
Hendryk Czech, Olli Sippula, Martin Sklorz, Thorsten Streibel, Ralf Zimmermann

Introduction / Experimental setup

The carbonaceous fractions of fine particulate matter (PM) from a ship diesel engine burning heavy fuel oil (HFO) and conventional diesel (light fuel oil, LFO) at complete motor cycles as well as four different single loads have been investigated within a field campaign at the faculty of engineering of the University of Rostock. Ship diesel particulate emissions impact climate by changing the radiative budget of the Earth, and human health by causing respiratory ailments, carcinogenesis and cardiovascular diseases [1]. To develop effective strategies for reducing these impacts, emissions of particulate matter have been collected on quartz fiber filters and analyzed by a thermo/optical carbon analyzer (fig. 1 & 2), which has been coupled to a time-of-flight mass spectrometer (TOFMS) using single photon (SPI) and resonance-enhanced multi photon ionization (REMPI) [2]. Due to the stepwise heating of the sample in account with the “improveA” temperature protocol, four fractions of organic carbon (OC1 – OC4) and three fractions of elemental carbon (EC1 – EC3) are obtained and quantified by a flame ionization detector (FID). In addition to the sum parameters OC, EC and the total carbon content TC, the coupling to the TOFMS using soft photoinization enables the detection of individual compounds in each fraction on a molecular level. SPI allows to ionize all compounds with an ionization energy below 10.49 eV, whereas REMPI is known to be very selective for (poly-)aromatic hydrocarbons.

Results and Discussion

Three kinds of datasets have been obtained from the analyses of five HFO and LFO particulate matter samples collected on quartz fiber filters. Single fractions of organic and elemental carbon have been condensed to established quantities OC and EC (fig. 3). Moreover, mass spectra of OC1 and OC2, which are regarded as thermodesorption-like, have been averaged to OCd, and normalized to total ion count to warrant comparability. Hereinafter, SPI- and REMPI-spectra (fig. 6 & 7) of HFO- (blue) and LFO-derived (red) combustion aerosols are discussed.

- **Single Photon Ionization @118nm**
  - SPI spectrum of HFO is dominated by alkylated PAH such as phenanthrene, chrysene and benz[a]pyrene, but the homologue series of dibenzothiophene as well
  - LFO-derived particle feature a variety of compounds
  - Fatty acid methyl – and ethyl esters (FAEE & FAEE) from biodiesel refer to be as the most abundant species
  - Naphthalic anhydride is observed as a major component on LFO-derived particulate emission

- **Resonance-enhanced Multiphoton Ionization @266nm**
  - REMPI results of HFO exhibit many PAH, including large basic structures of aromatics and high alklylation
  - Phenanthrene and chrysene series are most abundant
  - REMPI spectrum of LFO is less complex than SPI
  - Only alkylated phenanthrenes and naphthalenes together with C12 to C14-pyrene are found
  - Large polyaromatic structures are absent

Conclusion

- **HFO combustion leads to more than the double quantity of particulate emissions of OC and TC**
- **LFO particulate emissions are characterized by a fourfold higher quantity of EC**
- **Due to contrary trend of OC and EC in HFO and LFO particulate emission, both kinds of emission can be distinguished by their ratios OC/EC**

Reference:
[1] Mladenova, J; Field, Z; Prokhorcheva, O; Dombradi, D; Tonkova, V; Fucikova, A; Pena, C; Characterization of particulate matter and gaseous emissions from a large ship diesel engine. Atmospheric Environment, 2019

[2] Grabowsky, J; Strelt, T; Sleto, M; Chow, J C; Widen, J; Mihalisin, A; Zimmermann, R; Comparison of a carbon analyzer to photo-ionization mass spectrometry to unravel the organic composition of particulate matter of a molecular level. Analytical & Bioanalytical Chemistry, 2011

Contact: hendryk.czech@uni-rostock.de, ralf.zimmermann@uni-rostock.de, ralf.zimmermann@helmholtz-muenchen.de

Universität Rostock, Institute of Chemistry, Division of Analytical Chemistry & Joint Mass Spectrometry Centre, 18059 Rostock, Germany

University of Eastern Finland, Department of Environmental Sciences, Fine Particle and Aerosol Technology Laboratory, P.O. Box 16271 FI-70211 Kuopio, Finland

Joint Mass Spectrometry Centre, Institute of Ecological Chemistry, Helmholtz Zentrum München, 85764 Neuherberg, Germany