Chamber measurements of α-pinene SOA constituents using two different Extractive Electrospray Ionization (EESI) set-ups

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Introduction

- POA/SOA known as large contributors to aerosol particle matter[1]
- Detailed chemical composition largely unknown – need for real-time particle measurements → recent method Extractive Electrospray Ionization (EESI)-ToF-MS[2]
- α-pinene: most emitted monoterpene[3] – oxidation under day-/nighttime conditions

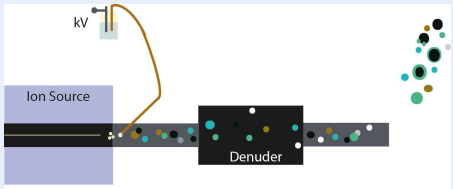


Fig. 1: Schematic of the EESI Source attached to the Orbitrap Q Exactive Plus.

- Comparison EESI-TOF with EESI-Orbitrap setup – higher mass resolution of Orbitrap
- Testing stability of instruments
- Investigation of further oxidation pathways with NO_x/SO_2

Experimental Setup: ACD-Chamber

- ACD-C: 19 m^3 cylindrical chamber
- Steady-state reaction conditions:
  - RH: 60% (±2%)
  - α-pinene: 60 ppb
  - SO_2: 15 ppb
  - Nighttime oxidant: NO_3-radicals from pre-reactor (O_3+NO_2)
  - Daytime oxidant: OH-radicals (from H_2O_2 photolysis)
  - For daytime: NO 15 ppb
- Two EESI instruments
- State-of-the-art instrumentation

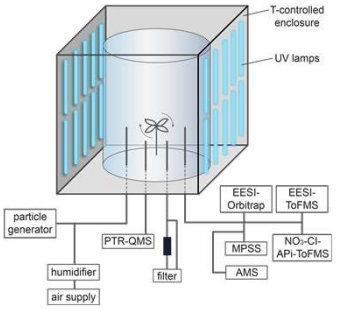


Fig. 2: Schematic of the ACD-C with the employed instruments during this project.

Results

Comparison between particle and gas phase

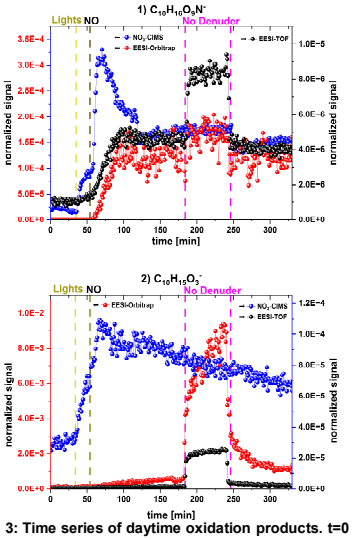


Fig. 3: Time series of daytime oxidation products. t=0 is α-pinene injection. Comparison of both EESI instruments with gas-phase CIMS.

- 1) Organonitrate $C_{10}H_{16}O_9N^-$ ($[M-H]^-$ 294.0825) particle increase corresponding to gas phase decay – possible coupling by uptake
- 2) $C_{10}H_{15}O_3^-$ ($[M-H]^-$ 183.1021) shown to be detected only in the gas-phase
- Pink: phase without denuder – sampling both gas- and particle-phase with EESI
- Multiple overlaying processes: particle uptake + decay + formation slowing down
- Qualtitative signal partitioning factor ($signal_{particle}/signal_{whole}$):
  - Orbitrap: 1) 0.74 2) 0.071
  - TOF: 1) 0.55 2) 0.055

Comparison of EESI-TOF and EESI-Orbitrap

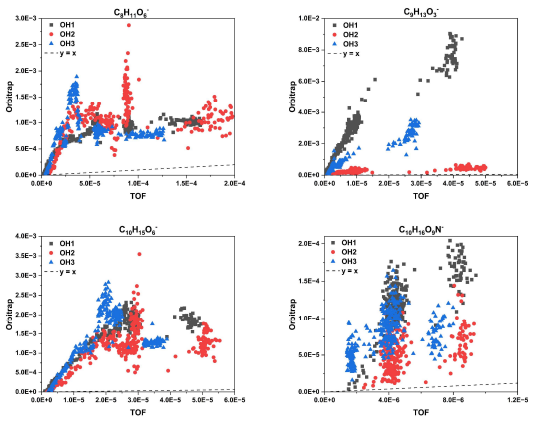


Fig. 4: Comparison of signal for multiple SOA products from daytime odixation in both EESI instruments. For better comparability: intensities are TIC normalized, dotted line y=x

- **Different oxidation products:**
  - Sensitivity differences of both EESI devices – Orbitrap much higher sensitivity
  - Signal correlation mostly linear in beginning – deviation towards end of experiment
  - Ionization efficiency different for CHO/CHON compounds
- **Signal variability throughout the days:**
  - Slopes variability between days – low for most targets
  - Shows if signal spiked in only one instrument

Target analysis

- Results for both EESI instruments:
  - Very good detection of CHO compounds – 9-10 during daytime runs and 7-10 during nighttime runs
  - Good detection of CHON in both devices – all 6 detected in daytime runs and 2 compounds in nighttime runs
  - No detection of CHOS/CHONS during all online measurements
- Day vs night: lower SOA mass with NO_3 – less targets detected in particles
- Without denuder: compounds present in gas-phase during NO_3 experiments → Confirms SOA suppression by less condensation
- Non-target analysis Orbitrap: still no CHOS but further suspected CHON species

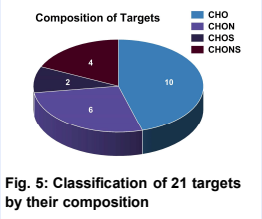


Fig. 5: Classification of 21 targets by their composition

Nighttime vs daytime α-pinene oxidation

- Average daytime SOA (from AMS): 54.6 µg m^{-3}
- Average nighttime SOA: 10.6 µg m^{-3} – one fifth SOA mass
- Possible explanations:
  - Less oxidant – slower reaction to form NO_3-radicals → SOA formation delayed
  - High NO_x conditions (NO_2 >15ppb) – suppression of SOA formation[4], compounds gas-phase only

→ Overall low EESI signals during all NO_3 experiments

- Comparison with offline filters to see: sensitivity problem or no formation

→ First filter results: enrichment of particles – detection of CHOS/CHONS possible

Summary

- Comparison of EESI-Orbitrap and EESI-TOF: qualitative agreement - sensitivity of Orbitrap higher
- Real-time tracking of SOA particles: uptake and formation linked to gas-phase changes
- During nighttime experiments less products partition to particle phase than during daytime conditions.
- Sensitivity and quantitation with online methods remains a challenge

References

1Tsimpidi. A.P., et al. Aerosol composition trends during 2000–2020: in-depth insights from model predictions and multiple worldwide near-surface observation datasets, Atmos. Chem. Phys., 25, 10183–10213, https://doi.org/10.5194/acp-25-10183-2025, 2025. **2Luo, X., et al.,** Practical Applications of Secondary/Extractive Electrospray Ionization (SESI): A Versatile Tool for Real-Time Chemical Analysis. Mass Spectrometry Reviews, 45: 392-428. https://doi.org/10.1002/mas.21938, 2026. **3Sindelarova, K.,** et al., Global data set of biogenic VOC emissions calculated by the MEGAN model over the last 30 years, Atmos. Chem. Phys., 14, 9317–9341, https://doi.org/10.5194/acp-14-9317-2014, 2014. **4Zhao, D.**, et al., Effects of NOx and SO2 on the secondary organic aerosol formation from photooxidation of α-pinene and limonene., Atmos. Chem. Phys., 18, 1611–1628, https://doi.org/10.5194/acp-18-1611-2018, 2018.