Can Particle Size Magnifiers detect HOMs with carbon numbers between C_{10} and C_{30}?

Wiebke Scholz[1,2], Birte Rörup[3], Markus Leiminger[1,2], Gerhard Steiner[1,4], Katrianne Lehtipalo[3], Juha Kangasluoma[3] and Armin Hansel[1,2]

1 Institute for Ion Physics and Applied Physics, University of Innsbruck, Austria.
2 Ionicon Analytik GmbH, 6020 Innsbruck, Austria
3 INAR – Institute for Atmospheric and Earth System Research, University Helsinki, Finland
4 GRIMM Aerosol Technik Ainring GmbH & Co. KG, 83404 Ainring

EGU2020, 6.05.2020

Motivation: Particle Size Magnifier (PSM)

- The PSM detects particles from charged Silver- and Tungsten oxide with diameters down to ~1 nm with high sensitivity

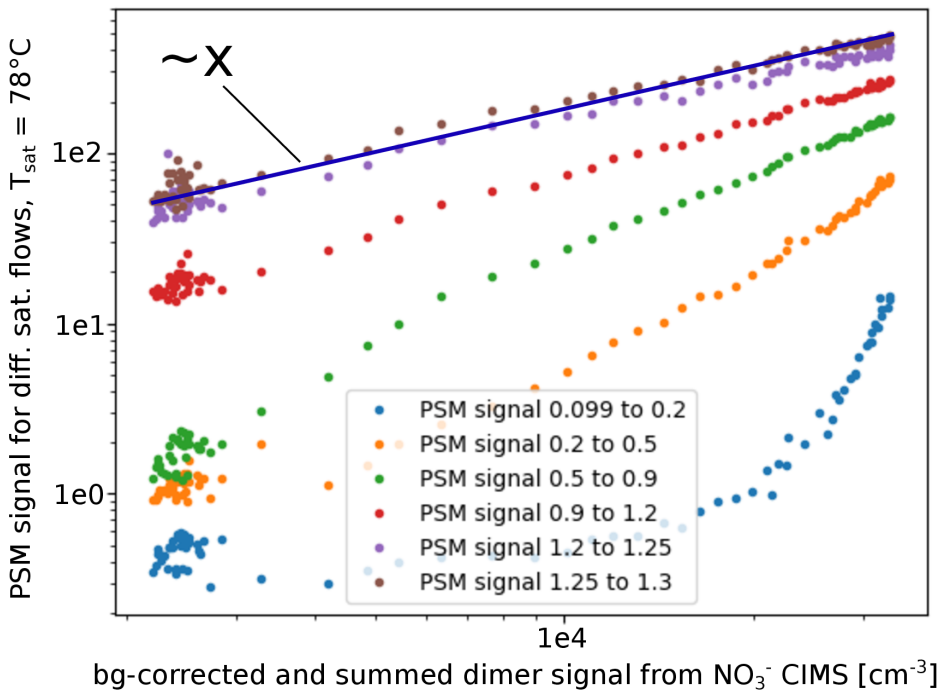
Vanhanen et al., AS&T, 2011

But what about particles formed from highly oxygenated molecules (HOMs)?

- Previous studies suggest a higher cutoff size for organic particles compared to particles from salts or tungsten oxides

Kangasluoma et al., AMT, 2014 *and* ***JoAS, 2015***

- During CLOUD experiments with beta-Caryophyllene ($C_{15}H_{24}$) ozonolysis we observed that the **signal of particles, activated only at high saturator flow depended linearly on summed HOM dimer concentration**



- HOM dimers are formed from peroxy radicals (RO_2) by self and cross reaction following

  $RO_2 + R'O_2 \rightarrow ROOR' + O_2$

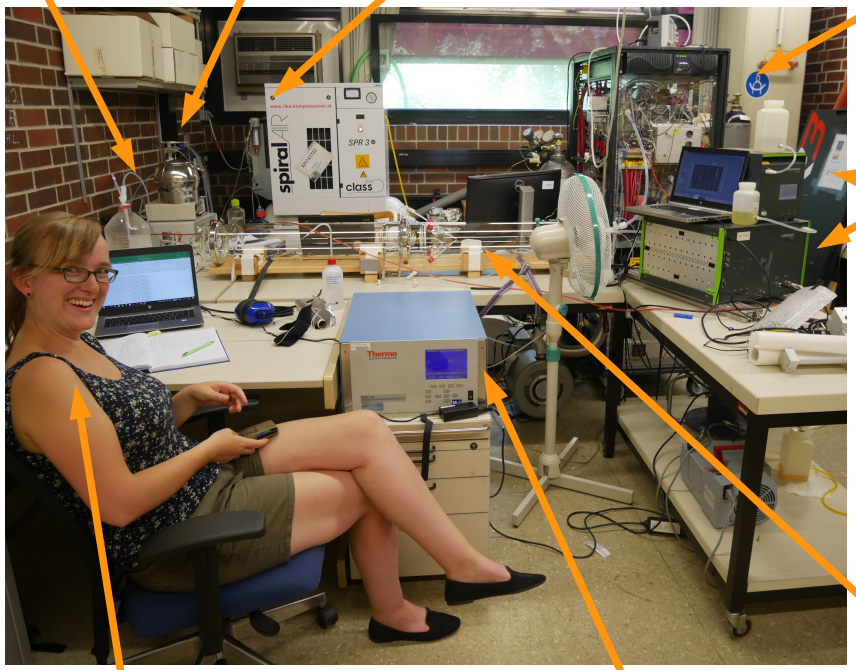
  Berndt et al., Angew. Chem. Int. Ed., 2018

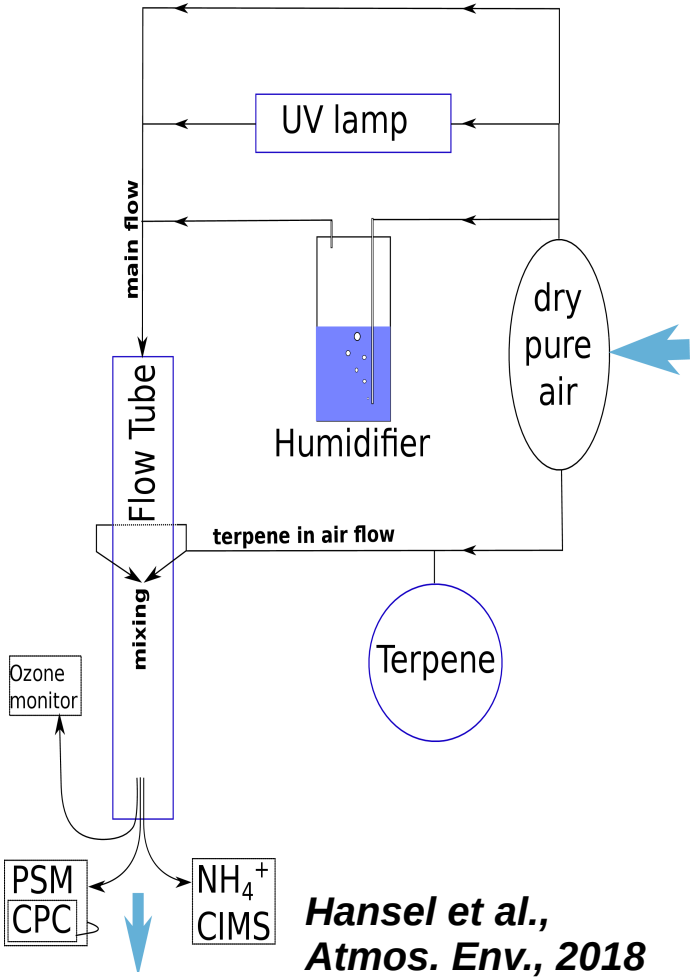
Experimental Setup

Reagents: alpha-Pinene ($C_{10}H_{16}$), beta-Caryophyllene ($C_{15}H_{24}$), Ozone (O_3)

Reaction Environment: Innsbruck continuous flow tube reactor of 9 sec. reaction time with negligible wall contacts.

The terpenes are mixed into the center of the laminar O_3-carrying main air flow by four impinging air jets, that create localized turbulence.





Hansel et al., Atmos. Env., 2018

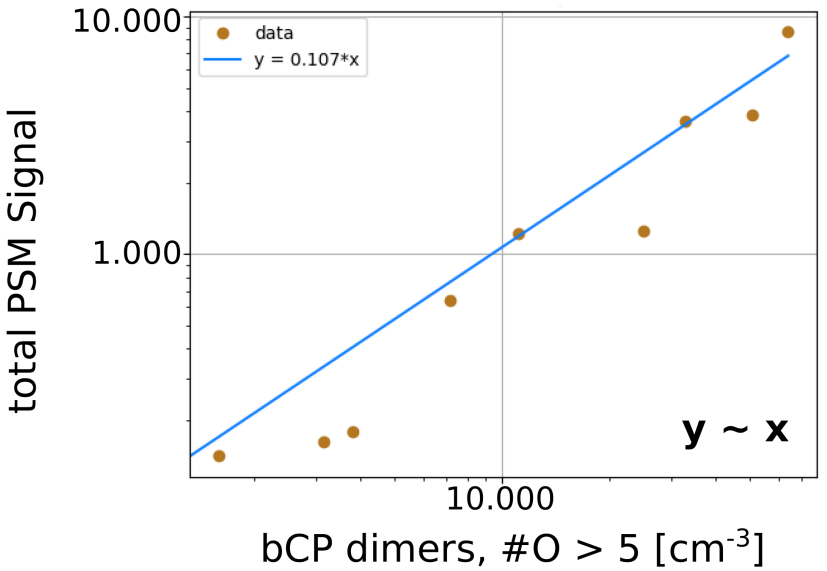
Detecting HOM dimers with the PSM

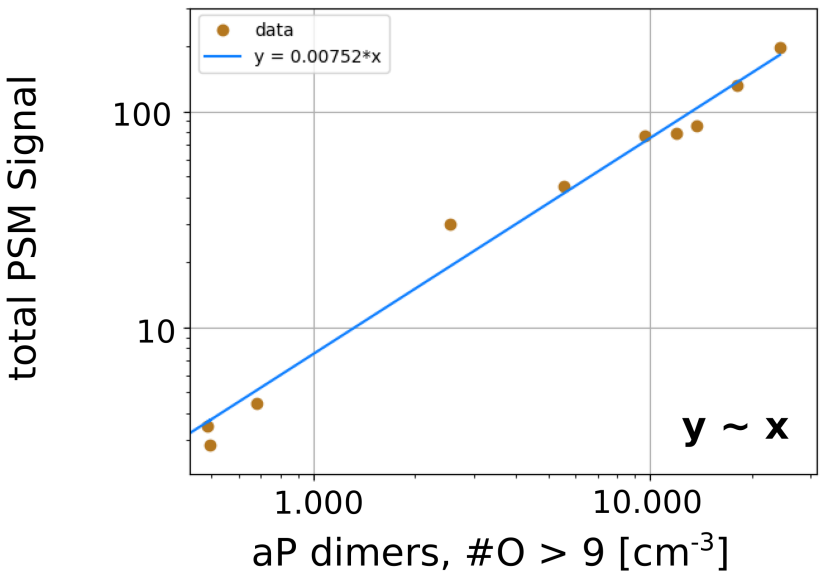
RH = 0% (DP -50°C)
Reaction Time 9s
PSM: Saturator Temp. 80°C
Saturator Flow 1.3 slpm

β-Caryophyllene (bCP):
(2.3 - 28) × 10^{10} molecules cm^{-3}
Ozone: **4.15 × 10^{12} molecules cm^{-3}**

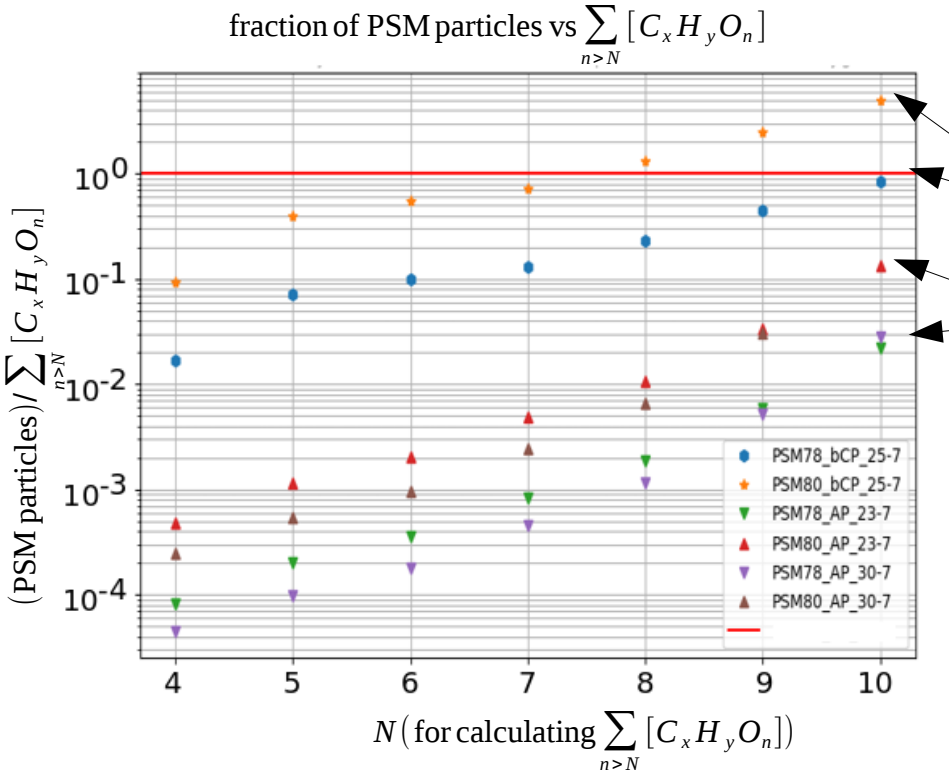
α-Pinene (aP): **(1.2 – 14) × 10^{12} molecules cm^{-3}**
Ozone: **(5 - 42) × 10^{11} molecules cm^{-3}**

- **The relationship between HOM dimers and the PSM signal is linear!**
  - **The PSM detects bCP HOM dimers ($C_{28-30}H_{44-48}O_{x>5}$) with reasonable sensitivity**
  - **aP HOM dimers ($C_{19-20}H_{28-32}O_{x>9}$) are still detected but with very low sensitivity**





Effect of Size, Oxygen number and Volatility



Prefactor of linear realationship between NH_4^+-CIMS and PSM for

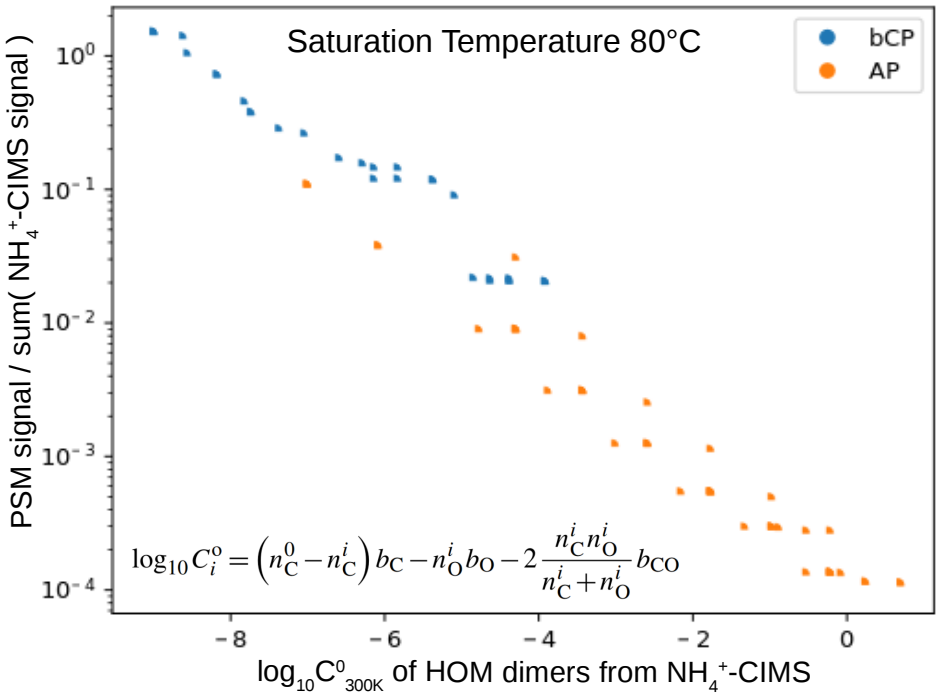
bCP HOM dimers $C_{28\text{-}30}H_{44\text{-}48}O_{n>N}$

and aP HOM dimers $C_{19\text{-}20}H_{28\text{-}32}O_{n>N}$

Each at 78°C and 80°C PSM saturator temperature, sat. flow 1.3 lpm, RH = 0%

Volatility Basis Set

- to estimate the volatility of oxidized organics based on their size and oxidation state ***Donahue, ACP, 2011***
- relates concentrations of highly oxidized molecules and growth rates of nanoparticles ***Stolzenburg, PNAS, 2018***

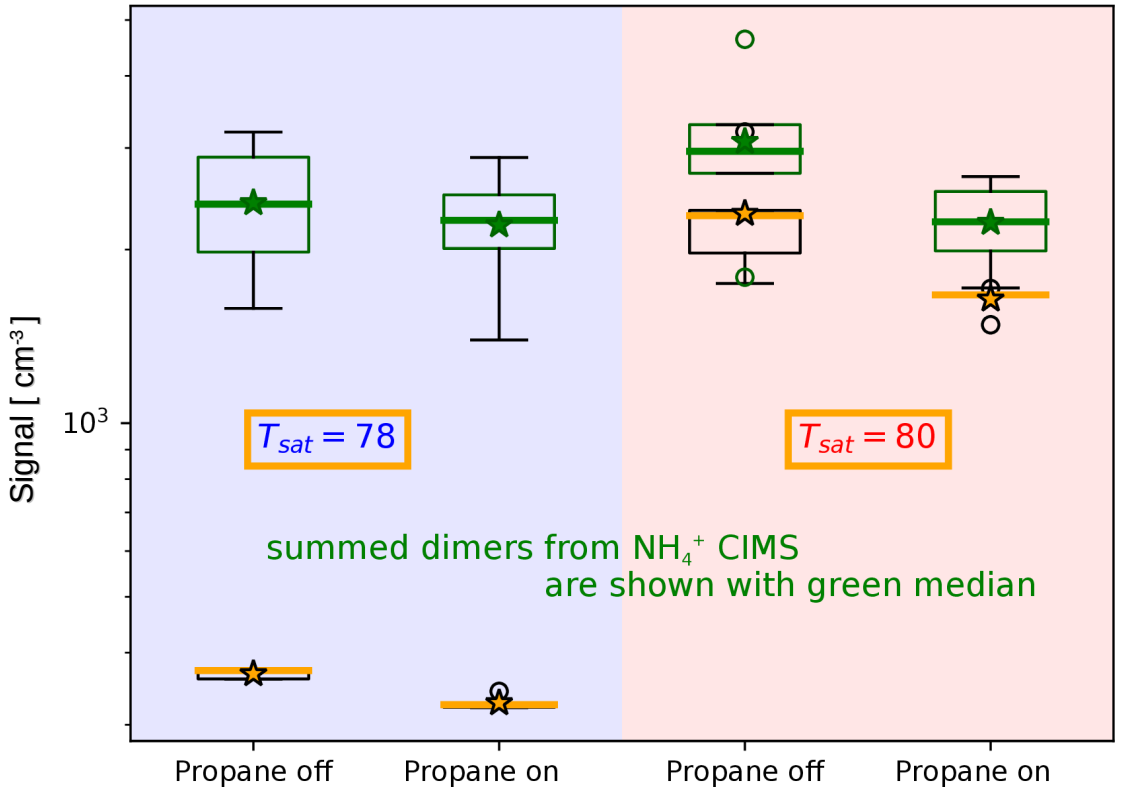


Effect of oxidation with OH

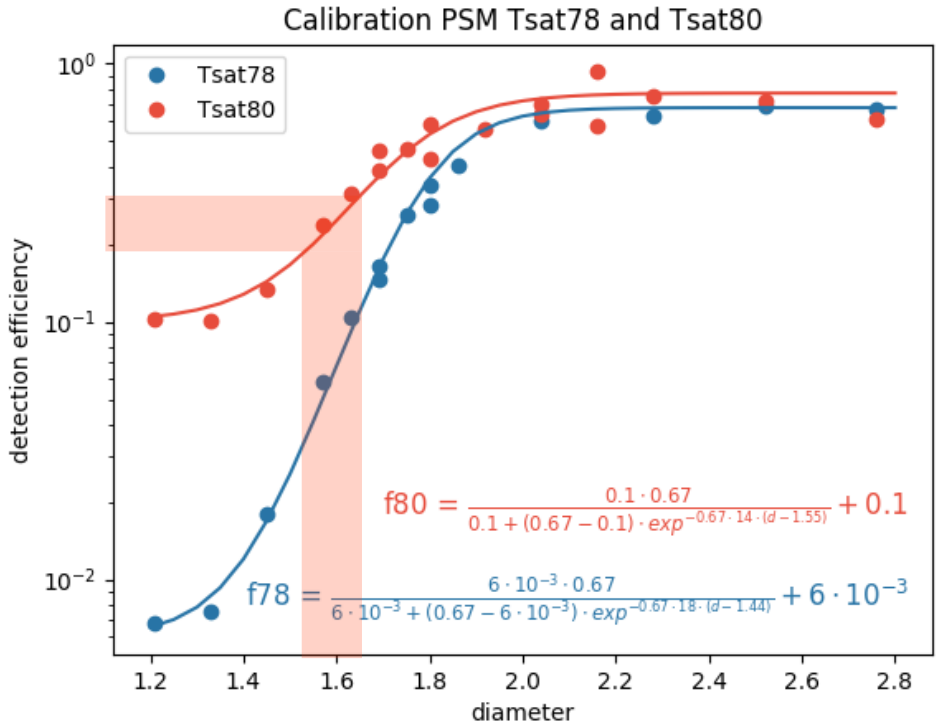
- **Propane** is used as an **OH scavenger** in some experiments to study, if the **structural differences** between dimers formed **from OH or Ozone initiated reactions matter to their detection by the PSM**

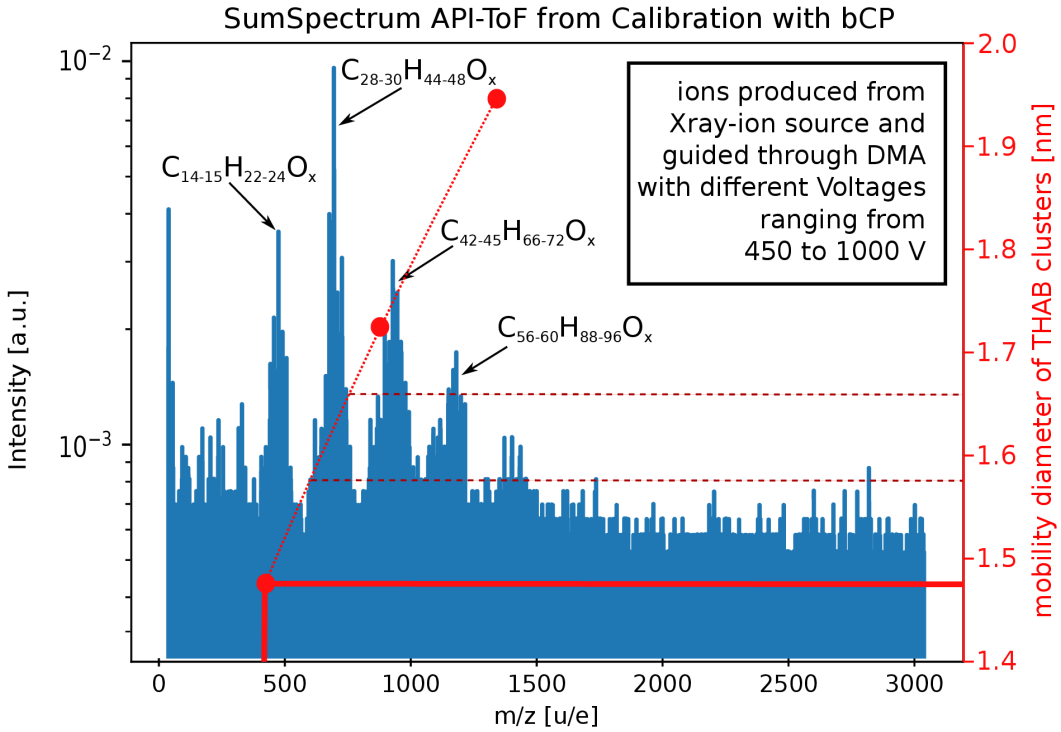
- The signal decrease of summed dimers from the NH_4^+-CIMS and the PSM is comparable

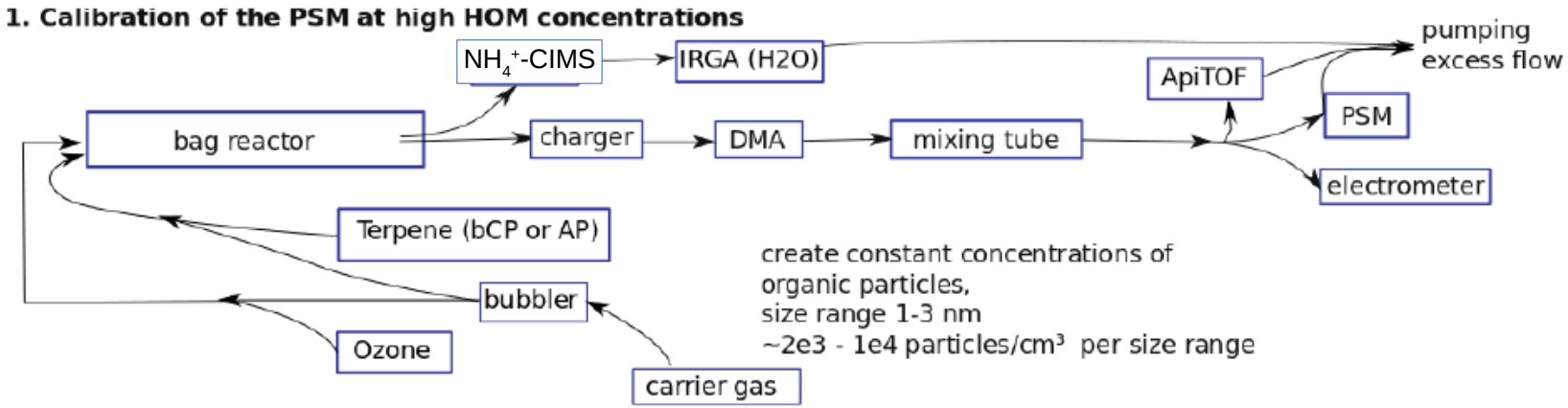
- From this experiment no significant effect of the structural differences on the detection efficiency can be found



HOM Dimers in the PSM‘s calibration curve



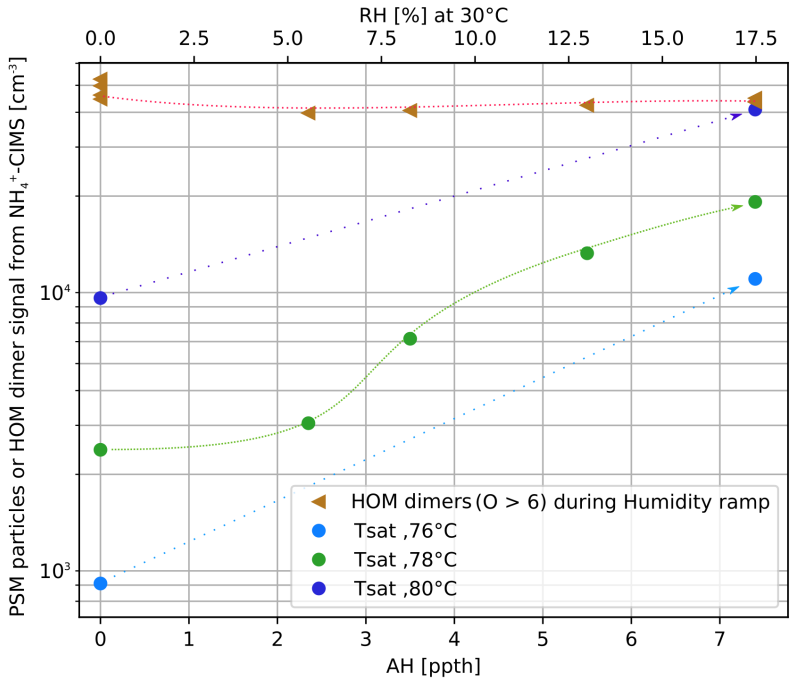


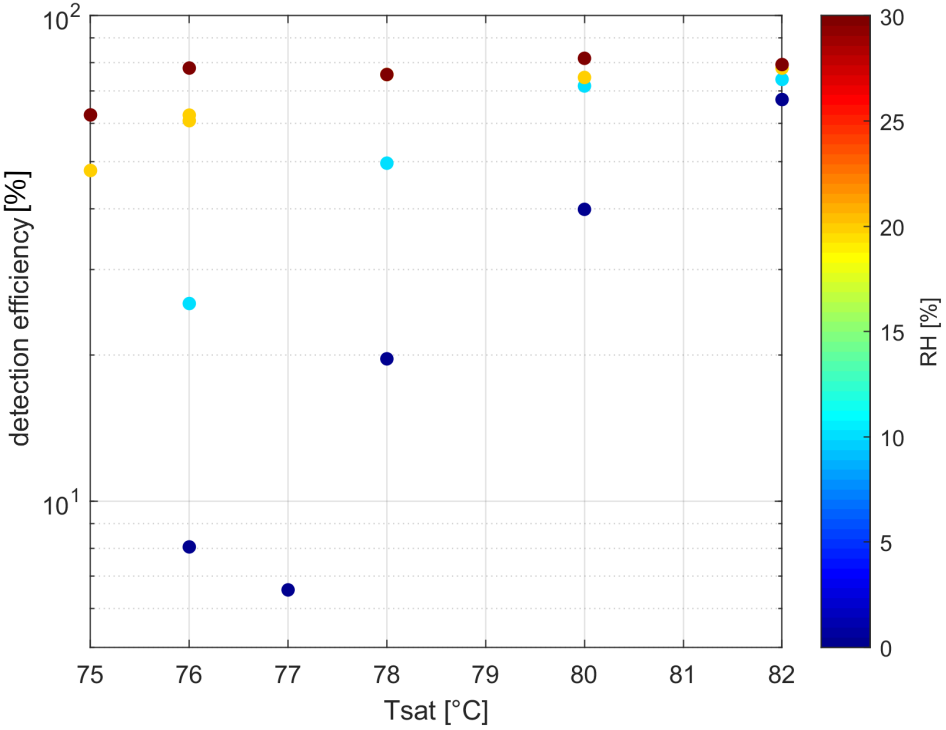


Humidity dependence of PSM detection of HOM dimers

Activation of HOM Dimers:

- Is strongly absolute humidity (AH) dependent
- humid conditions are more favorable for activation of HOM dimers
- effect stronger, the lower the saturation temperature





Activation of 1.7nm sized particles:

- Strongly dependent on humidity.
- At low humidity the saturation temperature matters dramatically, while at high humidity it is nearly independent on saturator temperature

Summary

- The PSM can detect HOM dimers of both alpha Pinene ($C_{19-20}H_{28-32}O_n$) and beta-Caryophyllene ($C_{28-30}H_{44-48}O_m$)
- For HOM dimers from beta-Caryophyllene the detection efficiency is in the range of tens of percent up to 100%, depending on the PSM settings and humidity
- Detection of HOM dimers as well as of small organic „particles“ is very humidity and saturation temperature dependent
- OH scavenging didn‘t affect the PSM detection efficiency, when including all HOM dimers

Thank you for your interest!

- Please feel free to chat to me in the session AS3.1, Tuesday, 05 May 2020, 10:45-12:30

I am happy for any questions and feedback - Wiebke