CHARON PTR-ToF-MS: a new method for real-time measurement and molecular-level characterization of submicron organic aerosol

Philipp Eichler[1], Markus Müller[1,2], Andreas Klinger[2], Alfons Jordan[2] and Armin Wisthaler[1,3]

[1] Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Innsbruck, AUSTRIA

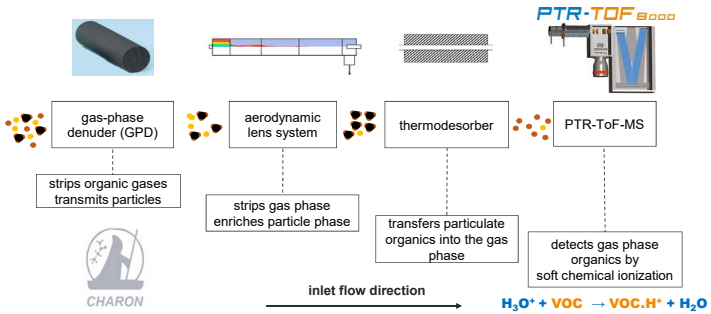
[2] IONICON Analytik GmbH., Innsbruck, AUSTRIA

[3] Department of Chemistry, University of Oslo, Oslo, NORWAY

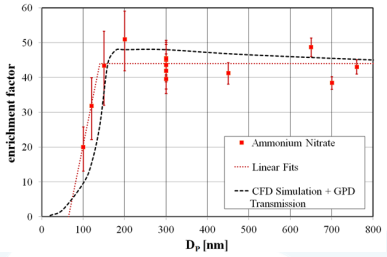
Introduction

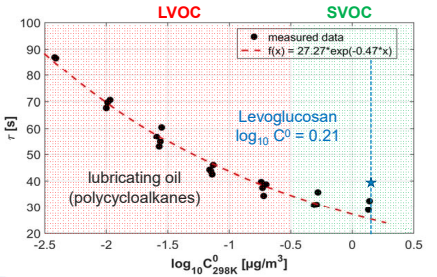
A quantitative characterization of the organic fraction of atmospheric particulate matter is still challenging. Available off-line techniques are typically slow, labor intensive and often prone to analytical artifacts. Emerging on-line mass spectrometric techniques suffer from low limits of detection, intensive fragmentation or lack true real-time capabilities. Herein we present the novel modular "**CHemical Analysis of aeRosol Online**"; (CHARON) inlet system designed to be coupled to a proton-transfer- reaction time-of- flight mass spectrometer (**PTR-ToF- MS**) that quantitatively detects most organic analytes and ammonia in **real-time** by chemical ionization with hydronium reagent ions. [1]

CHARON PTR-ToF-MS: Working Principle



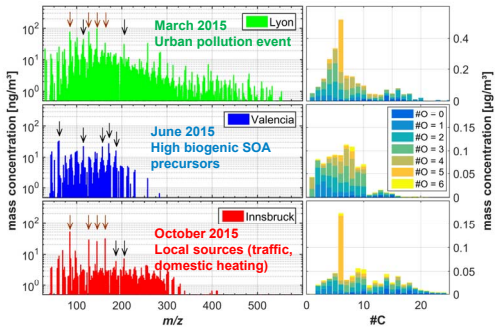
Performance Overview

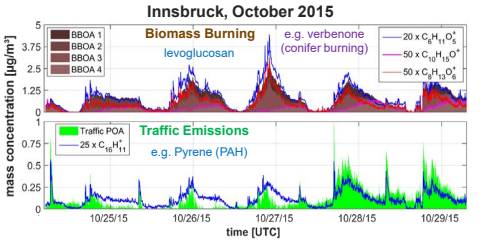




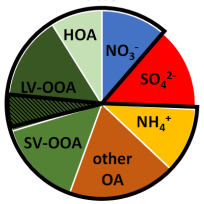
- Particle Enrichment: **Factor ~ 44** (D_p > 150 nm)
- Denuder **VOC adsorbtion** > 99.999%
- Response: sec. **(lVOC)** to single min. **(LVOC)**
- Limit-of-Detection: **single digit ng m^{-3}** (1 min)

Urban Particulate Organic Matter

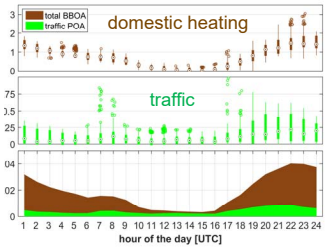




- Non-refractory urban particulate organic matter is composed of a **complex mixture**
- Contributions from contenental and regional (e.g. **SV-** and **LV-OOA**) backgrunds and urban sources (**HOA** from traffic, **BBOA** from domestic heating)
- Chemical characterization of organic PM by CHARON in **Lyon** (France), **Valencia** (Spain) and **Innsbruck** (Austria).
- Several **molecular tracers** were monitored quantitatively including **levoglucosan** (biomass burning tracer) and carcinogenic **PAHs** (traffic and biomass burning)



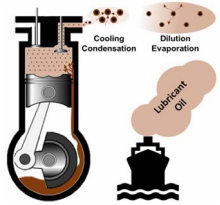
Detectable fraction by CHARON PTR-ToF-MS

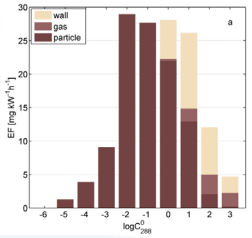


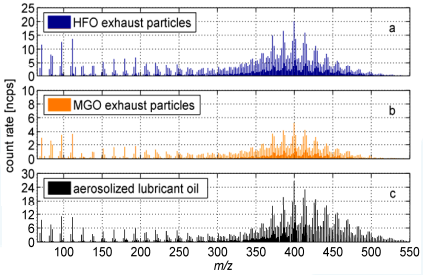
- Molecular tracer information was used for interpreting **positive matrix factorization** (PMF)
- **Sources** of particulate organic matter can be apportioned and emissions can be quantified.
- 73% of all detected **carcinogenic PAHs** are emitted from **domestic heating** in western Innsbruck.

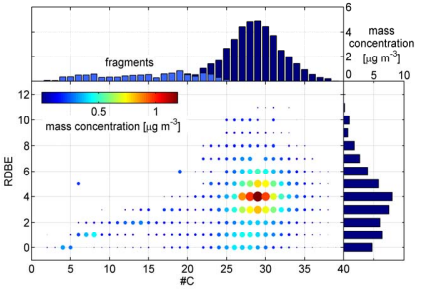
Lubricating Oil Emissions From Ship Engines

- First molecular level characterization of **ship engine exhaust** primary organic aerosol [2]
- CHARON PTR-ToF-MS mass spectra from **Heavy Fuel Oil** (HFO) and **Marine Gas Oil** (MGO) engine exhaust were dominated by **polycycloalkanes** in the C20-to- C39 range, which are typical main constituents of **lubricating oils**
- **Volatility distribution** of the organic fraction of the particles could be measured by **thermo-denuder** experiments
- Estimation of total **emission factors** (EF) including the particulate, gas and wall phases









CHARON PTR-ToF-MS is a powerful tool for on-line and real-time characterization of organic particulate matter

References

[1] Eichler, P., Müller, M., D'Anna, B., and Wisthaler, A.: A novel inlet system for online chemical analysis of semi-volatile submicron particulate matter, Atmos. Meas. Tech., 8, 1353-1360, doi:10.5194/amt-8-1353-2015, 2015.

[2] Eichler, P., Müller, M., Rohmann, C., Stengel, B., Orasche, J., Zimmermann, R., and Wisthaler, A.: Lubricating Oil as a Major Constiutent of Ship Exahust Particles, Environ. Sci. Technol. Lett, 4 (2) 54-58, doi: 10.1021/acs.estlett.6b00488, 2017

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