A versatile laminar-flow oxidation reactor for studying multiple-day oxidation of atmospheric organics

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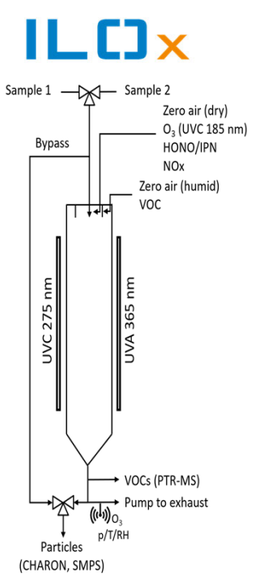
IONICON Laminar-Flow Oxidation Reactor



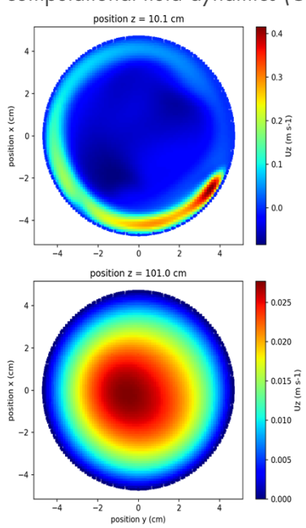
The automatable IONICON Laminar-flow Oxidation Reactor (ILOx) consists of a 110 cm long Quartz glass tube with a total internal volume of 8 l. Typical residence times range from 2 to 8 min. All materials are optimized for purest experiments possible (Quartz glass, Teflon and passivated surfaces only). To achieve a laminar flow condition inside the reactor, the carrier gas is injected by a circular motion, suppressing any formation of injection jets. Various oxidants can be supplied via multiple customizable inlet ports. To maintain stable temperatures inside the ILOx reactor active cooling via a set of fans is fully sufficient.

Three types of UV lamps power the photooxidation:

- An external UVC lamp (185 nm): production of O_3 from 0 to 3 ppmV
- Two dimmable UVC LEDs (275 nm): for photolysis of O_3 to produce OH in ILOx
- A dimmable UVA LED (365 nm): for photolysis of e.g. HONO or Isopropylnitrite (IPN) for OH formation and NOx cycling

Flow Conditions

The geometries for optimal sample injection and extraction were optimized via 3D computational fluid dynamics (CFD) simulations using OpenFOAM (openfoam.org).



➢ *Inlet*

Our 3D CFD simulations resulted in a best initial mixing and following optimal laminar flow conditions via a dual radial injection of the buffer gas and the sample. A benefit of this radial injection is the prevention of a formation of a jet at the center of the reactor.

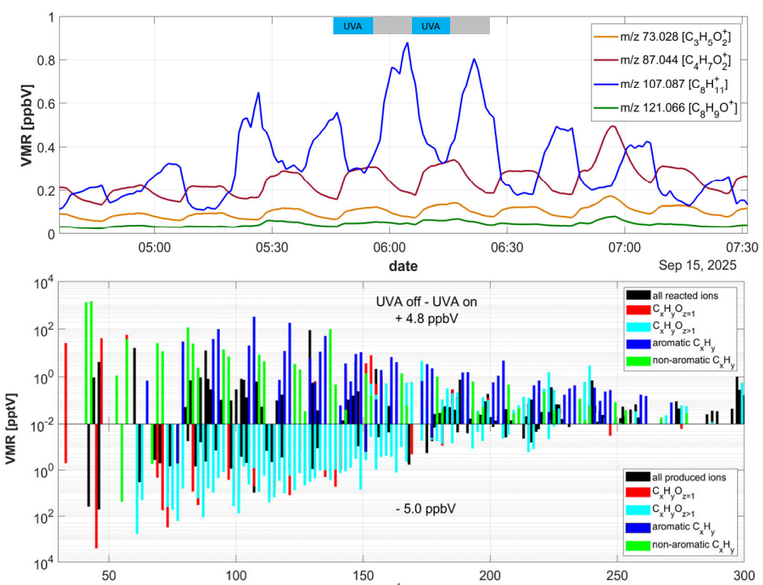
➢ *Reactor*

We have chosen a length-to-diameter ratio of > 10 for reaction conditions that resemble a traditional aerosol-flow-tube reactor. With the optimized inlet geometry optimal laminar flow conditions can be reached at various residence times.

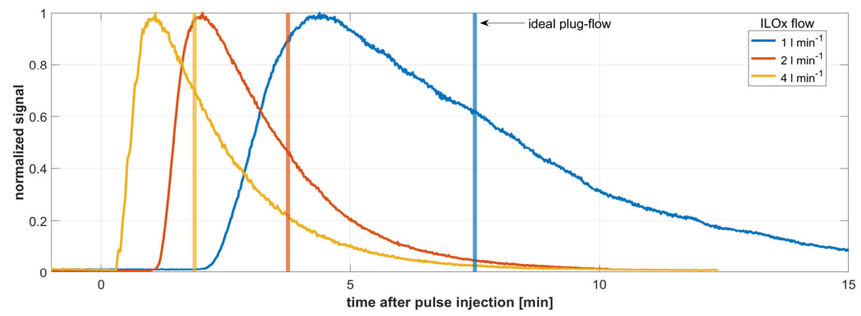
➢ *Outlet*

A conical outlet is followed by a core sampling of VOCs to minimize the loss of low volatiles while simultaneously transmitting the particles at highest efficiencies.

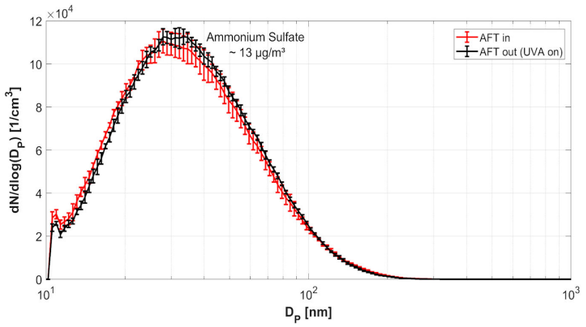
Atmospheric Multiple-Day Oxidation



Laminar-Flow Characterization



Particle Transmission Efficiency



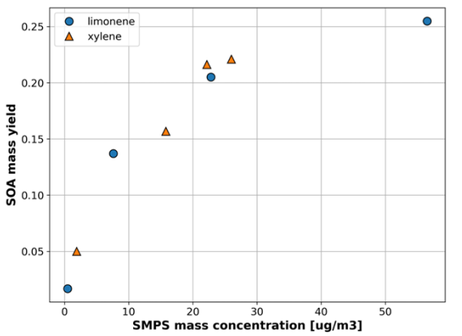
➢ Measurement of Ammonium Sulfate (AS) particles before and after ILOx.

➢ Excellent transmission of AS particles almost independent of particle size.

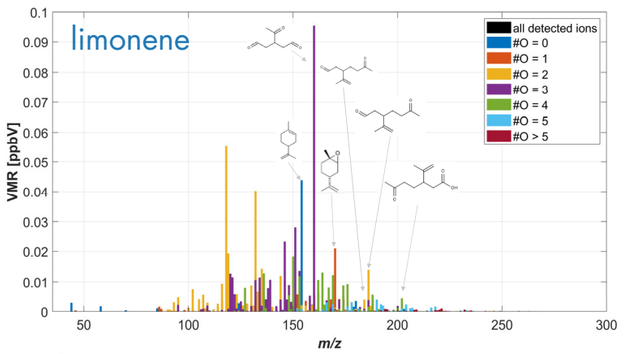
Characterization of SOA Mass Yield

➢ Limonene and xylene precursors were oxidized without seed in ILOx via photolysis of ozone.

➢ SOA mass yields match expectations from OFR and smog chamber experiments.



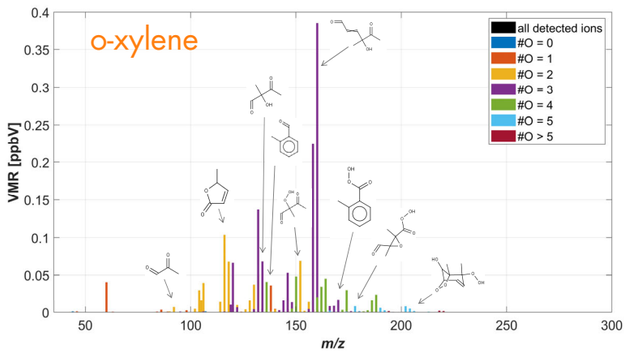
Gas Phase Oxidation: Molecular Insights



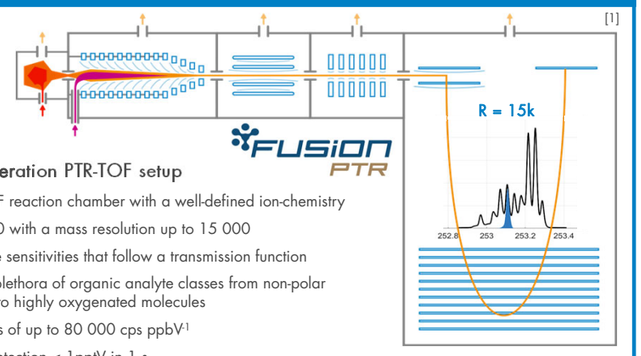
➢ Soft adduct ionization with NH_4^+ conserves the chemical compositions of oxidation products – no interferences with fragments hinder the interpretation of the recorded mass spectra.

➢ We injected limonene and o-xylene into ILOx to oxidize them with OH and ozone.

➢ Chemical compositions of the oxidation products match well with MCM 3.3.1 predictions.



FUSION PTR-TOF



A Next-Generation PTR-TOF setup

- FUSION RF reaction chamber with a well-defined ion-chemistry
- TOF-MS 10 with a mass resolution up to 15 000
- Predictable sensitivities that follow a transmission function
- Detects a plethora of organic analyte classes from non-polar aromatics to highly oxygenated molecules
- Sensitivities of up to 80 000 cps $ppbV^{-1}$
- Limits of Detection < 1pptV in 1 s

References

[1] Tobias Reinecke, Markus Leiminger, Alfons Jordan, Armin Wisthaler, and Markus Müller, 2023, Ultrahigh Sensitivity PTR-MS Instrument with a Well-Defined Ion Chemistry, Anal. Chem., 95, 32, 11879–11884, https://doi.org/10.1021/acs.analchem.3c02669

[2] Tobias Reinecke, Markus Leiminger, Andreas Klinger, and Markus Müller, Direct detection of condensed particulate polycyclic aromatic hydrocarbons on a molecular composition level at low pg m-3 mass concentrations via proton-transfer-reaction mass-spectrometry, Aerosol Research, 2, 225–233, 2024.