

# **Puff resolved investigation of commercially available tobacco heating products using photo ionization mass spectrometry (PIMS)**

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## + Instrumental Setup

- Introduction: photoionisation - SPI and REMPI
- Puff parameters

## + Results

- TIC and nicotine release profiles
- Spectral overview
- Detailed release profiles in SPI and REMPI
- Dependency on storage conditions

## + Summary



**TOF-MS**  
CUSTOMIZED GAS  
ANALYZER



**LM2X**  
SMOKE ANALYZER



**TG-PIMS**  
THERMOGRAVIMETRY -  
PHOTOIONIZATION  
MASS SPECTROMETRY

# Experimental Setup

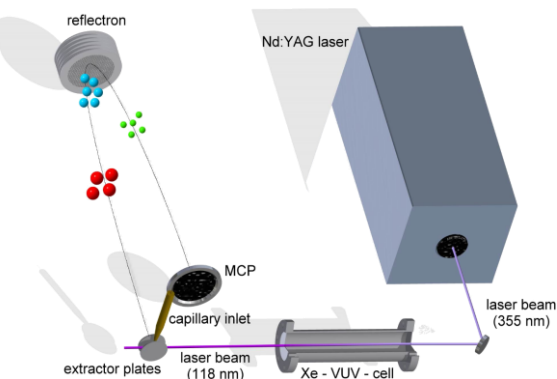
## Photoionisation ToF MS coupled to smoking machine

Single Photon Ionisation (**SPI**)  
118 nm (10.5 eV)

most organic compounds

Resonance-Enhanced Multiphoton Ionisation (**REMPI**)  
266 nm or 248 nm

aromatic compounds

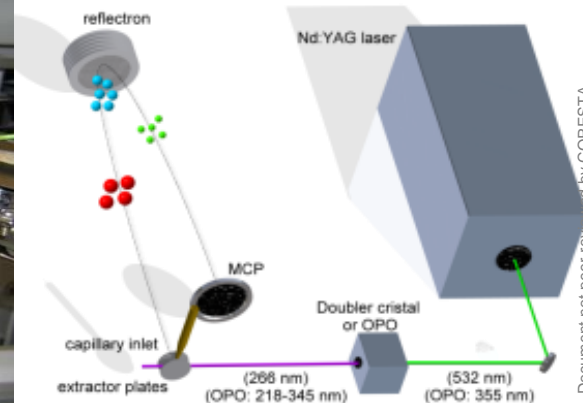
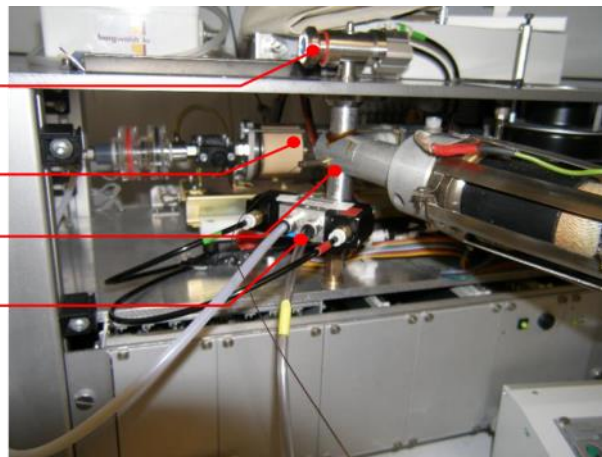


Cigarette holder

Syringe Pump

Coupling for ms  
with calibration  
gas inlet

Air backflush



# Experimental Setup

## Puff / smoking machine parameters

+

### General parameters:

Puff duration 3 s

Puff interval 30 s

Puff volume 55 ml

à 10 replicates @ 266 nm REMPI

à 10 replicates @ 248 nm REMPI

à 5 replicates @ 118 nm SPI

+

### THP product I:

First puff after 20 s

12 puffs



+

### THP product II:

First puff after 40 s

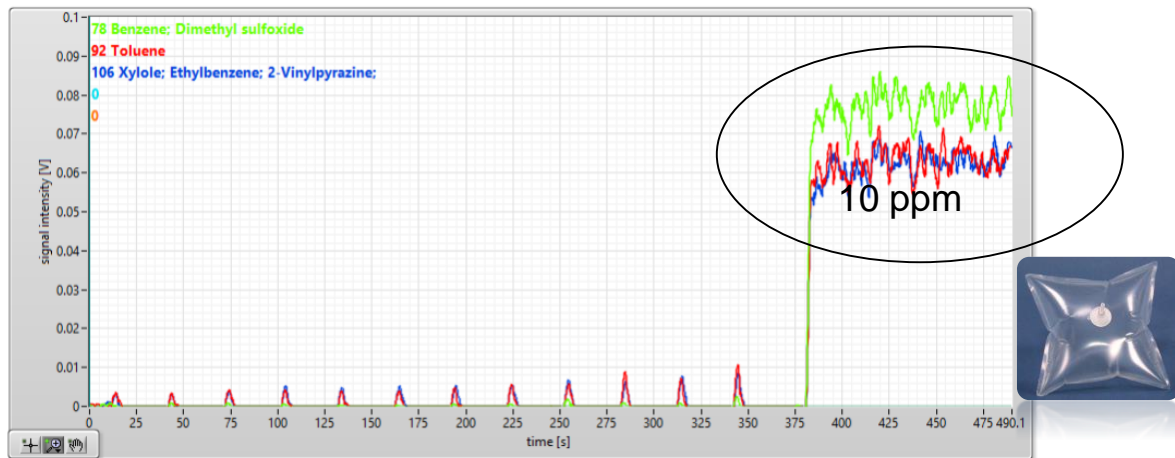
7 puffs

PHOTO-TOF-MS  
CUSTOMIZED GAS ANALYZER

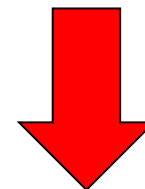


# Experimental Setup

## Normalisation and calibration



Every spectrum is calibrated and normalised by using a standard gas which contains Benzene, toluene and xylene



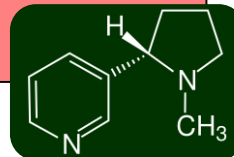
Crucial for reliable qualitative and semi-quantitative comparison

Alternative normalization basis for product comparison:

On smoke amount  
(e.g. by norm. on glycerin signal)



On nicotine signal as active compound of smoking

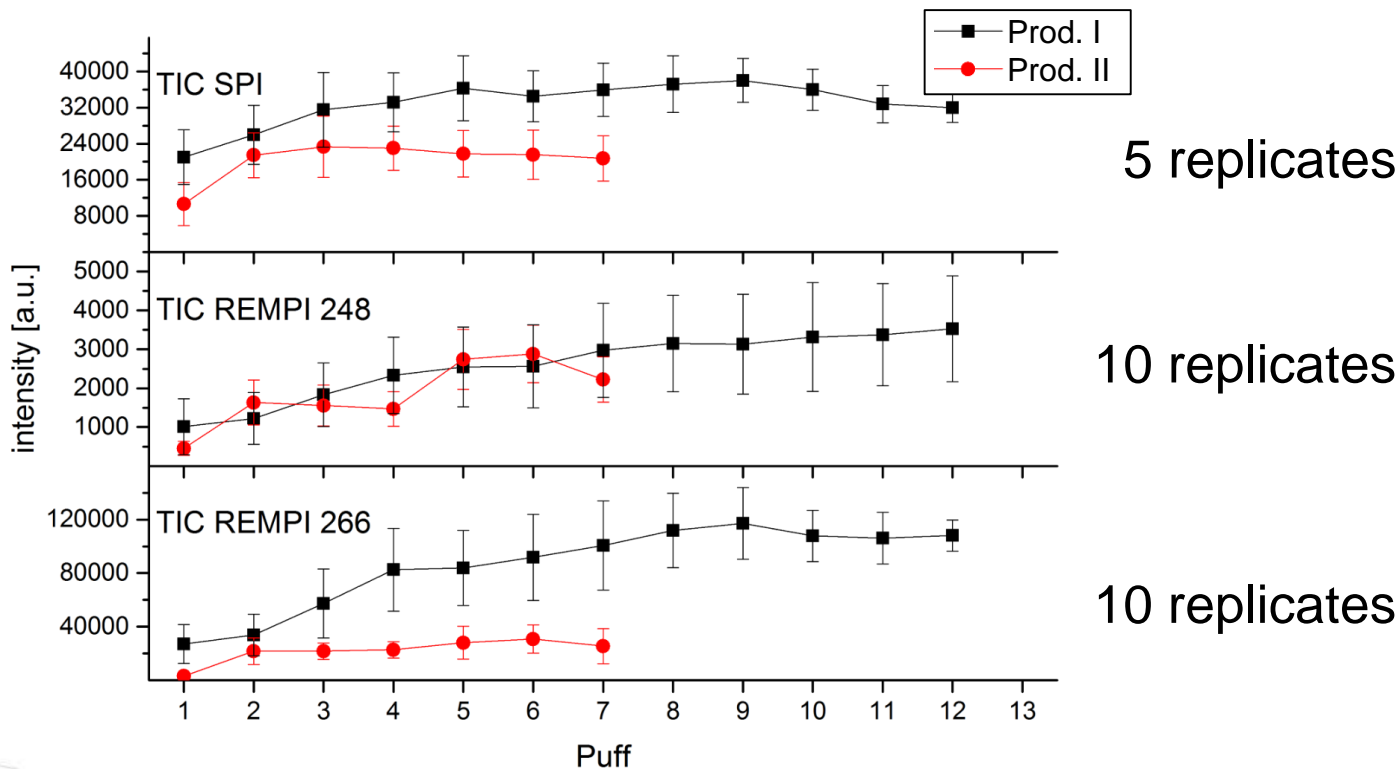


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# Results & Discussion

## Puff resolved release overview

### Total ion current



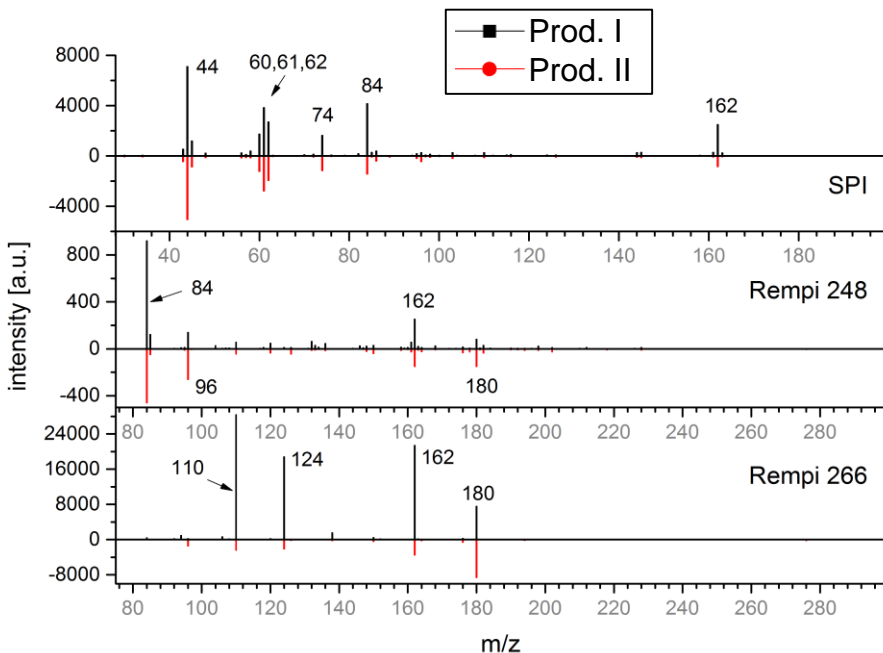
5 replicates

10 replicates

10 replicates

# Results & Discussion

## Spectral overview



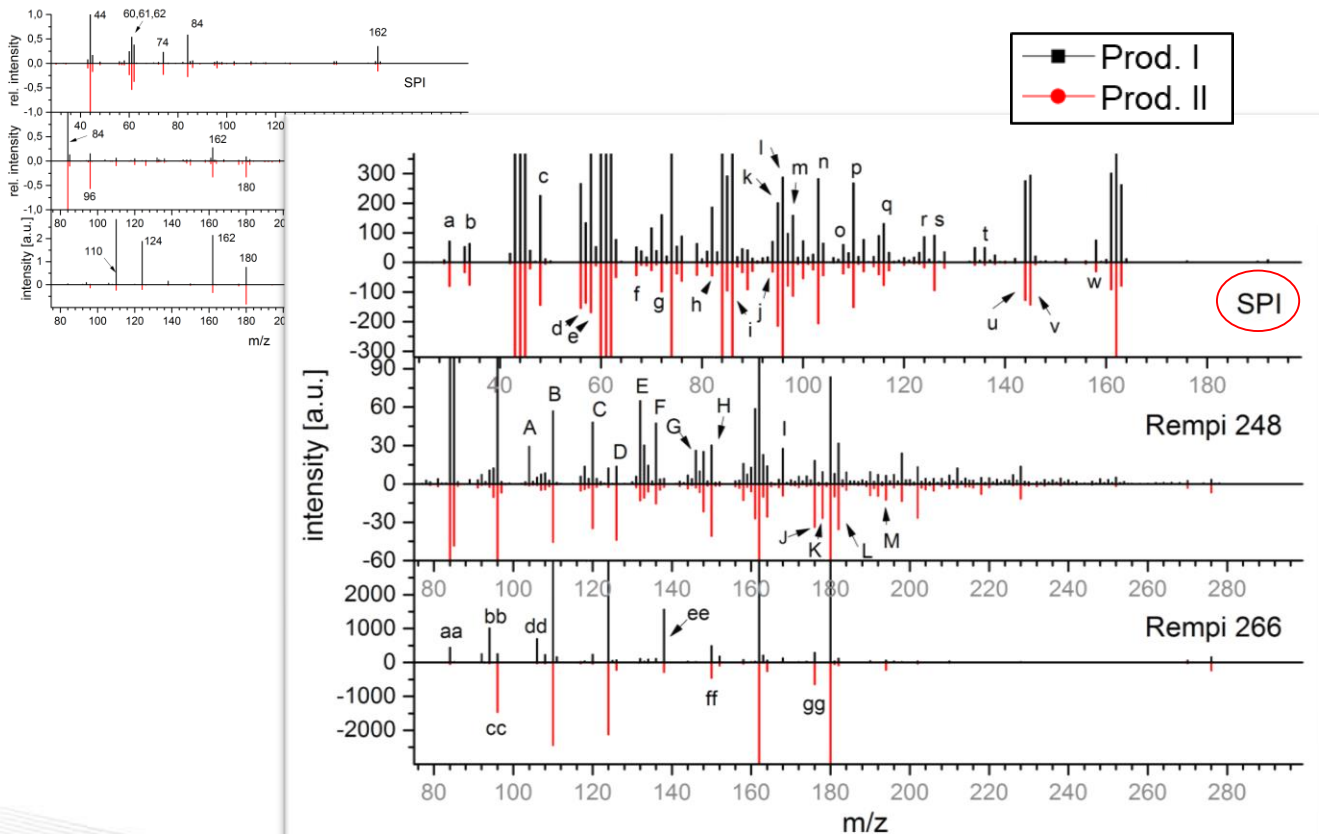
SPI	
Mass	Substance
44	Glycerol fragment, acetaldehyde
60	Glycerol fragment
61	Glycerol fragment
62	Glycerol fragment
74	Glycerol fragment
84	Nicotine fragment
162	Nicotine

REMPI 248	
Mass	Substance
84	Nicotine fragment
96	Dimethylfuran, furfural
162	Nicotine
180	1-Methyl-9H-fluorene, 9H-fluoren-9-one

REMPI 266	
Mass	Substance
110	Dihydroxybenzene
124	Guaiacol
162	Nicotine
180	1-Methyl-9H-fluorene, 9H-fluoren-9-one

# Results & Discussion

## Detailed spectra (SPI)

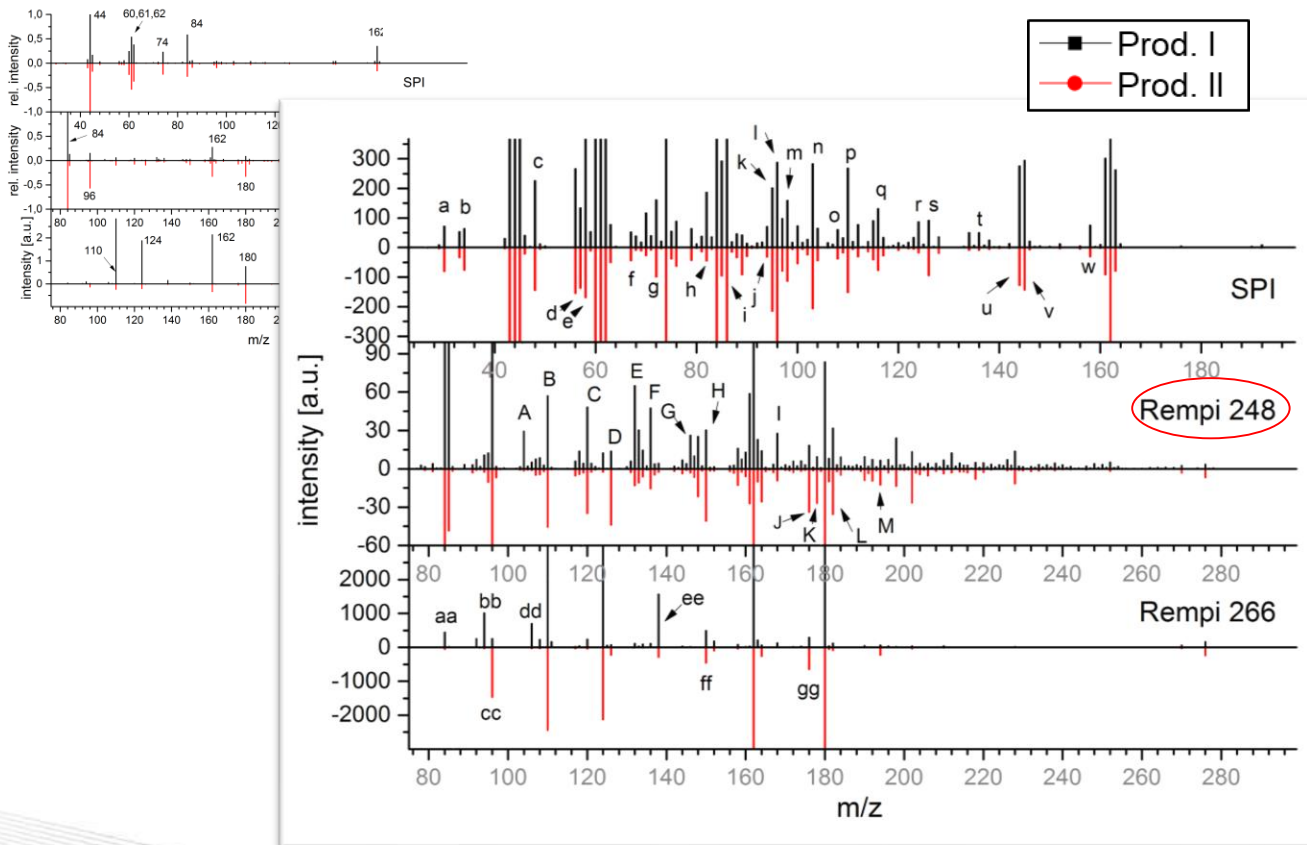


SPI		
Index	Mass	Substance
a	30	Nitric oxide
b	34	Hydrogen sulfide
c	48	Methanethiol
d	56	2-Propenal, butene
e	58	Acetone, propanal
f	67	Pyrrrole
g	72	Butanal, butanone, 2-Methylpropenal
h	82	Cyclohexene, 2-Cyclopenten-1-one
i	86	Methylfuran, Methylcyclopentene
j	94	Pentane, pentanone, 2,3-butadione
k	95	Methylbutanal, 3-Methyl-2-butanone
l	96	Phenol, 2-Vinylfuran
m	98	Pyridinol, Ethylpyrrol, Dimethylpyrrol
n	103	Dimethylfuran, Furfural
o	108	Furfuryl alcohol, Methyl-2-pental, Furanmethanol, 1,3-Cyclopentanedione
p	110	5-Methyl-2(5H)-furanone
q	116	Benzonitrile
r	124	Cresoles, Dimethylpyridine, Methylphenol
s	126	Anisol
t	136	Dihydroxybenzene, 2-Acetylfuran, Methylfurfural
u	144	Indene
v	145	Guaiacol, Dihydroxymethylbenzene
w	158	5-Hydroxymethylfurfural
		Limonene, Methoxybenzaldehyde
		2-Ethyl-5-methylphenol
		Naphthalenol, C2-alkylindene, Octanoic Acid
		Ethylindole
		?



# Results & Discussion

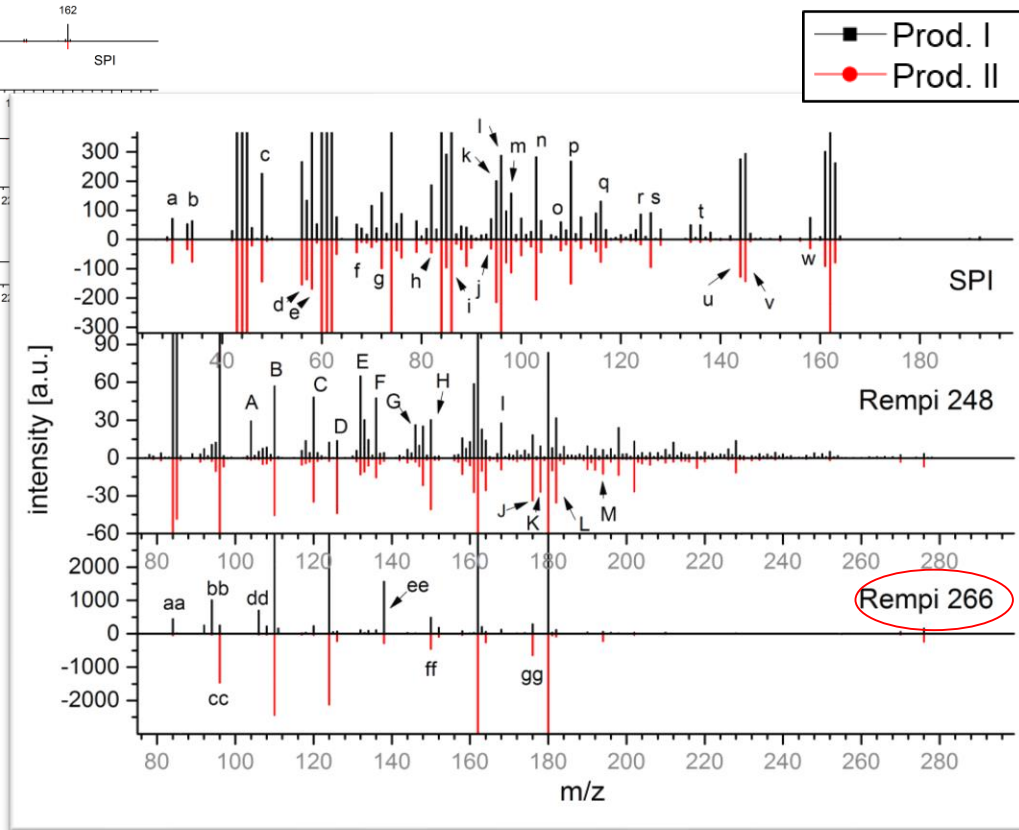
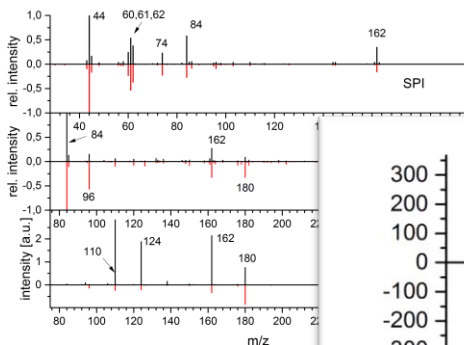
## Detailed spectra (248 REMPI)



REMPI 248		
Index	Mass	Substance
A	104	Styrene
B	110	Dihydroxybenzene
C	120	C3-Alkylbenzene, phenylacetaldehyde, acetophenone
D	126	5-Hydroxymethylfurfural
E	132	C2-Alkylstyrene
F	136	Limonen
G	146	Coumarin, myosmine, C3-alkylstyrene, C2-alkylindane
H	150	4-Vinylguaiacol, C4-alkylphenol
I	168	?
J	176	Cotinine
K	178	Anthracene, phenanthrene
L	182	Ethylbiphenyl, dimethylbiphenyl
M	194	Ferulic acid, C2-alkylfluorene

# Results & Discussion

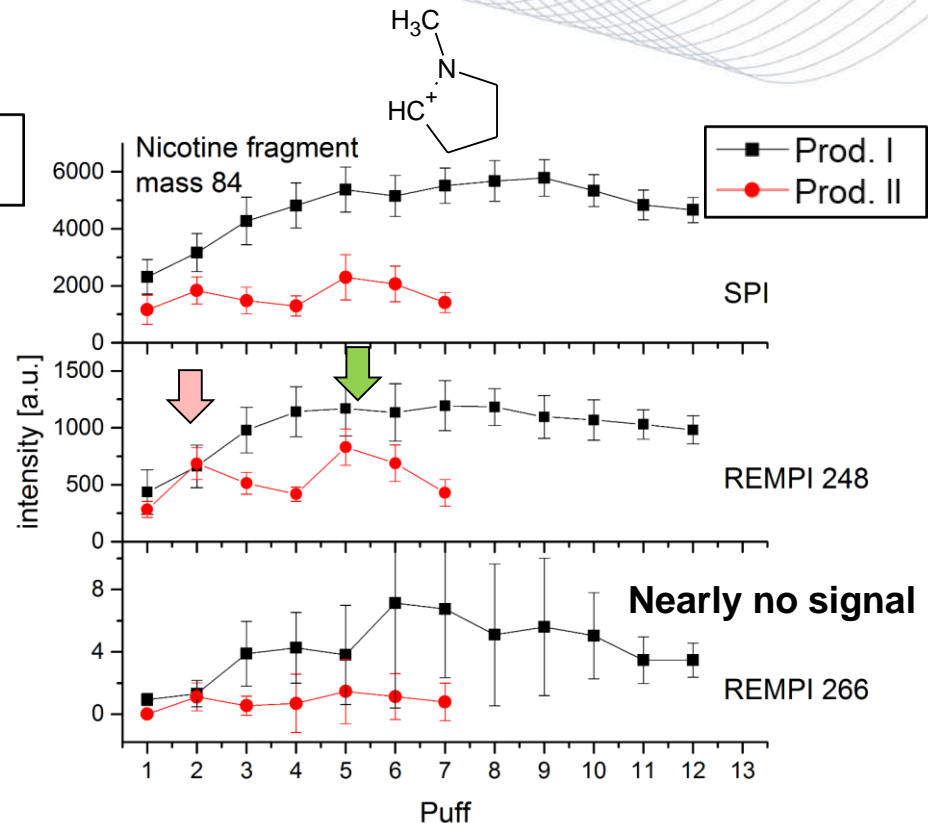
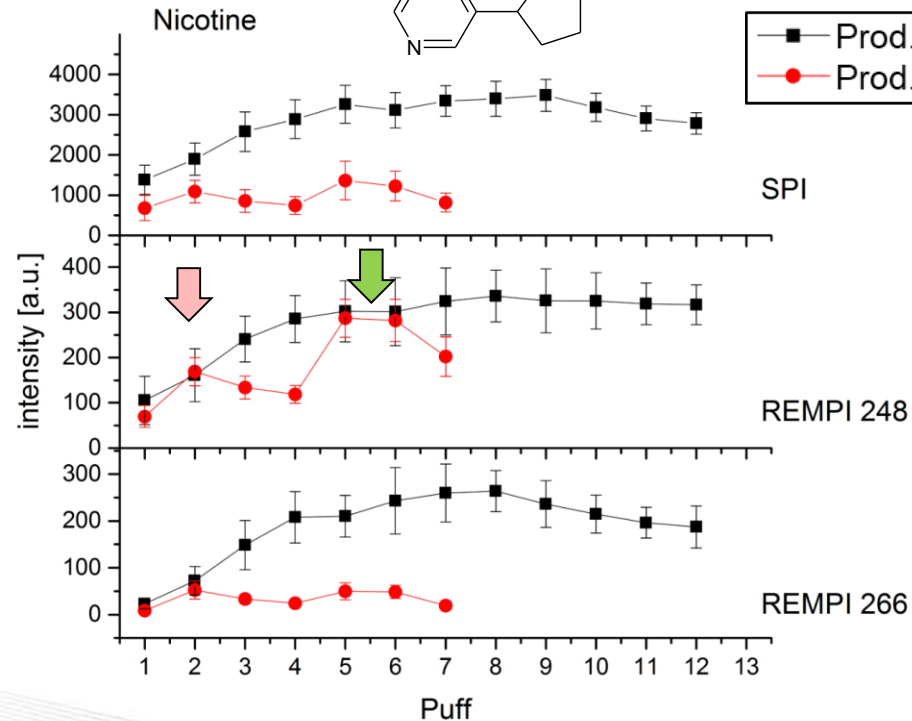
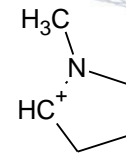
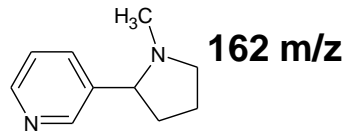
## Detailed spectra (266 REMPI)



REMPI266		
Index	Mass	Substance
aa	84	Nicotine fragment
bb	94	Phenol
cc	96	Dimethylfuran, Furfural
dd	106	Xylenes, ethylbenzene
ee	138	?
ff	150	4-Vinylguaiacol, C4-alkylphenol
gg	176	Cotinine, ?

# Results & Discussion

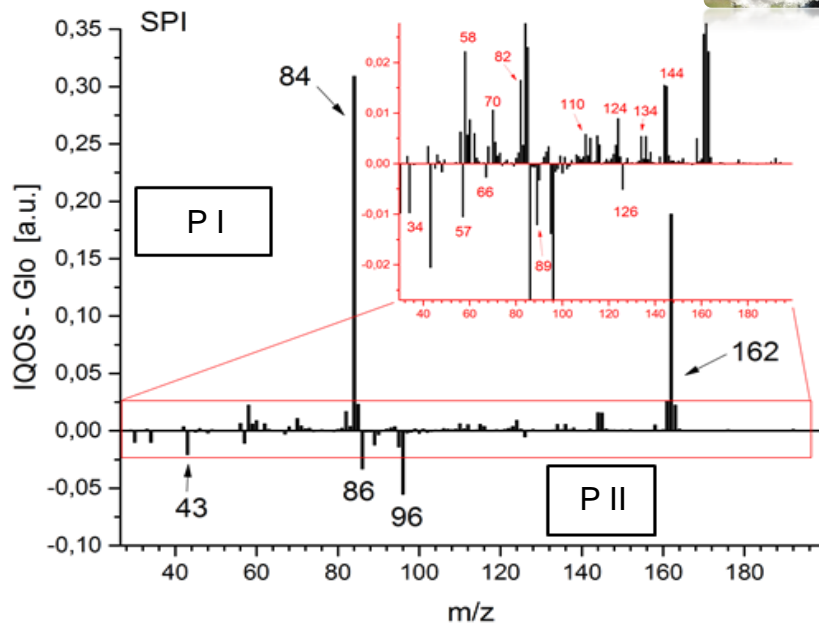
## Nicotine release profiles



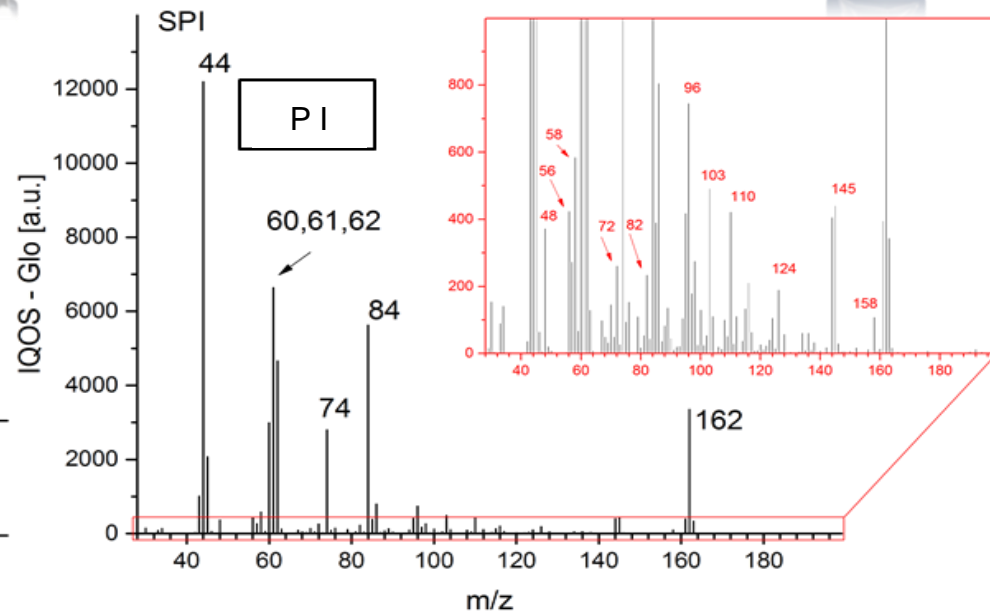
# Results & Discussion

## Difference spectra SPI

Normalised to mass 44



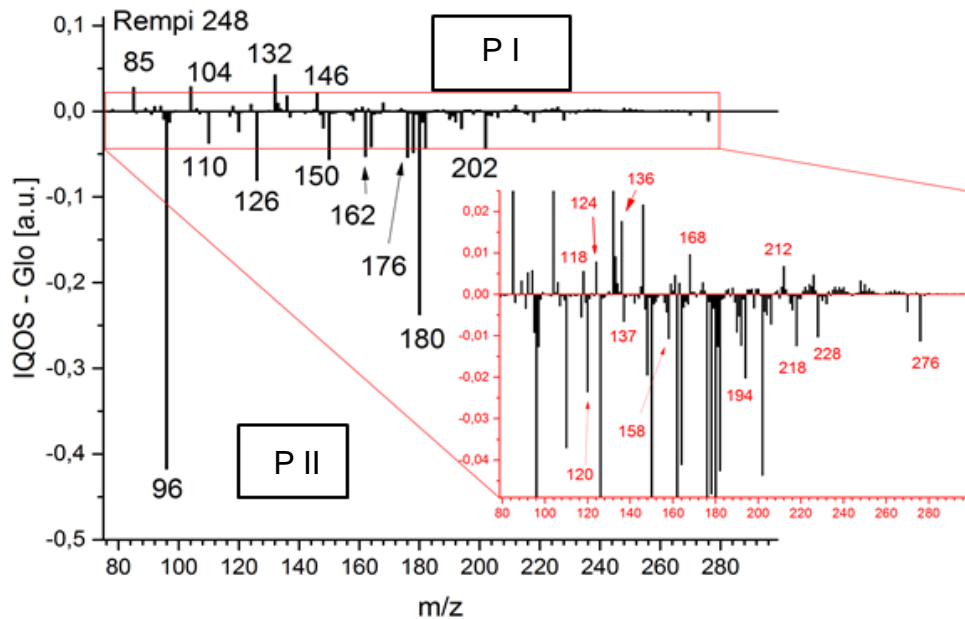
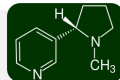
Normalised to toluene



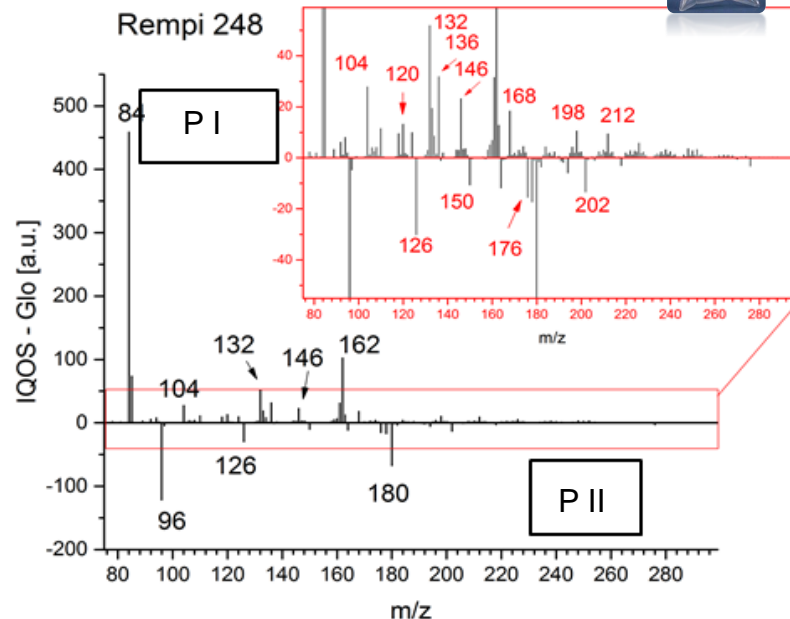
# Results & Discussion

## Difference spectra REMPI

Normalised to mass 84



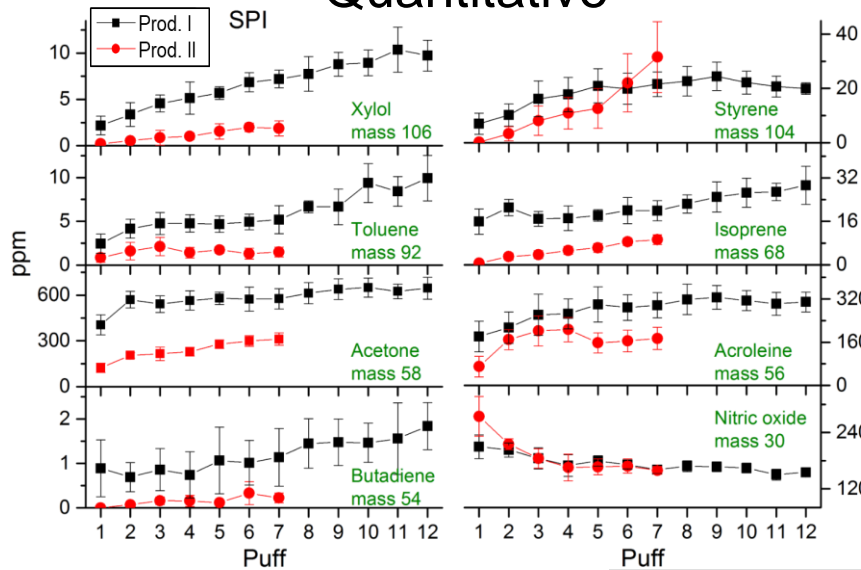
Normalised to toluene



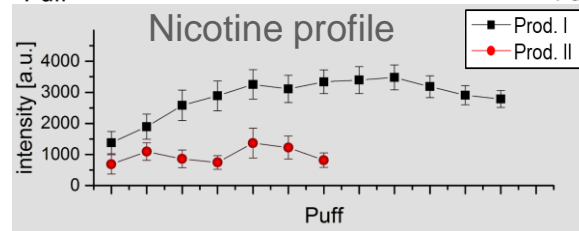
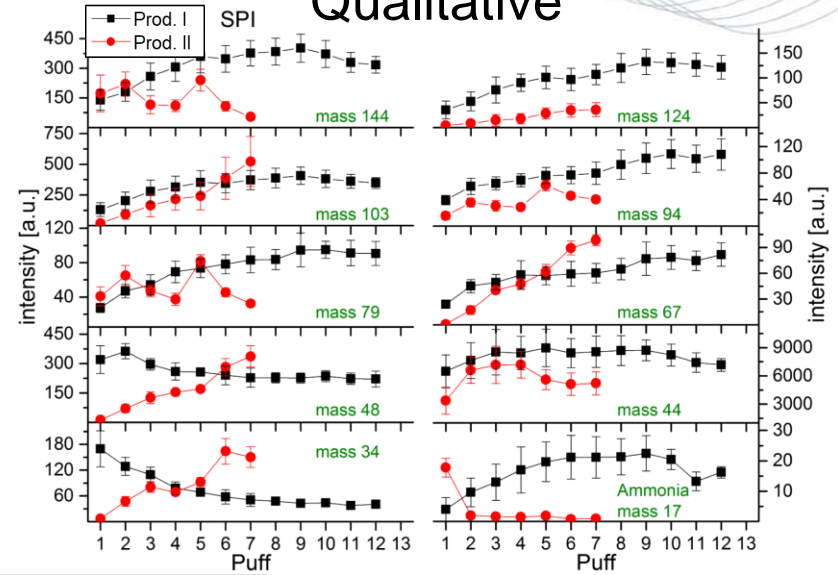
# Results & Discussion

## SPI release profiles

### Quantitative



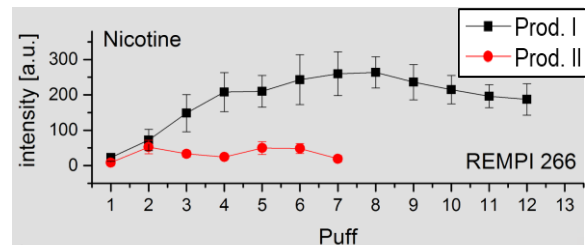
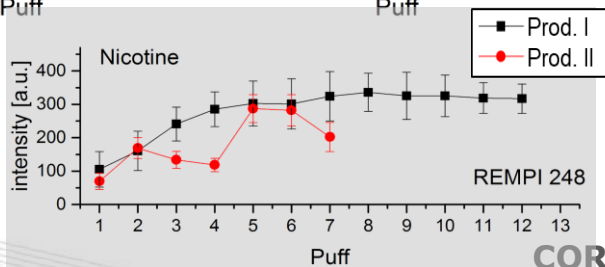
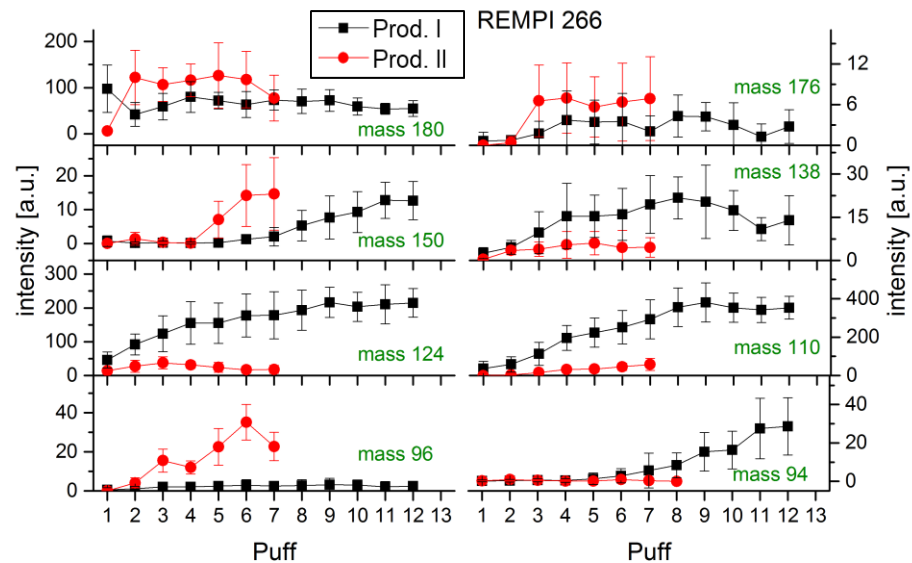
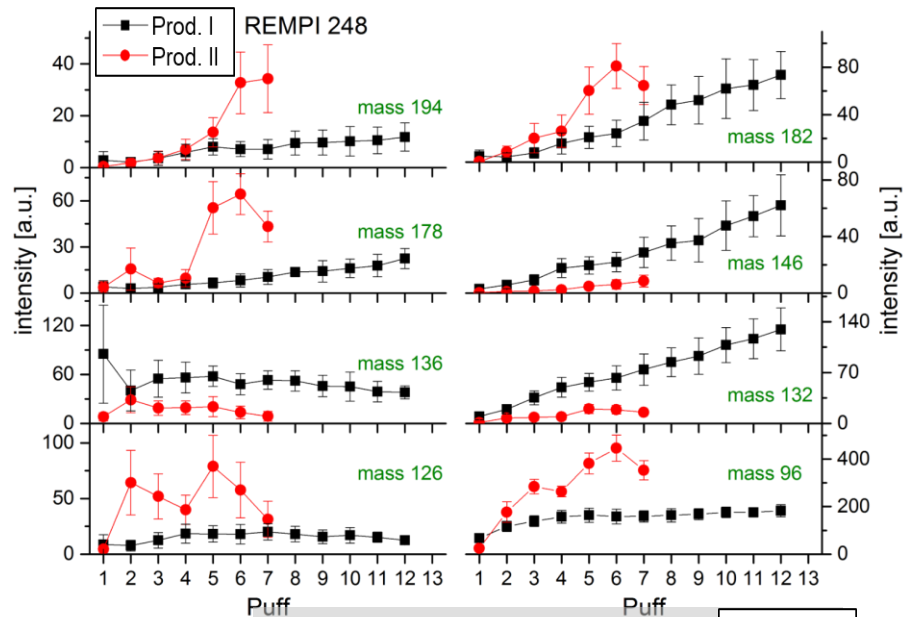
### Qualitative



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# Results & Discussion

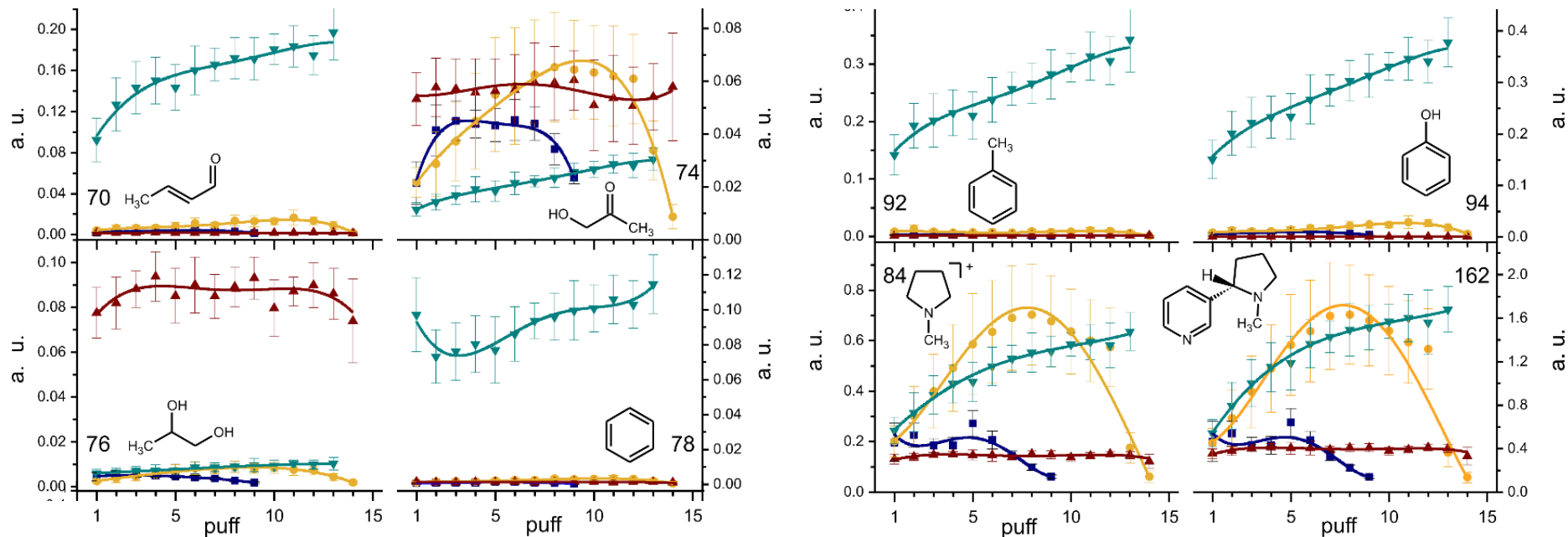
## REMPI release profiles



# Results & Discussion

## Comparison to further product classes

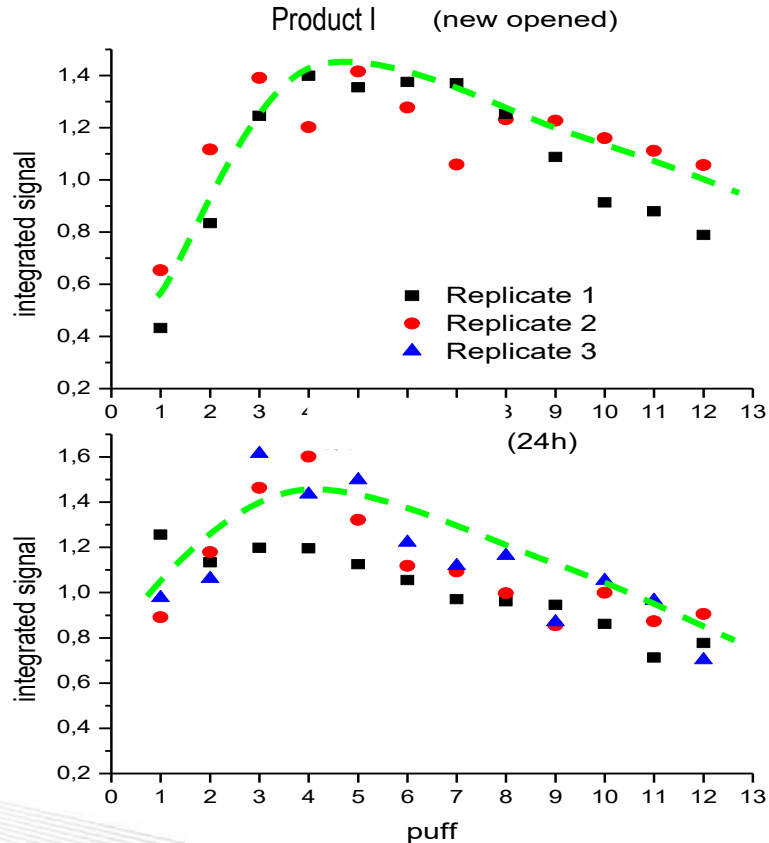
- THP product I
- ▲ E-cigarette\*
- THP product II
- ▼ Research cigarette



\*cartridge based e-cigarette with non-adjustable power/temperature

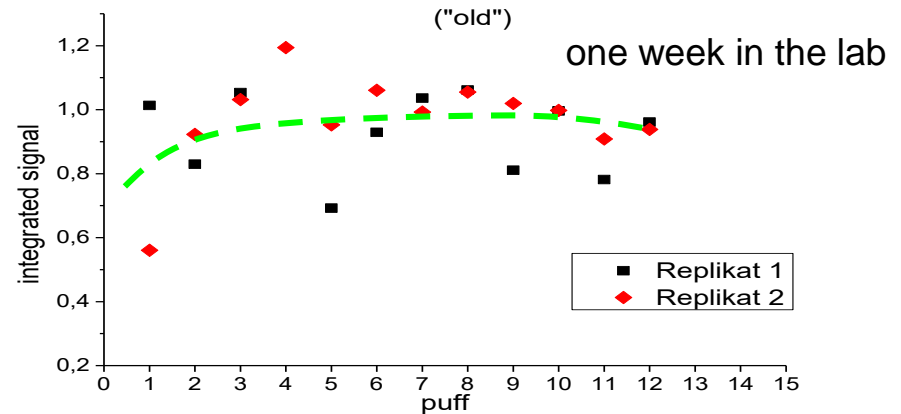


## Influence of 'aging' on nicotine release



⊕ Stability and nicotine release environmental influenced (humidity...)  
**[correlation need to be investigated]**

⊕ **Conditioning vs. consumer?**



# HnB/THP

## Puff resolved nicotine release

Product I

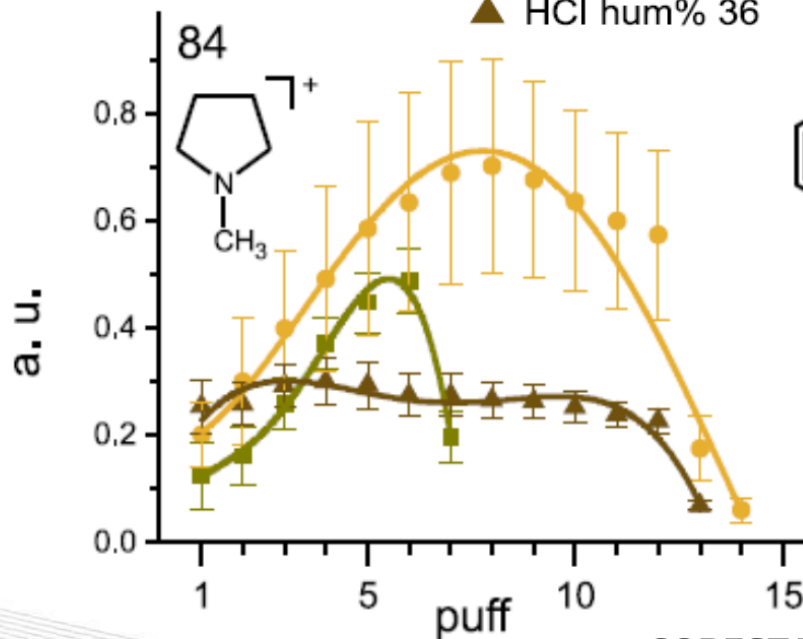
■ ISO

● HCl hum% 60

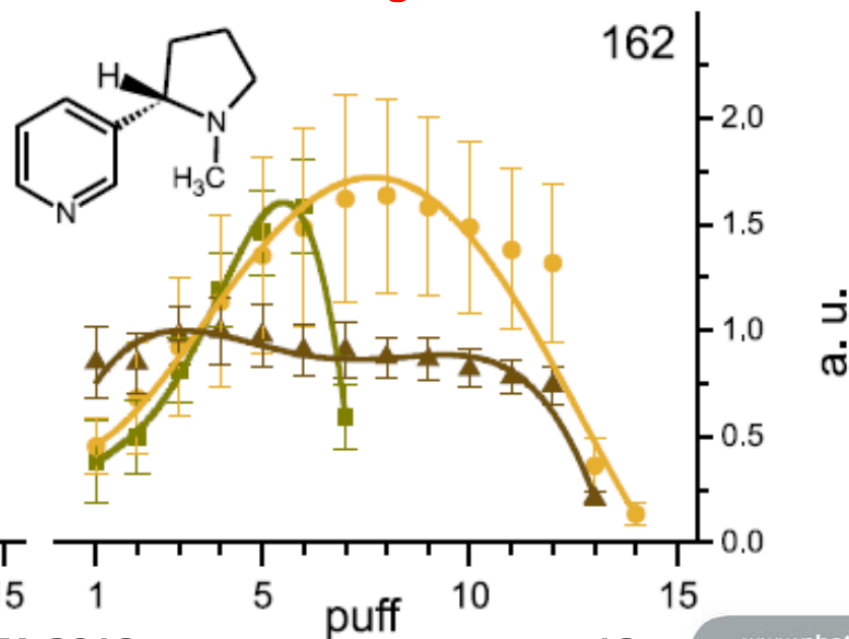
▲ HCl hum% 36

- ⊕ Stability and nicotine release environmental influenced (humidity...)

- ⊕ **Conditioning vs. consumer?**



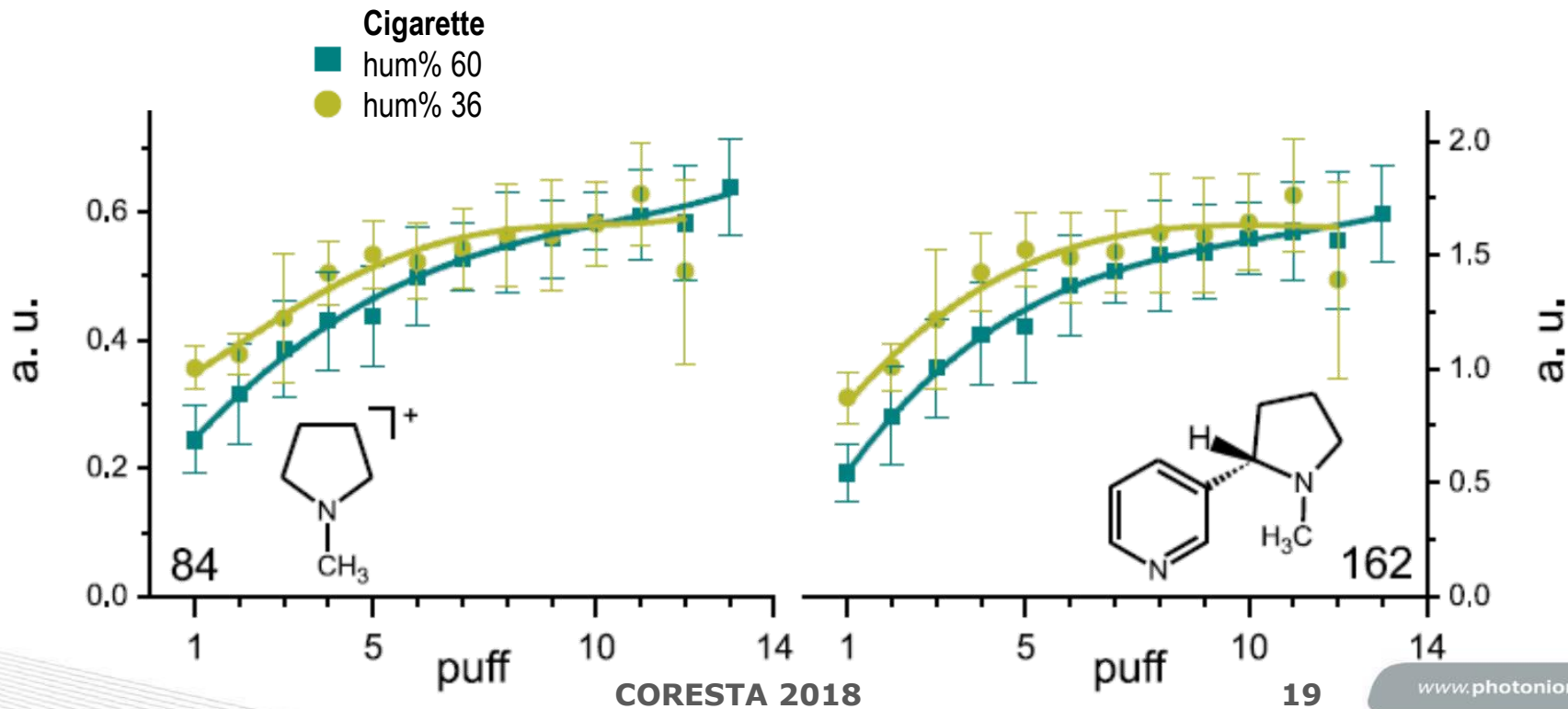
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# HnB/THP

## Puff resolved nicotine release



# Summary

## Online puff resolved **THP** product study

**TG-PIMS**  
THERMOGRAVIMETRY- PHOTOIONIZATION MS



- ⊕ Products show high differences in absolute amounts on gas phase compounds and nicotine
- ⊕ Main release glycerol and nicotine
- ⊕ Huge variety on less prominent compounds
- ⊕ Soft Photoionization (**SPI/REMPI**) Mass Spectrometry enables a **puff by puff resolved** investigation of smoking products

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



**SMOKE-TOF-MS**  
TOBACCO SMOKE ANALYZER



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



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



# Acknowledgement

Special Thanks to  
**Prof. Dr. Ralf Zimmermann**  
and members of the **JMSC**  
(Joint Mass Spectrometry Centre)



JOINT MASS SPECTROMETRY CENTRE

**TG-PIMS**  
THERMOGRAVIMETRY- PHOTOIONIZATION MS



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



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



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



## Thank you for your attention!

*Thursday talks*

**ST 43:** Overview of time resolved smoke analysis

**ST 45:** Chemical cigarette mapping

**STPOST49:** Photoionization for smoke analysis

**SMOKE-TOF-MS**  
TOBACCO SMOKE ANALYZER



# Products

## Overview of PI MS related products

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



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



**SMOKE-TOF-MS**

TOBACCO SMOKE ANALYZER



**PHOTONEX**

POWERFUL EXCIMER LASER IONISATION SOURCE



**PHOTO-TOF-MS**

CUSTOMIZED GAS ANALYZER



**A-TOF-MS**

SINGLE PARTICLE AEROSOL ANALYZER



**Photo-oa-TOF-MS**

COMPACT CUSTOMIZED GAS ANALYZER



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**TG-PIMS**

THERMOGRAVIMETRY-PHOTOIONIZATION MS



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