

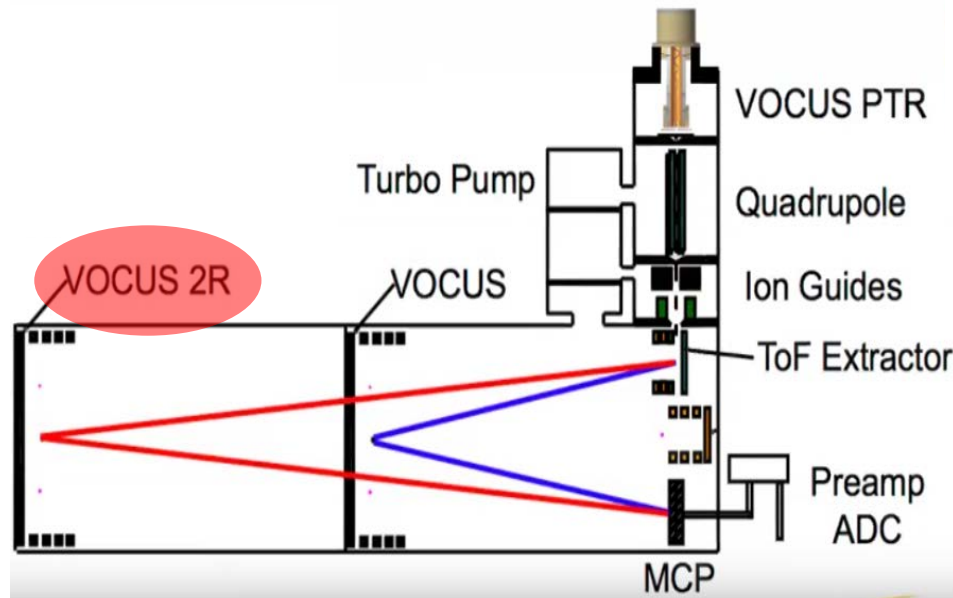


Milestone 10.10

Milestone 10.10: Instrumentation for the detection of oxygenated / nitrogenous / highly functionalized species made available at chambers

Achievements:

- New instruments for HO₂ and CH₃O₂ detection based on cavity ring-down spectroscopy (CRDS) developed for HIRAC (NCAS-Leeds)
- New instruments for radical detection based on chemical ionization mass spectrometry (CIMS) in HELIOS (CNRS-ICARE), at TROPOS and in SAPHIR (FZJ)
- New chemical modulation system developed for OH instrument based on laser-induced fluorescence (LIF-CHEM) in SAPHIR (FZJ)

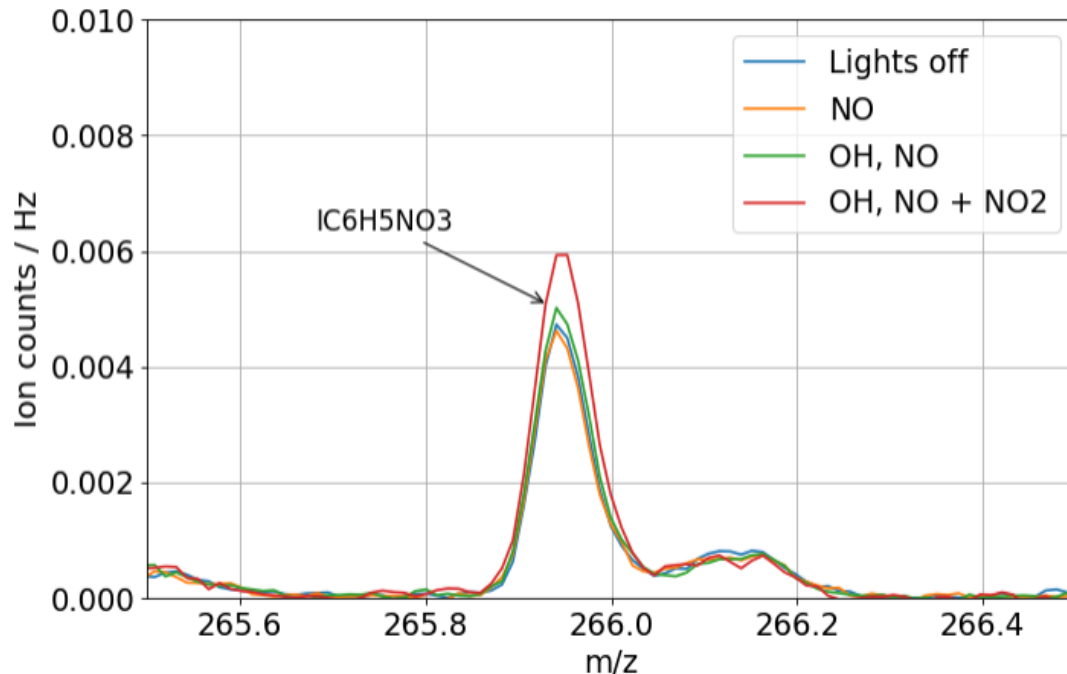


Installation of two new mass spectrometry instruments at the SAPHIR chamber

- Aerodyne VOCUS PTR-TOF-MS
- Aerodyne TOF-MS with custom-built Br⁻ CIMS inlet

- Detection of organic hydroperoxid species (tested for isoprene derived hydroperoxides)
- Detection of organic nitrogen oxide species (tested for products from isoprene + NO₃)

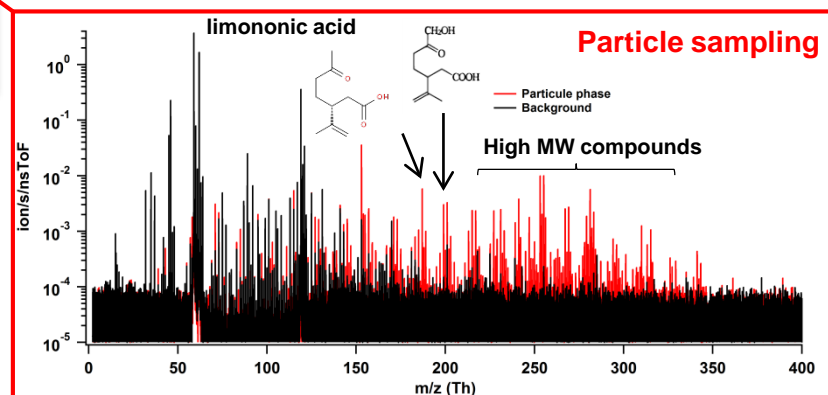
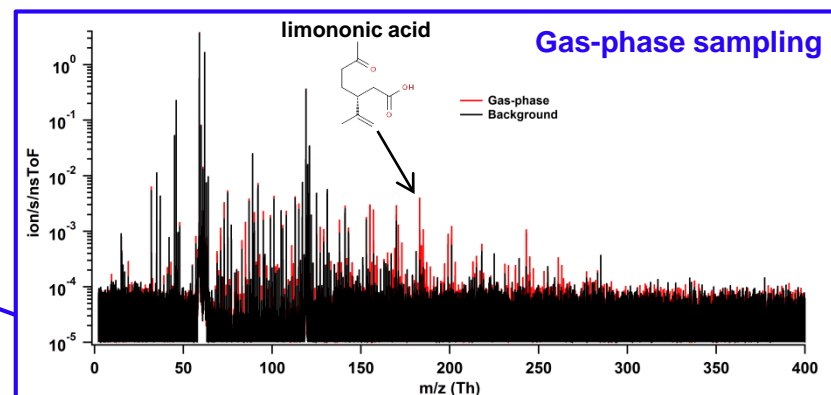
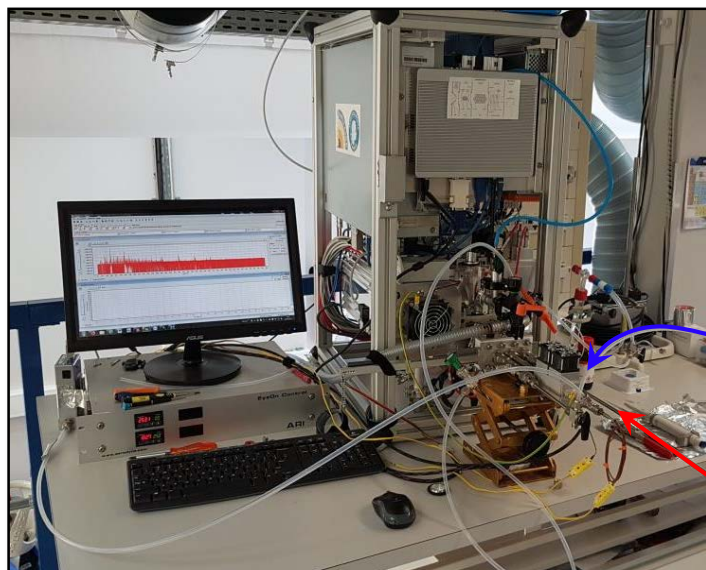
- TOF-CIMS utilising an iodide chemical ionisation scheme has been used to identify and quantify OVOCs including organic acids and organic nitrates in alpha-pinene SOA.
- The formation of organic nitrates during the oxidation of benzene using hydroxyl radical in the presence of nitrogen oxides has also been investigated.



Formation of organic nitrate in the benzene oxidation system: growth of a peak corresponding to $C_6H_5NO_3$ identified as nitrophenol. Similarly, the growth of $C_6H_4N_2O_5$ and $C_6H_3NO_4$ identified as dinitrophenol and nitrobenzoquinone, respectively followed the same trend as nitrophenol.

Task 10.4.2: New measurement technology towards a carbon balance

Limonene ozonolysis in the presence of SO₂ using acetate Figeero-HR-ToF-CIMS



- Increase in high molecular-weight compounds in the particle phase corresponding to lower volatility compounds partitioning to aerosols

- Development of a CEAS system for measuring Glyoxal and m-Glyoxal at EUPHORE. Set-up under progress
- HPLC system, with Fluorescence detection, has been optimised. Samples can be taken every 5 minutes automatically, reducing the sampling time. Measurements of hydroperoxides as part of the EUPHORE's auxiliary mechanism
- Improvement of on-line techniques for the detection and quantification of highly oxygenated compounds in the gas-phase by means of SPME-GC-MS (solid phase micro-extraction plus gas chromatography -mass spect.) with double derivatization. Already used to measure small oxygenated comps within the small OVOCs intercomparison at EUPHORE

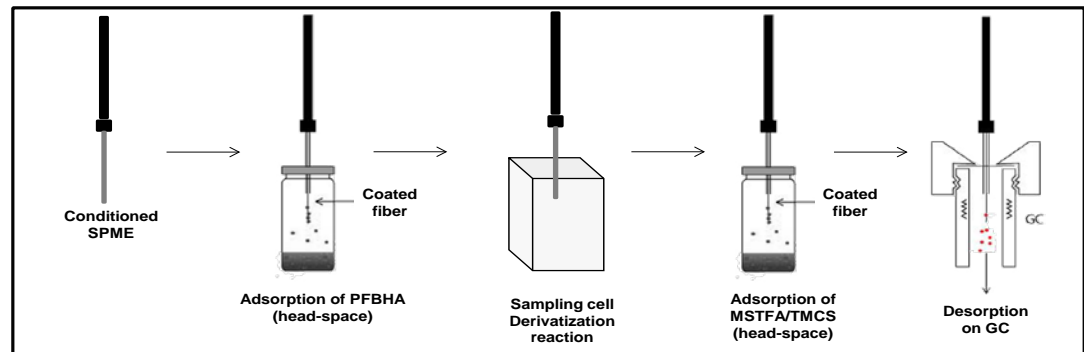
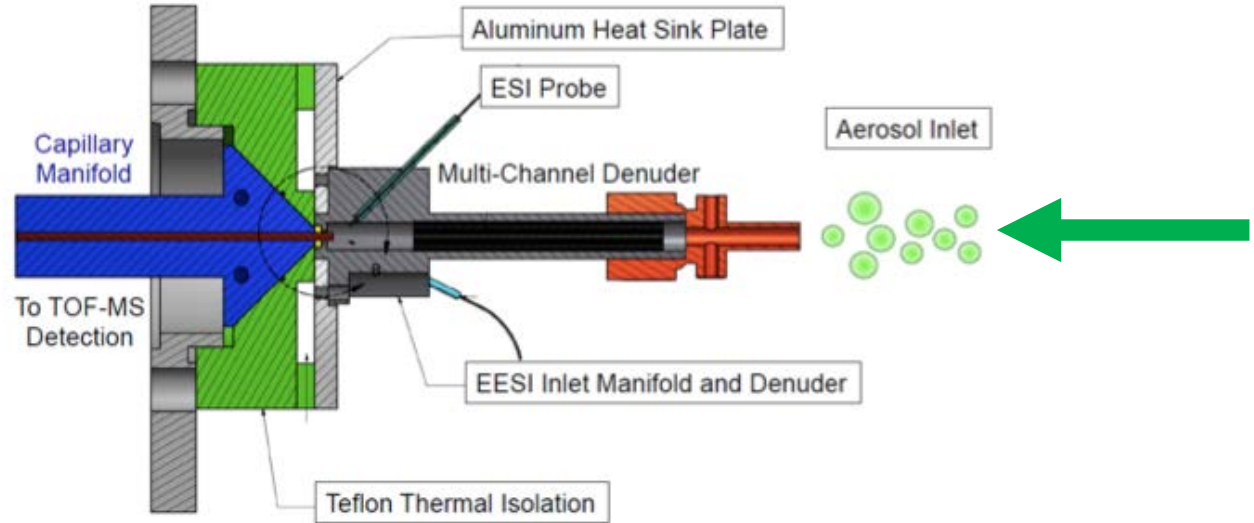
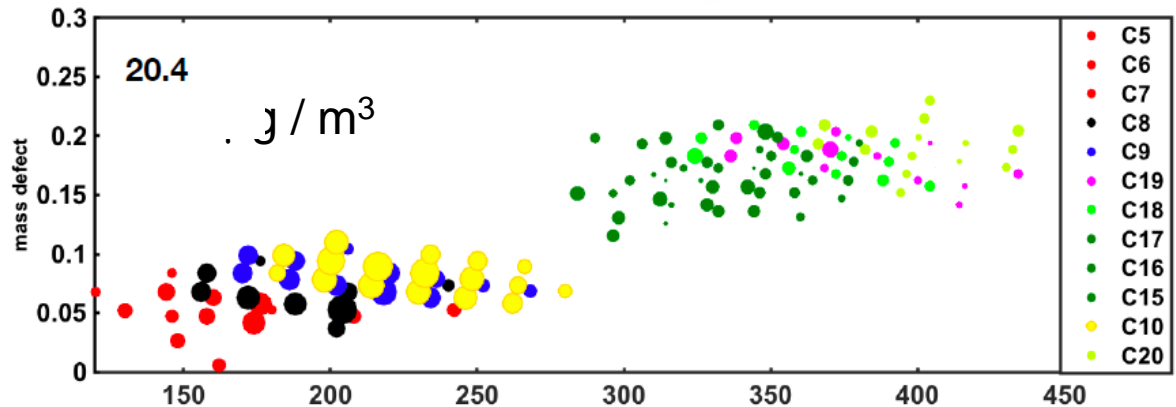
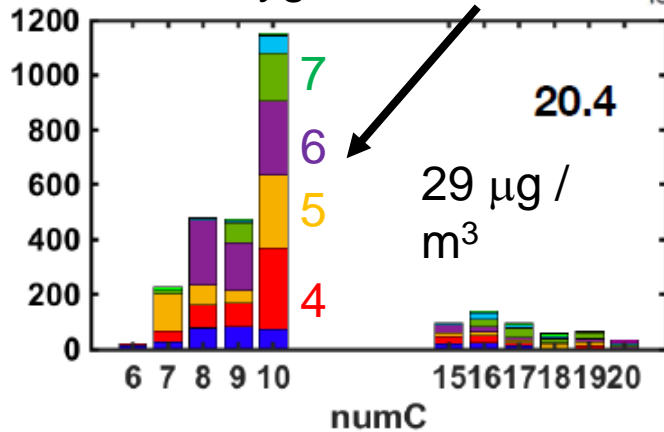


Fig: Derivatization protocol for hydroxy-carbonyl compounds



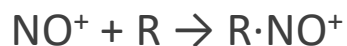
Ionization and Evaporation Extraction Gas Phase Removal Filter Blank Sample Valve

Oxygen Number



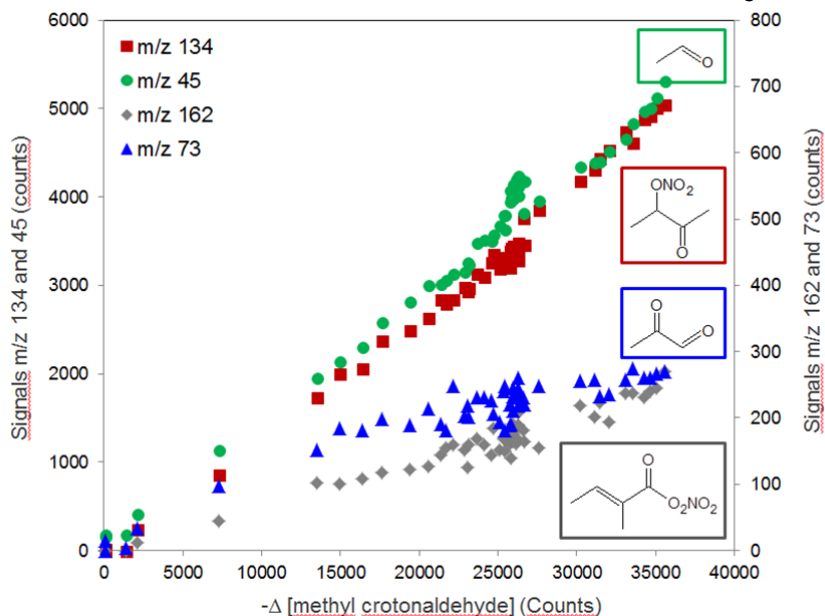
Organic nitrates (ON) difficult to detect by "classical" analytical techniques: unstable (decomposition + fragmentation in PTR) + no commercial standards

- Use of two ionization modes: H_3O^+ and NO^+ :
 - Low electric field to reduce fragmentation

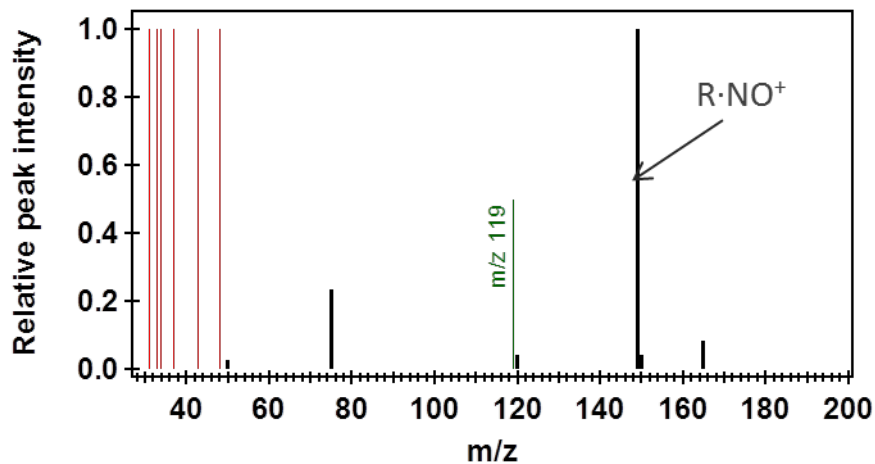


- Method tested and validated with standards of different types of ON: alkyl nitrates, carbonyl nitrates, hydroxy-nitrates, PANs

Detection of ON during a reaction aldehyde+ NO_3



Mass spectrum of nitroxyacetone in NO^+ ionization mode



(Duncan et al., AMT, 2017)