Thermal desorption/laser photo-ionisation aerosol mass spectrometry for on-line monitoring of molecular organic compounds from individual aerosol particles

M.Bente1,2, M.Sklorz1,2, T.Streibel1,2 and R.Zimmermann1,2,3

1Institute of Ecological Chemistry, Helmholtz Zentrum München, D-85764, Oberschleißheim, Germany
2Chair of Analytical Chemistry, University of Rostock, D-18051, Rostock, Germany
3bifa-Umweltinstitut, D-86167, Augsburg, Germany

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Within the last decade, aerosol mass spectrometry has evolved to a versatile tool for applied and fundamental aerosol research. Up to now, however, the detection of molecular organic species by aerosol mass spectrometry is very difficult. Recently a new single particle laser ionisation mass spectrometer, using a two-step laser-desorption photo-ionization approach for detection of aromatic molecular compounds on individual particles was developed and successfully tested (Bente 08). Tracked and sized individual single particles (SP) herein firstly are laser desorbed (LD) on the fly within the ion source of the mass spectrometer by a IR-laser pulse (CO2-laser, 10.2 µm). After some microseconds the released aromatic molecules are selectively ionized by an intense UV-laser pulse (ArF excimer, 248 nm) in a resonance enhanced multiphoton ionisation process (REMPI). The ions are detected in a time of flight mass spectrometer (TOFMS). With this setup (i.e. laser desorption – REMPI-ionisation – single particle – Time-of-flight mass spectrometry or LD-REMPI-SP-TOFMS) it is possible to detect profiles of polycyclic aromatic hydrocarbons (PAH) and their derivatives which are predominantly bound to the ambient fine particulate matter (PM). It could be shown, that source specific molecular indicators for diesel car emissions, gasoline car emissions as well as for biomass burning (soft/hard wood) are detectable. As PAH and their derivatives may show both, chronic toxicity (i.e. many PAH are potent carcinogens) as well as acute toxicity (i.e. inflammatory effects due to oxidative stress) and are discussed to be relevant for the observed health effects of ambient PM, a better understanding of the occurrence, dynamics and particle size dependence of particle bound-PAH is of particular interest. In this context it was decided to make the LD-REMPI-SP-TOFMS aerosol mass spectrometric technology for organic monitoring more suited for field measurements. For this purpose the laser desorption step (LD) is substituted by a thermal desorption (TD) step, similar as in case of the Aerodyne AMS technology (Bente 2009). However, due to the features of the pulsed REMPI photo-ionisation a single particle detection of molecular organic compounds remains possible. With the current aerosol inlet system particles from about 400 nm to 10 µm are accessible. The novel thermal desorption – REMPI-ionisation – single particle – Time-of-flight mass spectrometry approach (TD-REMPI-SP-TOFMS) was tested with standard aerosol in the laboratory (re-dispersed wood ash). Furthermore real-world combustion aerosols were investigated (diesel/gasoline car emissions). Finally ambient measurements were performed using a virtual impactor enrichment unit to increase the detection frequency of ambient particles in the covered size range. It was possible to find distinct differences in the pattern of PAH and PAH derivatives in the single particle mass spectra from different sources (e.g. gasoline, wood combustion and diesel emissions). In Figure 1 a TD-REMPI-SP-TOFMS mass spectrum from ambient air (winter) is shown. The results obtained with the novel on-line thermal desorption method are comparable to the ones obtained by the earlier, more sophisticated two laser-technology. In conclusion, on-line thermal desorption laser photo-ionization single particle mass spectrometry (TD-RTEMPI-SP-TOFMS) represents a promising technology for field measurements and source apportionment studies based on single particle organic analysis. It is planned to apply the technology at the Augsburg aerosol monitoring super-site of the Helmholtz-Zentrum München.