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JOINT MASS SPECTROMETRY CENTRE

ON-LINE PUFF RESOLVED ANALYSIS OF CIGARETTE SMOKE, E-CIGARETTE VAPOUR AND VAPOUR OF TOBACCO HEATING PRODUCTS

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Introduction & Method

Within the last years e-cigarettes and other new smoking/vaping products became more and more commonly used. An on-line puff by puff resolved analysis of thermal degradation products has the challenge to enable an analyte search without pre-separation although the starting point of the thermal decomposition process is a complex organic matrix and will provide multiple reaction pathways. With the increased (legal) availability of marijuana/cannabis and THC containing smoking products not only for medical purposes, the interest in understanding the release processes of the active smoke constituents beside potentially harmful compounds is increasing as well.

Soft Photo-ionization-mass-spectrometry (PIMS) is well suited for on-line characterization of complex gaseous mixtures. Environmental matrix gases such as oxygen, nitrogen or water vapor can be suppressed efficiently. The measurements in this study were mainly performed using a modified Borgwaldt-KC LM1 smoking machine coupled to a laser-photo-ionization time-of-flight mass spectrometer. The modification of the smoking machine refers to a 'cold-spot'-free sampling without affecting flow velocities and volumes using a side stream for MS analysis. The smoking machine was coupled to a PIMS (Photonion GmbH; Germany). It is equipped with a laser-SPI (Single-Photon-Ionization) source at 118 nm [10.5 eV] and a Laser-REMPI (Resonance-Enhanced-Multi-Photon-Ionization) source at 266 nm. Regarding quantification of specific compounds such as nicotine or Delta-9-THC the relative cross sections related to toluene where determined within a parallel experiment for the 266 nm REMPI radiation. Our study was conducted with cannabis products provided by the responsible governmental authorities.

Figure 1: Experimental setup with the commercial available SPI/REMPI ToF-MS of Photonion GmbH (Germany)

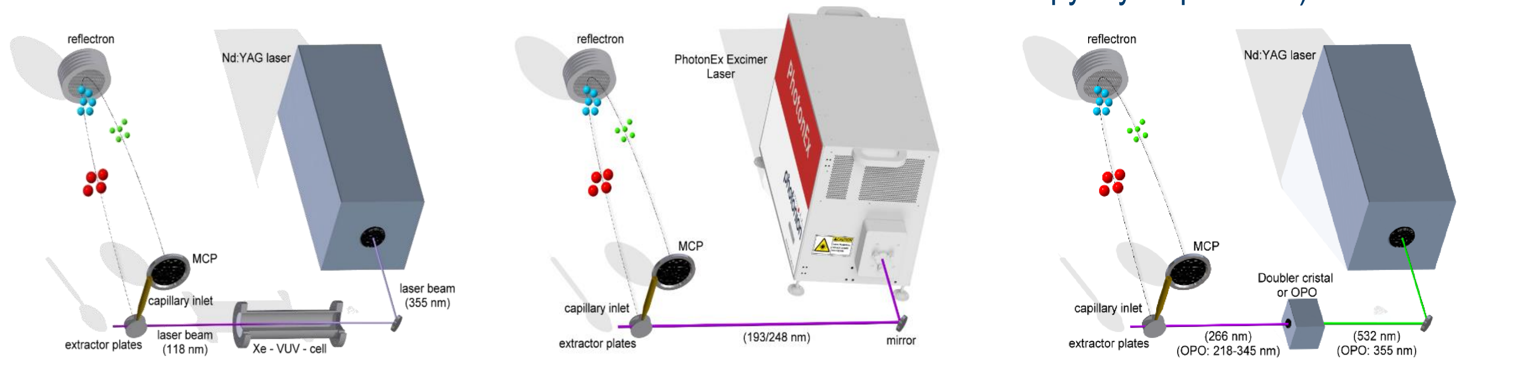


Figure 2: Schematic of a) Laser SPI using the tripling in a Xenon gas cell and a reflectron TOF MS b) Laser REMPI using the 248nm PhotonEx Eximer laser with high repetition rate of 1kHz c) Laser REMPI using 266nm or an OPO [Optical Parametric Oscillator] for the range of 218 nm to 345 nm with a reflectron TOF MS

Applications, Results & Discussion

New smoking products such as e-cigarettes and THPs

Actual tobacco heating products (THPs) are somehow hybrids between conventional cigarettes and e-cigarettes. Although the first representatives of their kind were coal heated and introduced decades ago, recent tobacco heating products are working mainly electrically.

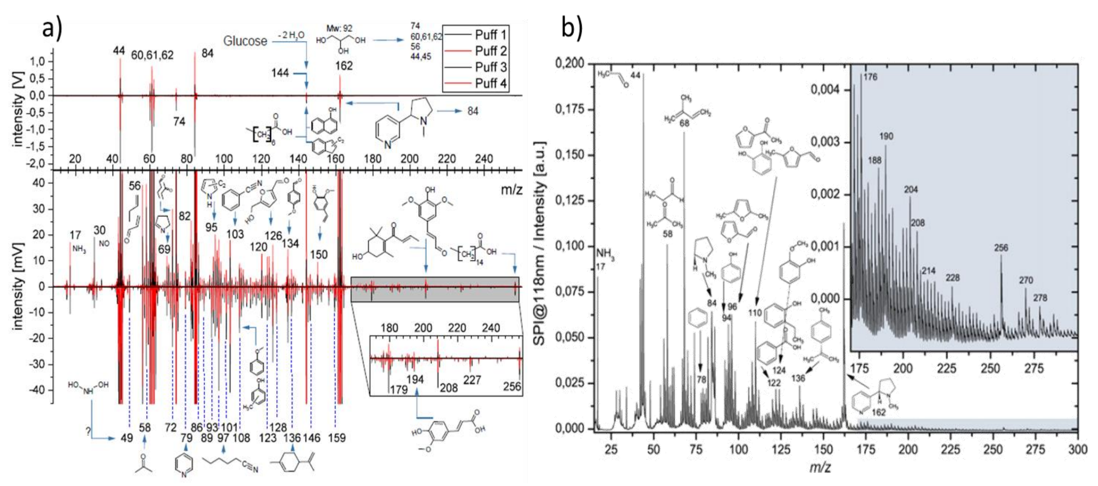


Figure 3: a) Puff averaged SPI mass spectra of the first four Puffs of a Heat-not-burn smoking device working at 180°C. Puff one and two as well as 3 and 4 are displayed together. b) An averaged mass spectrum sampled by the µ-probe from whole smoke inside of a 2R4F cigarette smoked under ISO puffing parameters (5 averaged replicates). The advantage of the direct sampling is clearly shown by the presence of masses up to m/z 300. (The shown chemical structures are proposals based on literature but were not tested with own analytical reference methods such as high resolution mass spectrometry.)

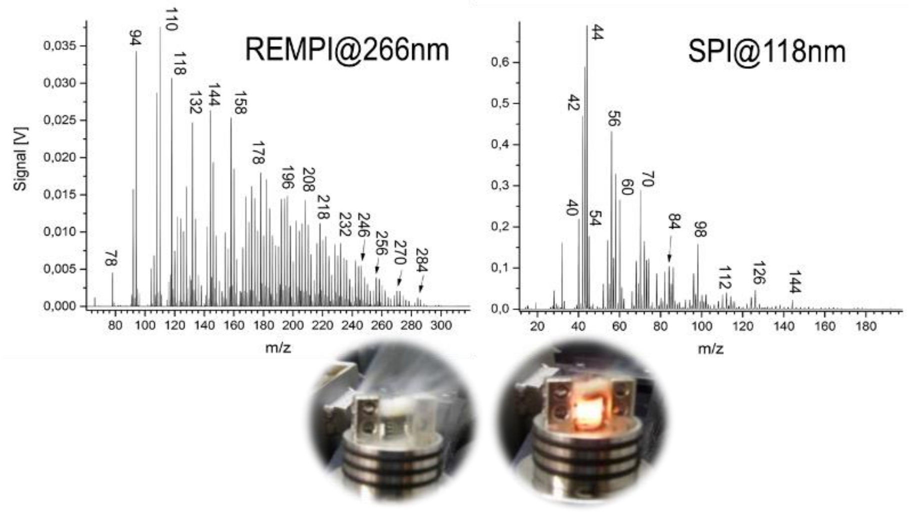


Figure 4: Intentional dry-burn of a cotton wick observed with REMPI (problematical aromatic species e.g. PAHs) and SPI (various smaller pyrolysis products) ionization.

On-line Investigation of THC containing smoking products

In the used preparation method of mixing tobacco with cannabis there are of course wide similarities in the spectral appearance shown in Figure below. But even without this artificially induced congruence respective similarities could be expected due to the fact that main process in a joint or cigarette is pyrolysis of organic material. The most interesting aspects are the differences in the spectra. Of course in the blank pure tobacco sample neither Delta-9-THC (m/z 314) nor Cannabinol (m/z 310) could be observed. For the cannabis containing samples always both compound can be seen but in different ratio. The Cannabinol concentration in the hashish sample is about 10 times higher than in weed or marijuana.

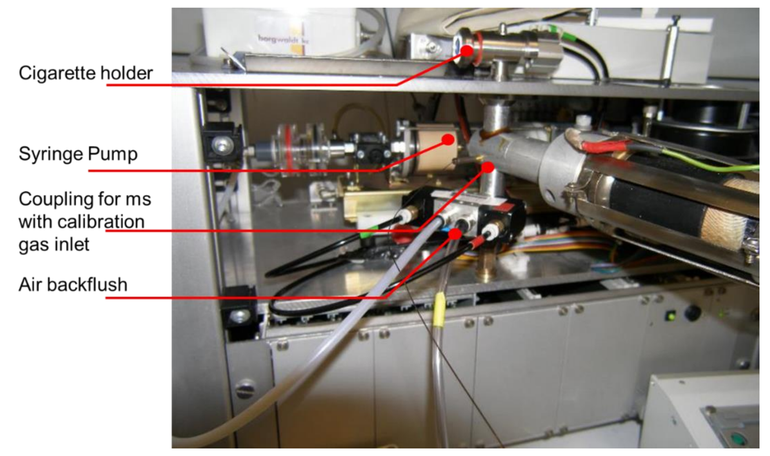


Figure 5: Experimental setup a) Smoking machine with heated adapter to the PIMS system, sucking mouth, syringe pump and pneumatically controlled backflush valves with calibration gas inlet

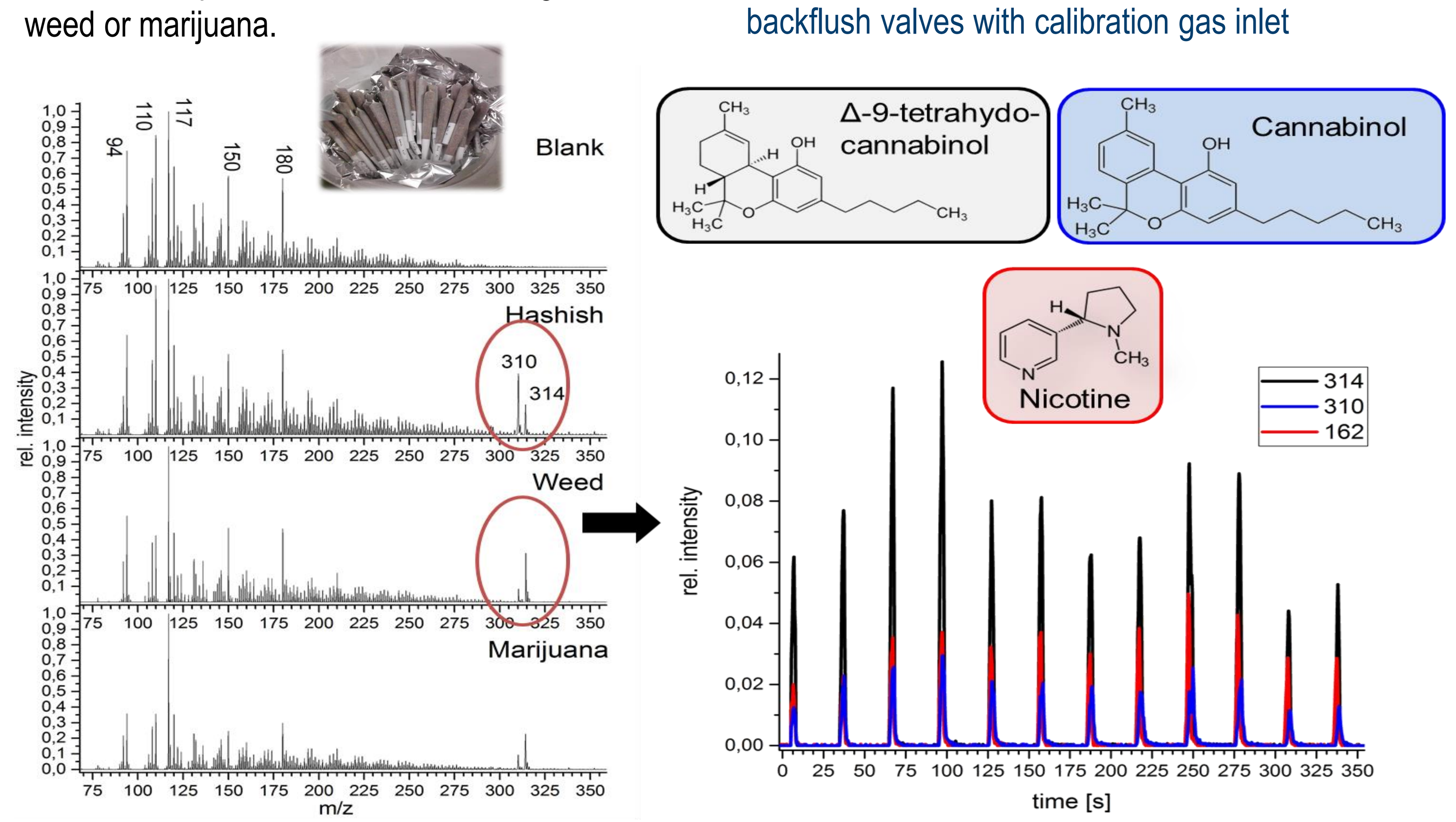
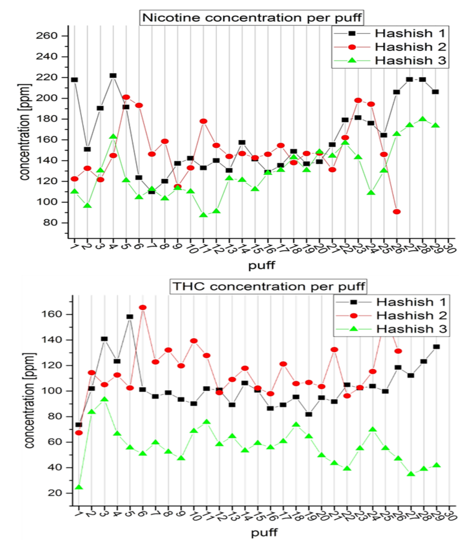
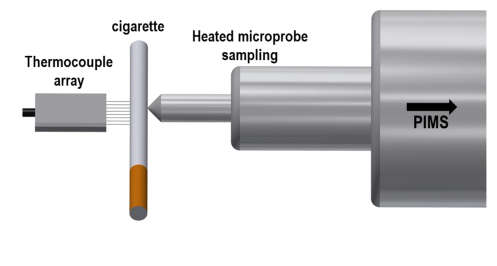


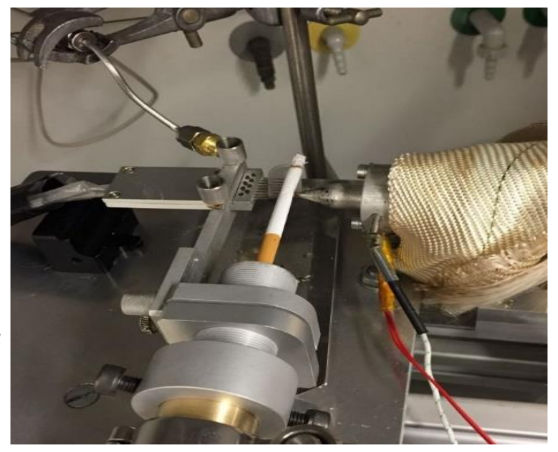
Figure 6 above: Spectral comparison of three different cannabis containing products/joints versus a pure tobacco containing blank sample. Remarkably is the change in the ratio between Delta-9-THC and Cannabinol between hashish and Weed/Marijuana flowers. The measurements were performed using REMPI ionization. **Below**: Puff by puff quantification of nicotine and Delta-9-THC in three different joints containing different hashish samples. Whereas the nicotine contents are quite comparable there are differences in the measured THC contents. Reference analytics confirm the trend of the online analysis; THC content: Hashish1: 16.7%; Hashish2: 17.3%; Hashish3 10.4%



Chemical mapping of combustion products in a cigarette

The majority of particulate matter in smoke is formed by incomplete combustion and pyrolysis of the tobacco biomass at temperatures of 300–600 °C. In-situ thermochemical and physiochemical mapping represents a powerful way to understand the complex combustion system inside the full biomass matrix. The temperature and pressure sensor arrays are combined with a microprobe for simultaneous sampling of the gas flow for chemical analysis by SPI-TOF-MS, an analytical technique that allows both real-time measurements of volatile organic compounds and on-line puff-by-puff monitoring of tobacco smoke constituents.





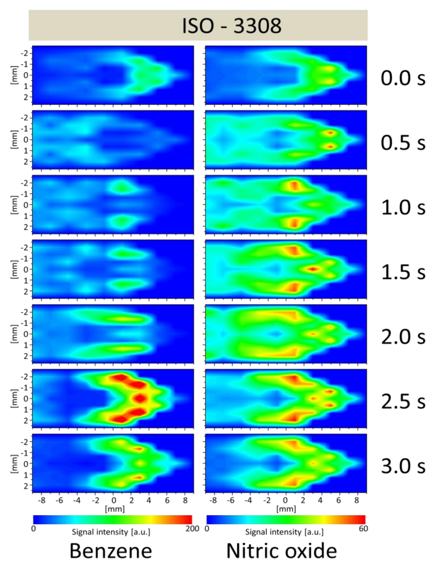


Figure 7 above: Experimental set-up. A, Diagram showing the thermocouple array and chemical sampling microprobe in relation to the cigarette. B, Image of the experimental set-up.
left: Time evolution of the substance concentration maps for NO and C_6H_6 in the cigarette tip/ash cone before and during an ISO puff of a super-slim commercial cigarette. The first row depicts the pre-puff situation. The following four rows show the situation in the first, second, third, and last quarter of the 2 s lasting puff. The last two rows illustrate the re-equilibration.

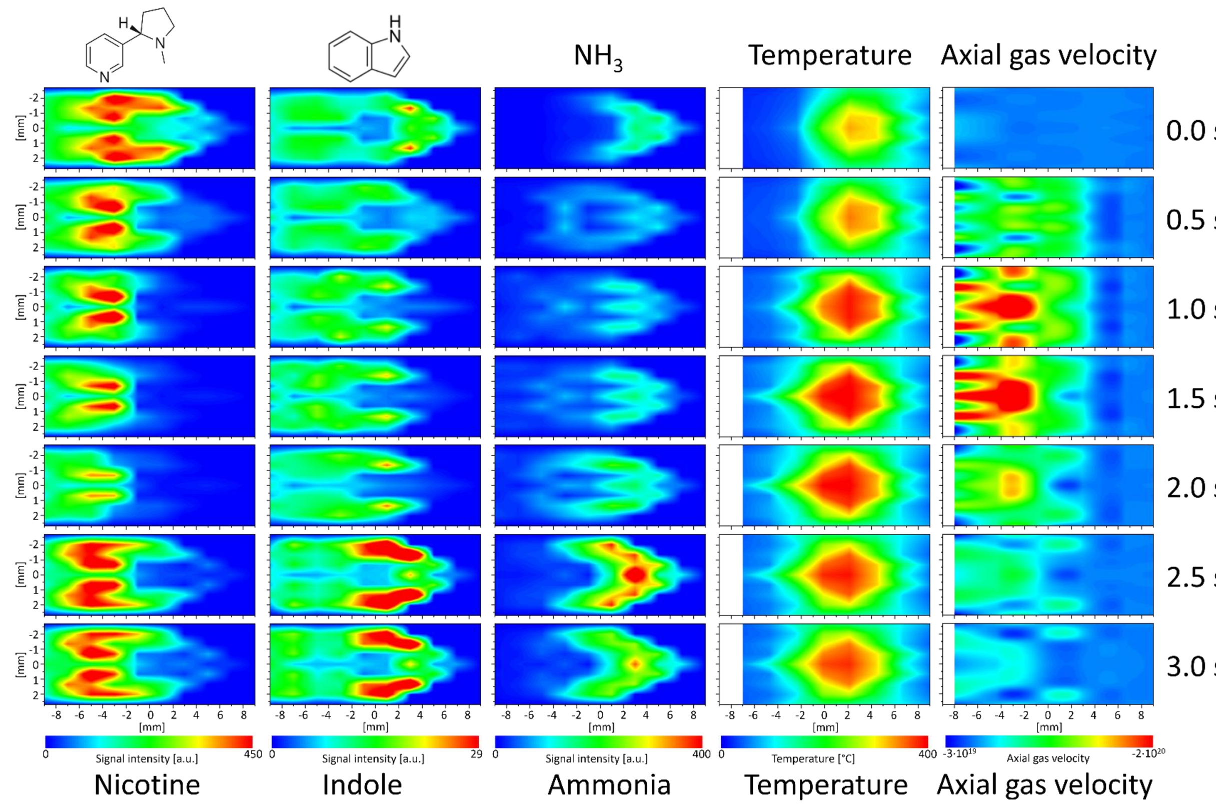


Figure 8 left: Time-resolved concentration/abundance maps of nicotine, indole and ammonia under ISO smoking conditions combined with change in gas-phase temperature and pressure fields within a burning super-slim cigarette. The nicotine desorption and degradation can be explained overlaying it with the temperature map.

Acknowledgements

photonion

Photonion GmbH is an innovative company providing customized solutions for monitoring of chemicals using mass spectrometry with soft ionization methods such as photo ionization.

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