Hyphenation of a Thermal/Optical Carbon Analyzer to photo-ionization mass spectrometry for determination of the organic content of aerosol particles

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The identification of carbonaceous fractions of particulate matter on a molecular level still provides an analytical challenge. Knowledge of organic composition is of great importance with respect to health effects or aerosol particles. The determination of sum parameters such as total organic and elementary carbon (OC and EC) following thermal desorption at different temperatures already yields valuable information. However, the method provides no insight of the molecular composition of the distinct thermal fractions. Therefore, hyphenation between a commercial thermal/optical carbon analyzer and a time-of-flight mass spectrometer equipped with photo-ionization has been developed. With this new setup, desorbed organic compounds can be analyzed prior to their oxidation to carbon dioxide by sidelining a small part of the gas flow. For this, the quartz tube between sample holder and oxidizer had to be modified. The new coupling piece extends into an aluminum box, which is heated to 230 °C to prevent condensation. The modified quartz tube is coupled inside the box to a capillary running inside a heated curing tube, which guides the molecules to the ion source of the mass spectrometer. In total a flow of 5 ml/min is led to the mass spectrometer. Ionization is carried out with two soft methods, viz. resonance enhanced multi photon ionization (REMPI), which is selective for (poly)aromatic compounds as well as single photon ionization (SPI), which allows a more universal analysis of aliphatic and aromatic species. By doing this, the molecular pattern of each organic fraction is obtained. Figure 1 depicts a scheme of the instrumental setup and an exemplary two-dimensional graph of the mass spectrometric pattern of a complete OC/EC experiment of diesel exhaust particles.

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With the new instrumentation ambient aerosols as well as source particles from combustion processes have been investigated. Furthermore, particles from smog chamber experiments with α- und β-pinene as precursors were analyzed. Ambient samples taken in winter showed a big influence from wood combustion, whereas samples taken in summer at the same location missed wood combustion markers, but were dominated by secondary organic aerosol (SOA). Comparison with smog chamber filter samples experiments revealed typical mass to charge signals (at m/z 58 and 82, respectively) that are not observable in any other sample. These could therefore be potential marker substances for SOA. Particles from cold start emissions of gasoline cars showed larger polycyclic aromatic hydrocarbons than those from diesel cars. With diesel cars, there was also a significant influence of the biodiesel content on the product pattern. In general, at higher desorption temperatures the spectra are shifted to smaller molecules, which are formed by thermal decomposition of larger oligomeric and polymeric species, suggesting the possibility to learn more about the nature of such larger structures.

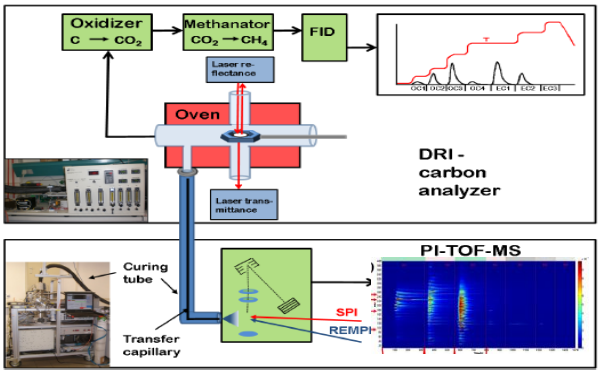

Figure 1: Experimental setup of the hyphenation between a thermal/optical carbon analyzer and photo-ionization mass spectrometry depicting a two-dimensional mass spectrometric pattern of a complete OC/EC analysis of diesel exhaust particles

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