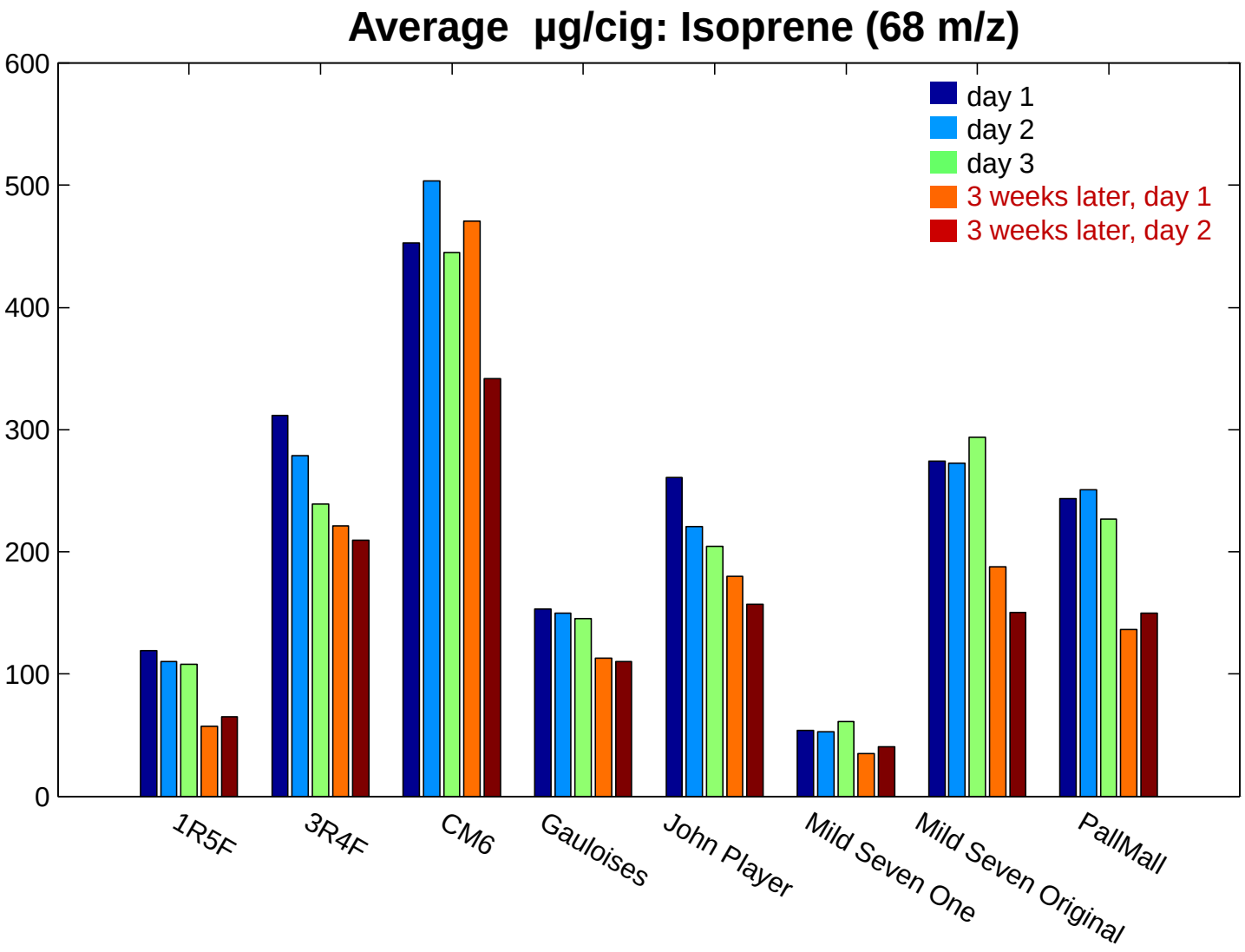
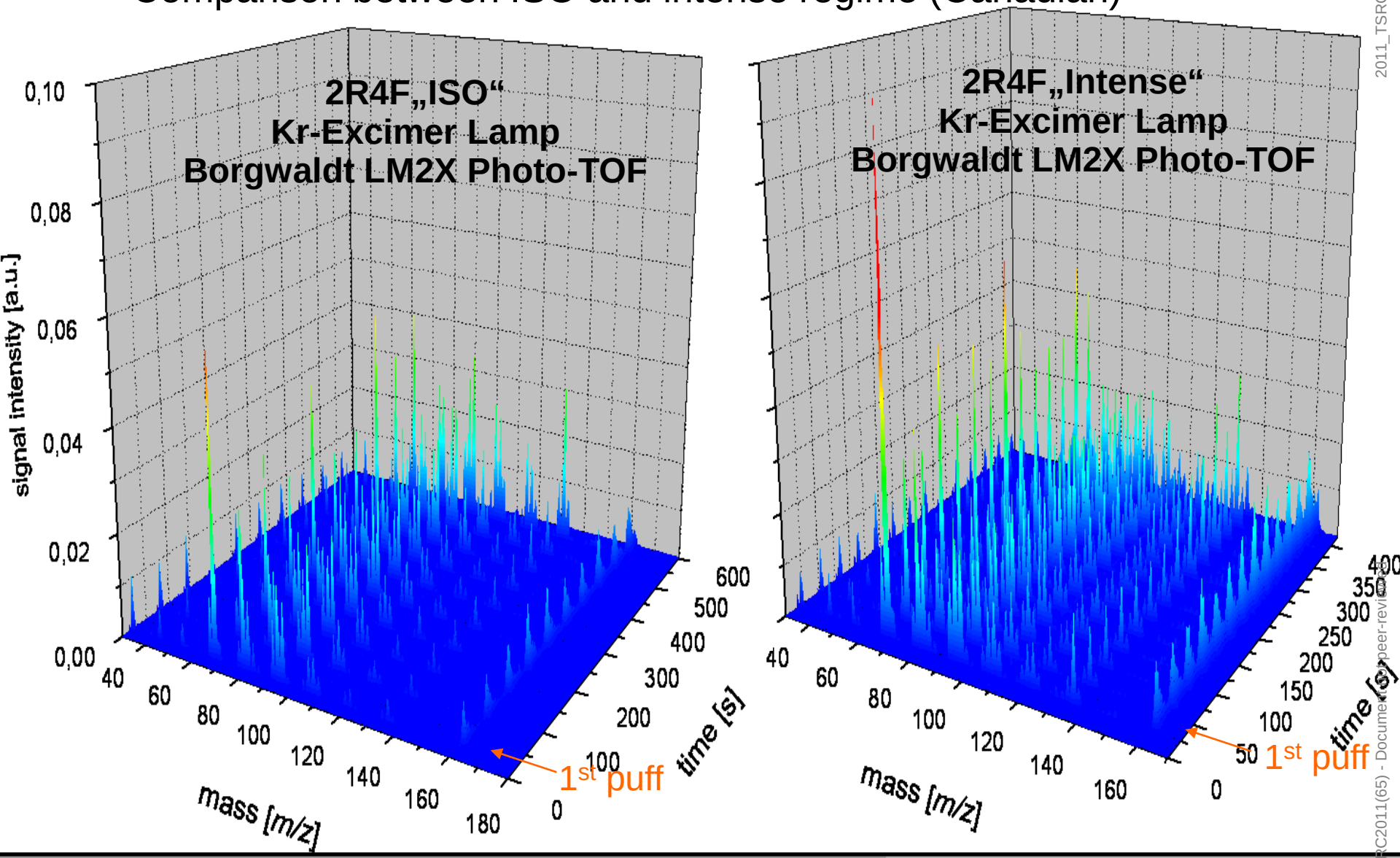


LM2x-TOF-MS Smoke Profiler: ISO and intense smoking

Comparison between ISO and intense regime (Canadian)



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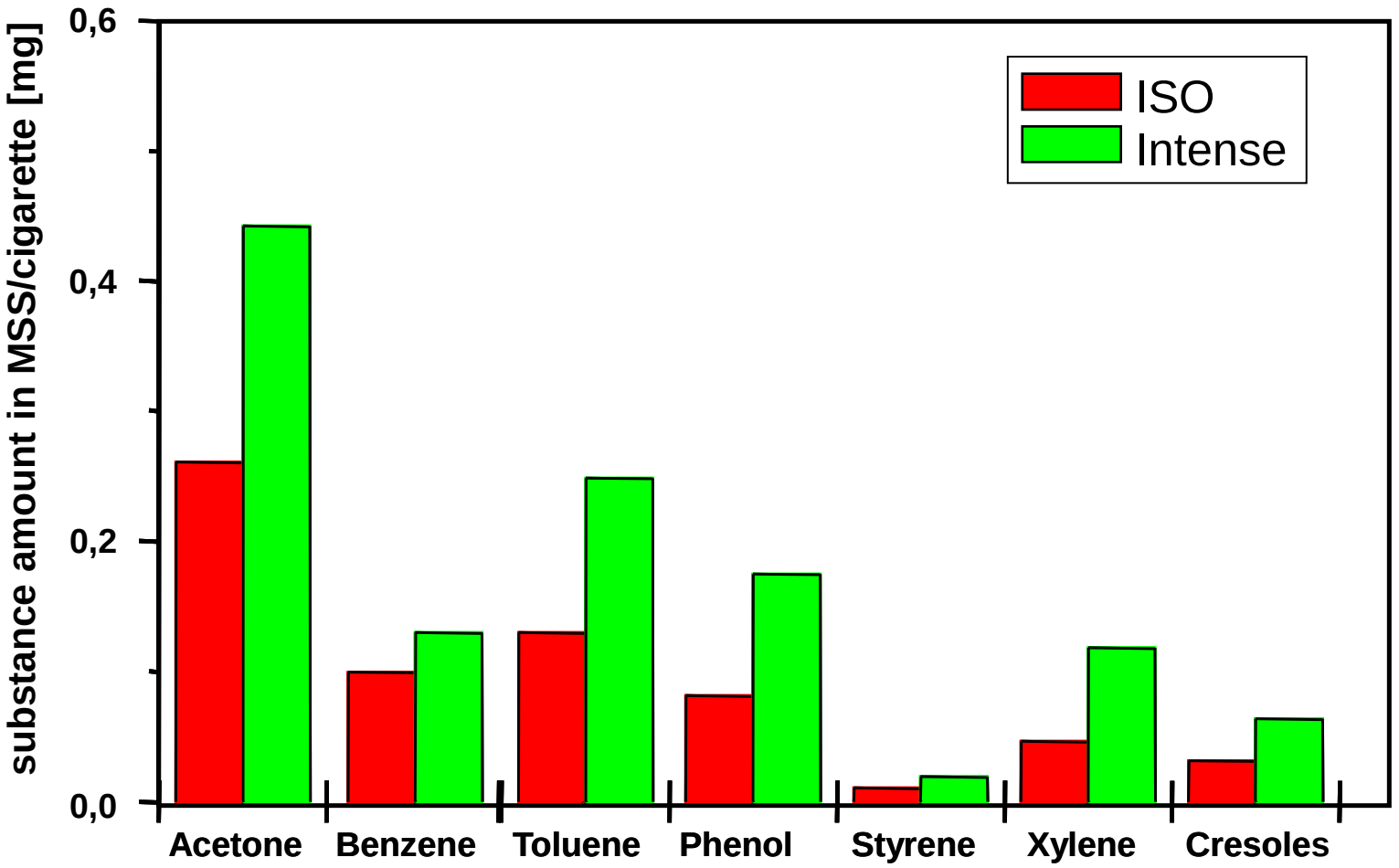

Puff-resolved on-line analysis of main stream cigarette smoke

A variety of compound classes can be on-line profiled by SPI-MS, Several can be quantified (whole smoke, depending on wavelengths):

Inorganic compounds: NO, NH_3,H_2S

Sulfur compounds: methylsulfide

Aliphatic hydrocarbons: alkenes, alkines, isoprene, butadiene etc.

Phenols: phenol, cresols, guajacols etc.

Carbonylic compounds: acetaldehyde, acetone etc.

Benzoid aromatics: benzene, toluene, xylenes etc.

Heterocyclics: pyrrole, pyridine, nicotine etc.

Polycyclic aromatics: naphthalene and derivatives

➡ **On-line tobacco smoke chemistry overview**

photonion

Contact: Info@photonion.de

Commercial Multi-Component Gas Analyzers

On-Line Mass Spectrometry with novel EBEL Photoionization Source

Applications

- Flexible Systems for Process and Quality Control: Photo-TOF und Photo-Quad
- Time Resolved Analysis of Cigarette Smoke (LM2X-TOF-MS, Borgwaldt KC)
- Evolved Gas Analysis of Organic Compounds in Thermal Analysis (TG-Photo-Quad, Netzsch GmbH)

borgwaldt kc

NETZSCH