REMPI-Laser-mass spectrometry: On-line and off-line analysis of the molecular signature of polycyclic aromatic hydrocarbons (PAH) in gas- and particle-phase of combustion aerosols

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Polycyclic aromatic hydrocarbons (PAH) and benzene derivatives represent important compound classes, present in combustion aerosols. On the one hand, PAH and their derivatives are known to be of high health relevance (chronic and acute lung and cardiovascular diseases). On the other hand, the signatures of the aromatic molecules in combustion aerosols characterize the combustion process and allows conclusion on the molecular formation mechanisms of soot and other pyrolysis and combustion by-products. Photoionisation mass spectrometry is an ideal approach for on-line-detection of the molecular signature of combustion aerosols. When the laser based resonance-enhanced multiphoton ionization method (REMPI) and a time-of-flight mass analyser (TOFMS) are used, unsurpassed sensitivities (ppb/ppt) and time resolutions (sub-second) are achieved for detection of aromatic molecular species. In Fig. 1A an on-line measured REMPI-TOFMS mass spectrum of wood combustion aerosol is depicted. The

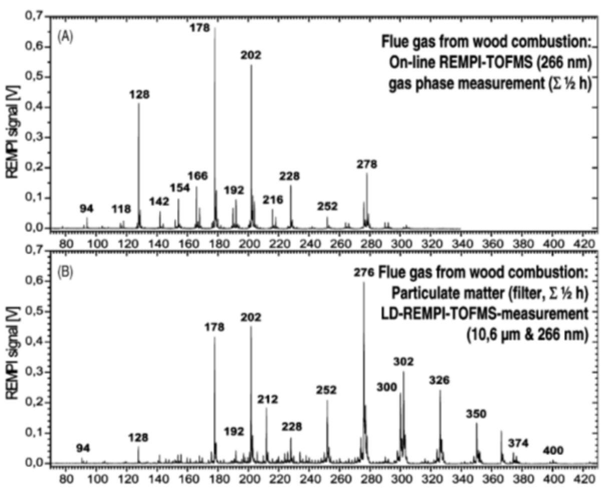

Figure 1) REMPI mass spectra of ***wood combustion aerosol***
A) Signal of the aromatic compounds in the ***gas phase*** *of a wood combustion experiments: more volatile aromatics are detected B) Laser desorption-REMPI mass spectrum of the aromatic compounds from the* ***particulate phase*** *(collected simultaneously to measurement of A): larger PAH are observed*

selectivity of the REMPI ionisation for aromatic compounds allows a straight-forward assignation of the observed mass peaks in the mass spectrum (e.g. for Fig. 1A: 94 m/z-phenol, 118 m/z-indane, 128 m/z-naphth-alene, 166 m/z-fluorene, 178 m/z-phenanthrene, 202 m/z-pyrene, 228 m/z-chrysene, 252 m/z-5-ring PAH including Benz[a]pyrene, 278 m/z 6-ring-PAH). By

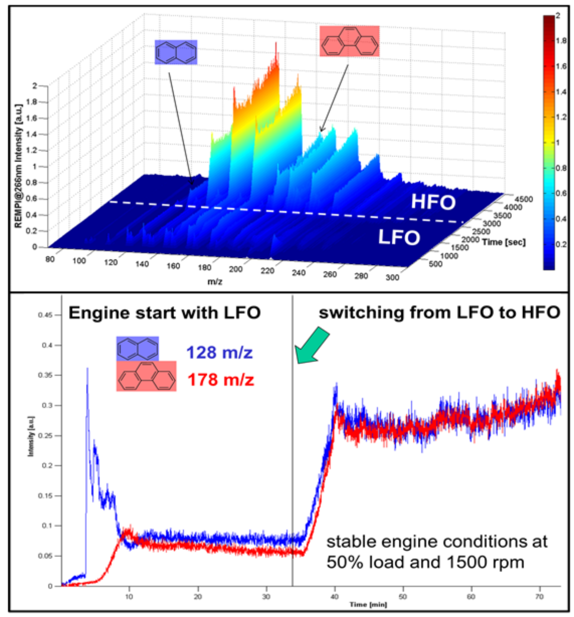

Figure 2 On-line measurement of the gas-phase aromatics (PAH and alkylated-PAH) in combustion aerosol from a ***ship diesel engine*** *operated with distillate fuel (light fuel oil, LFO) and residual fuel (heavy fuel oil, HFO) top) 3D-representation of the changes in aromatic REMPI mass spectral signature over time during a switch from "clean"LFO -fuel to"dirty" HFO-fuel. The lower part of the figure depicts the time-intensity curves for 2 selected PAH, naphthalene and phenanthrene.,*

using laser desorption (LD, e.g. direct from PM on filter) also the particle-bound aromatics can be rapidly analysed (Fig. 1B). It is obvious from Fig. 1 that the larger PAH are predominately particle bound.
During the HICE campaign at a ship diesel engine test bench, REMPI-TOFMS was used to follow the switch from LFO to HFO fuel in real time (Fig. 2). During the engine-start period, the large ship diesel engines are operated with LFO. The HFO fuel (melting point ~ 60 °C) is only introduced when the engine is at operational temperature. Fig. 2 shows clearly, that the emission of aromatic compounds, including the toxic polyaromatics, is increased significantly after the transition to HFO. The PM from ship diesel and wood combustion aerosol was furthermore investigated by a new coupling of an EC/OC-thermal analyser to a REMPI-TOFMS system, showing the aromatic signature of different thermal steps in the thermo-optical EC/OC measurement.

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