Fourier-transform-ion-cyclotron-resonance mass spectrometry with laser-desorption-ionization of primary ship diesel exhaust particles

C. Rüger[1], T. Schwemer[1,3], M. Sklorz[1,2,3], R. Zimmermann[1,2,3]

[1]Joint Mass Spectrometry Centre / Chair of Analytical Chemistry, University of Rostock, 18051 Rostock, Germany
[2]Joint Mass Spectrometry Centre, Cooperation Group Comprehensive Molecular Analytics, Helmholtz Zentrum München, Ingolstädter Landstr. 1, 85764 Neuherberg, Germany
[3]HICE – Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health – Aerosols and Health, www.hice-vi.eu

Keywords: ship diesel emissions, LDI, high resolution mass spectrometry, soot
Presenting author email: christopher.rueger@uni-rostock.de

Introduction

Negative effects on the health caused by combustion aerosols are known since a long time. One of the most underestimated sources are ship diesel emissions. The comprehensive chemical characterization of organic compounds in the particulate matter is the key for a deeper understanding of biological health effects.

The chemical composition of ship diesel combustion aerosol is poorly investigated. Due to the extreme high complexity of combustion aerosols high resolution mass spectrometry using laser-desorption-ionization is one promising tool for revealing components with the same molecular mass and assigning molecular sum formulas.

Experimental Section

The samples were taken during a measurement campaign at the Faculty of Mechanical Engineering and Marine Technology at University Rostock. The experiments were performed at a four-stroke one cylinder ship diesel engine with three liter cylinder capacity driven with heavy fuel oil (HFO) and light fuel oil (LFO) at different loads.

Exhaust gas was diluted by clean air and particles were collected by impaction on aluminum or stainless steel foils. Size classes of the applied low pressure impactor ranged from 30 nm up to 10 µm. Time traces were collected using a rotating drum impactor with cutpoints of 0.1 µm, 1 µm and 10 µm, respectively.

The measurements were carried out with a solariX Fourier-transform-ion-cyclotron-resonance mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7 Tesla superconducting magnet. The setup was used without further modification except of a self-made MALDI-Target to position the impactor foils directly in the ion source. The third harmonic of a Neodymium-YAG laser (355 nm) was used with moderate laser strength of 30 up to 70 % and various foci. Mass resolution was set to about 300˙000 @ m/z = 400.

Results and Discussion

The laser-desorption-ionization (LDI) mass spectra obtained show two types of ionized species: radical cations and protonated species. Most abundant are $CH^{\bullet+}$, $CHO^{\bullet+}$ and $CNH^{\bullet+}$ class compounds, in accordance to the results of Cho et al. (2012).

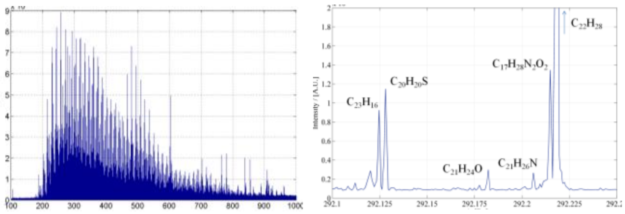

Figure 1: Broadband mass spectrum (left) and a blow up of m/z = 292.1 to 292.2 (right) of HFO-combustion particles sampled by ELPI obtained by (+) laser-desorption-ionization mass spectrometry

Direct LDI-measurements of the HFO feed indicates that the majority of the signals refer to products of incomplete combustion. Additionally, differences in the intensity of individual species and some new compounds were identified in the aerosol.

The high resolution mass spectrometry allows the determination of exact sum formula; thereby the signals can be assigned to alkylated, nitro- and oxo-PAH-species as well as to low abundant sulfur containing molecules. Because of the ionization method no aliphatic compounds were found.

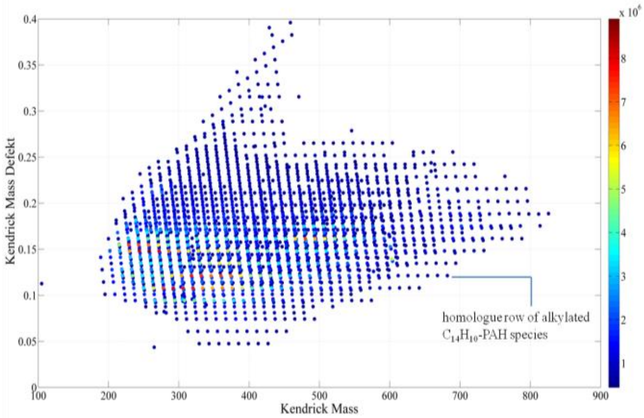

Figure 2: Kendrick Plot observed from HFO sample by (+) laser-desorption-ionization

Acknowledgements

This work was supported by the University Rostock and the Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE).

Cho, Y., Witt, M., Kim, Y. H., Kim, S. (2012) *analytical chemistry*, **84**, 8587 - 8594