

Chemical composition and volatility distribution of SOA formed by ozonolysis of β -caryophyllene between 213-313 K

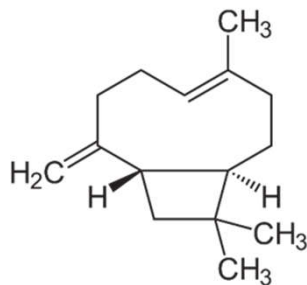
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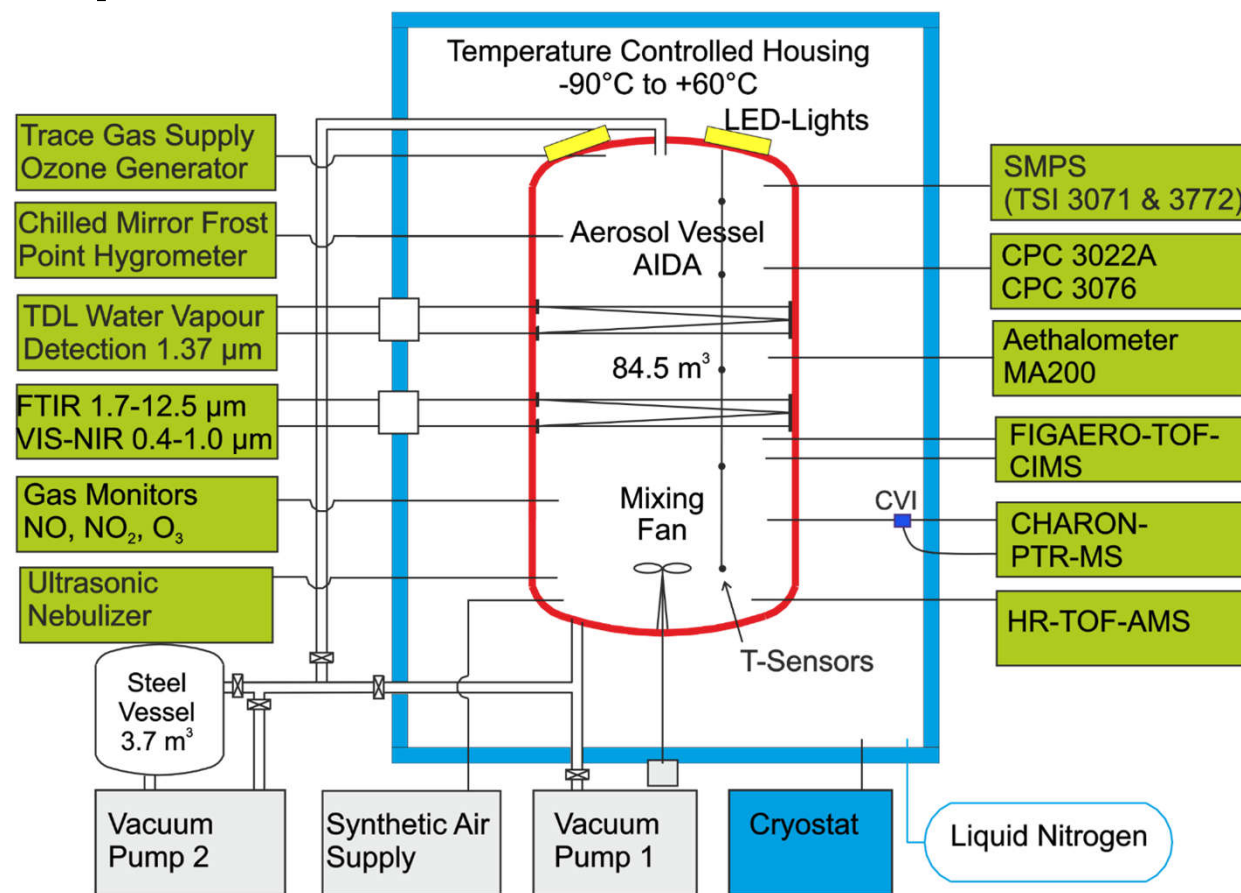


Introduction

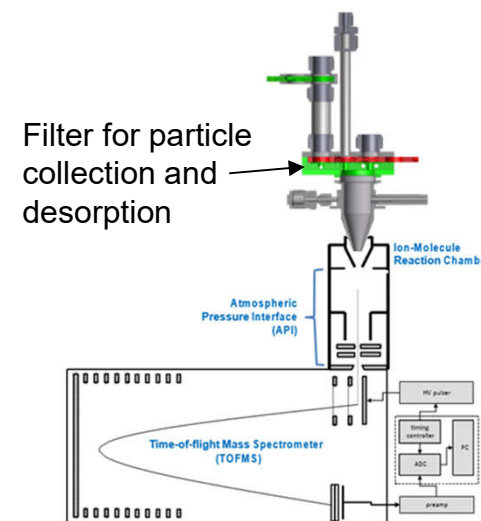


- β -Caryophyllene is the most common and abundant of the sesquiterpenes emitted into the atmosphere and more reactive and larger in size than monoterpenes. (Duhl et al., 2008).
- Their aerosol mass yields are large and result in a significant contribution to the SOA budget in the atmosphere (Tasoglou and Pandis, 2015).
- Therefore, we studied the composition of both gas and particle phases as well as phase partitioning of SOA from ozonolysis of β -caryophyllene in presence and absence of NO_x at five temperatures (213 K, 243 K, 273 K, 298 K and 313 K) in the AIDA aerosol simulation chamber (Wagner R et al., 2006).
- This work focusses on the characterization and volatility analysis of the SOA by mass spectrometry employing a FIGAERO-HR-TOF-CIMS (Lopez-Hilfiker et al., 2013) operated with iodide ions as well as a HR-TOF-AMS (Canagaratna M et al., 2007).

Experiment



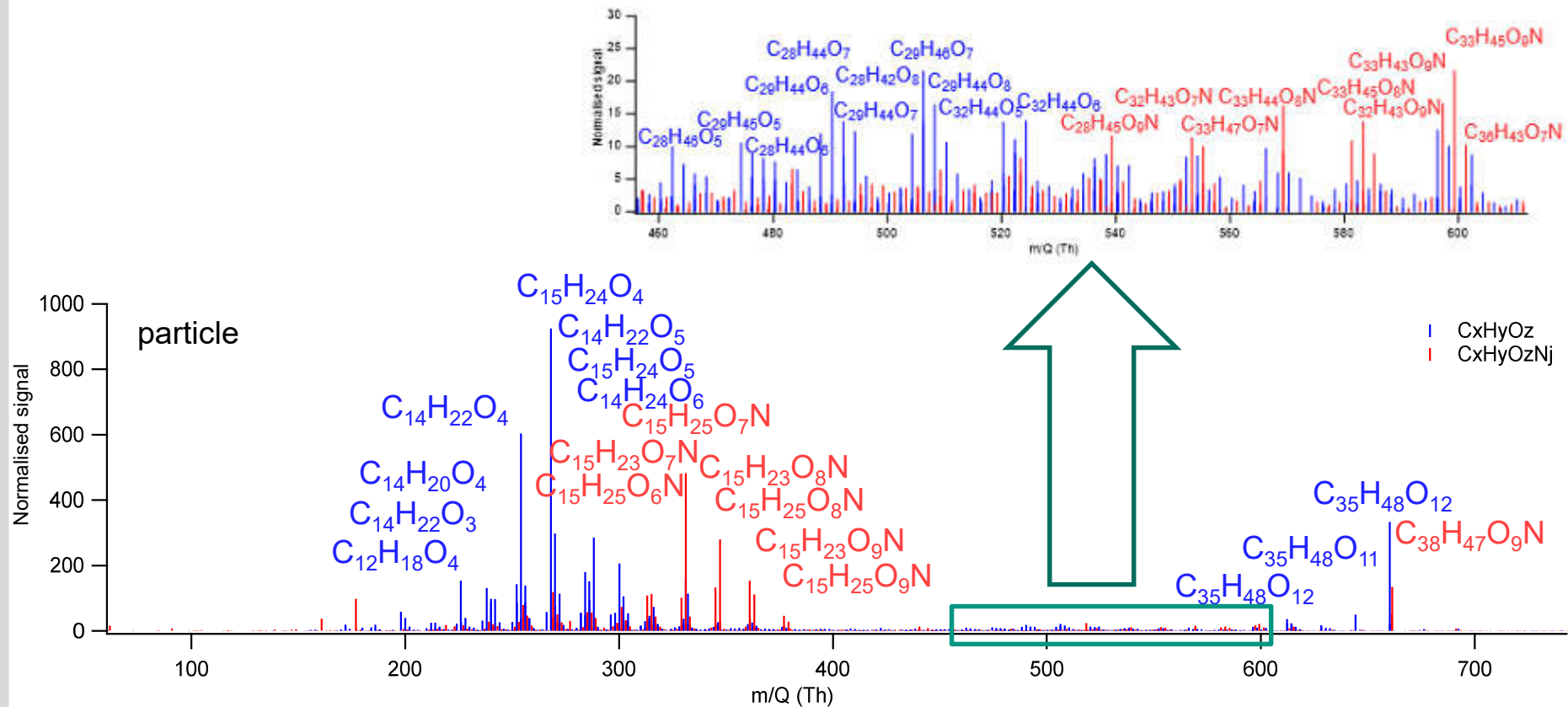
FIGAERO-TOF-CIMS



T [K]	RH [%]
313	13
298	28
273	67
243	88
213	96

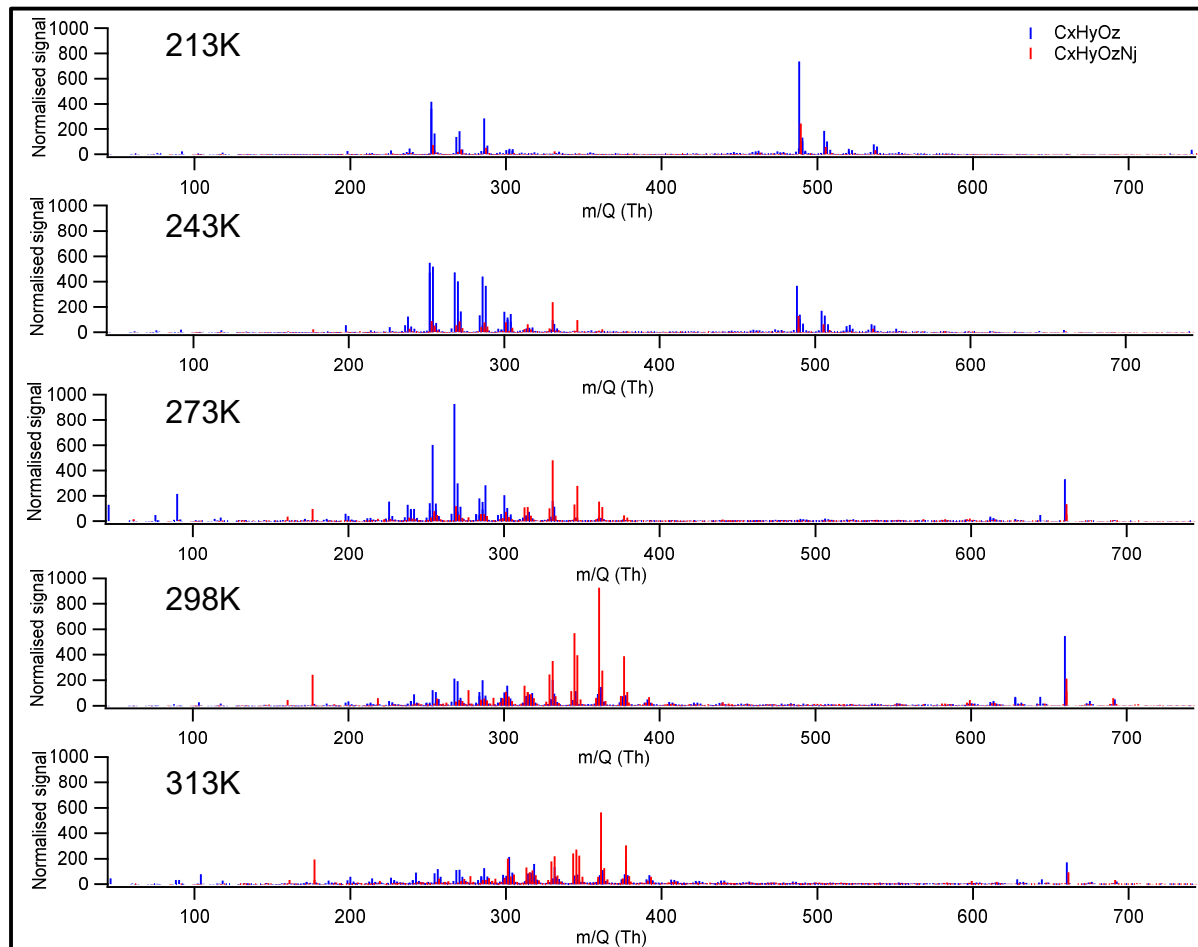
- β -Caryophyllene was oxidized by an excess of 317 ppb ozone in presence of 37 ppb of NO₂

Results: Mass spectrum of SOA formed at 273 K



- Main components are $C_{15}H_{24}O_{3-6}$, $C_{14}H_{22}O_{3-6}$, $C_{14}H_{24}O_{5-6}$, $C_{15}H_{25}O_{7-8}N$.
- Nitrogen containing species are marked in red.

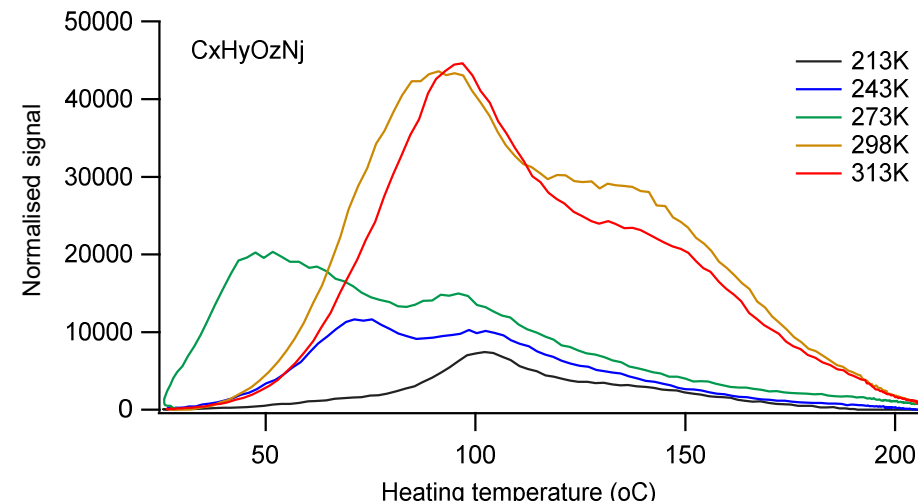
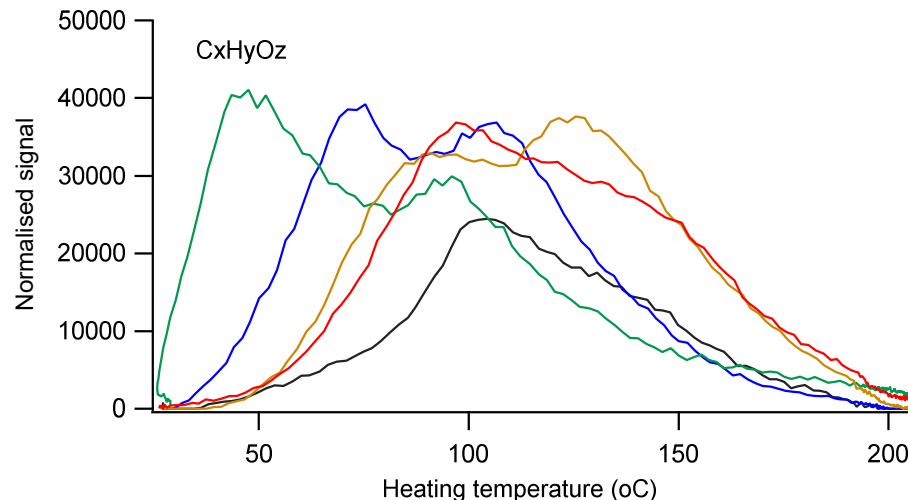
Results: Mass spectra of SOA formed at 213K-313K



(Signals are normalized to the reagent ion, I^-)

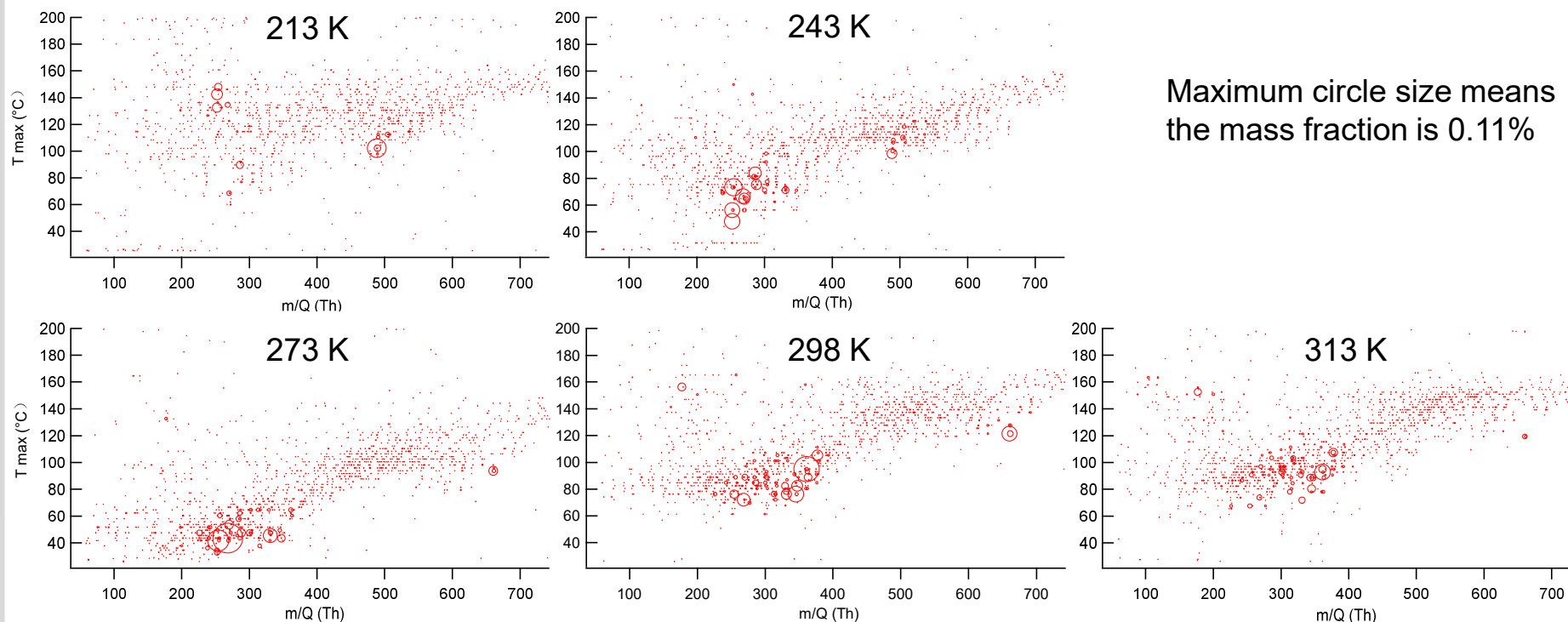
- With decreasing temperature the SOA contains more heavier masses at m/Q (400-540, dimers) and less at m/Q (200-400, monomers) as well as m/Q (540-700, trimers).
- More compounds in $C_xH_yO_zN_j$ ($j \geq 1$) are formed at higher temperatures. Their mass peaks are strongest at 298 K.

Results: Desorption of SOA from Filters



- The maximum of desorption temperatures (T_{\max}) of sum $C_xH_yO_z$ and sum $C_xH_yO_zN_j$ compounds show similar trends with temperature, going down from 213 K to 273 K, and then going up from 298 K to 313 K.
- Bimodal structures could be explained by two volatile groups (e.g. m/Q 200-400 and 600-700 at 273 K) for each filter. The fragmentation of heavier compounds during the heating procedure could also contribute to the first peak.
- At 213 K, the single but wide peak may be influenced significantly by the compounds at m/Q of 488.3 (excluding I⁻) and 489.3 (excluding I⁻), as these two compounds contribute most to $C_xH_yO_z$ group and $C_xH_yO_zN_j$ group, respectively.

Results: Desorption Temperatures



- The T_{\max} goes down from experiments at 213 K to 273 K, and then goes up from 298 K to 313 K. The T_{\max} keeps the lowest in experiments at 273 K. The mass peaks are more concentrated in the experiment at 273 K.
- At low temperatures, the product spectrum is smaller, which means these compounds have larger individual contributions to total mass.

Calculation of the saturation concentration C_{sat}^*

$$\lg C_{sat}^*(298K) = (n_{c0} - n_c) \cdot b_c - n_o \cdot b_o - 2 \cdot ((n_c \cdot n_o) / (n_c + n_o)) \cdot b_{co} - n_N \cdot b_N; \text{ (Li et al., 2016)}$$

where n_{c0} is the reference carbon number; n_c , n_o and n_N denote the numbers of carbon, oxygen and nitrogen atoms, respectively; b_c , b_o and b_N denote the contribution of each atom to $\lg C_{sat}^*$, respectively, and b_{co} is the carbon-oxygen nonideality.

Classes	n_C^0	b_C	b_O	b_{CO}	b_N	b_S
CH	23.80	0.4861				
CHO	22.66	0.4481	1.656	-0.7790		
CHN	24.59	0.4066			0.9619	
CHON	24.13	0.3667	0.7732	-0.07790	1.114	
CHOS	24.06	0.3637	1.327	-0.3988		0.7579
CHONS	28.50	0.3848	1.011	0.2921	1.053	1.316

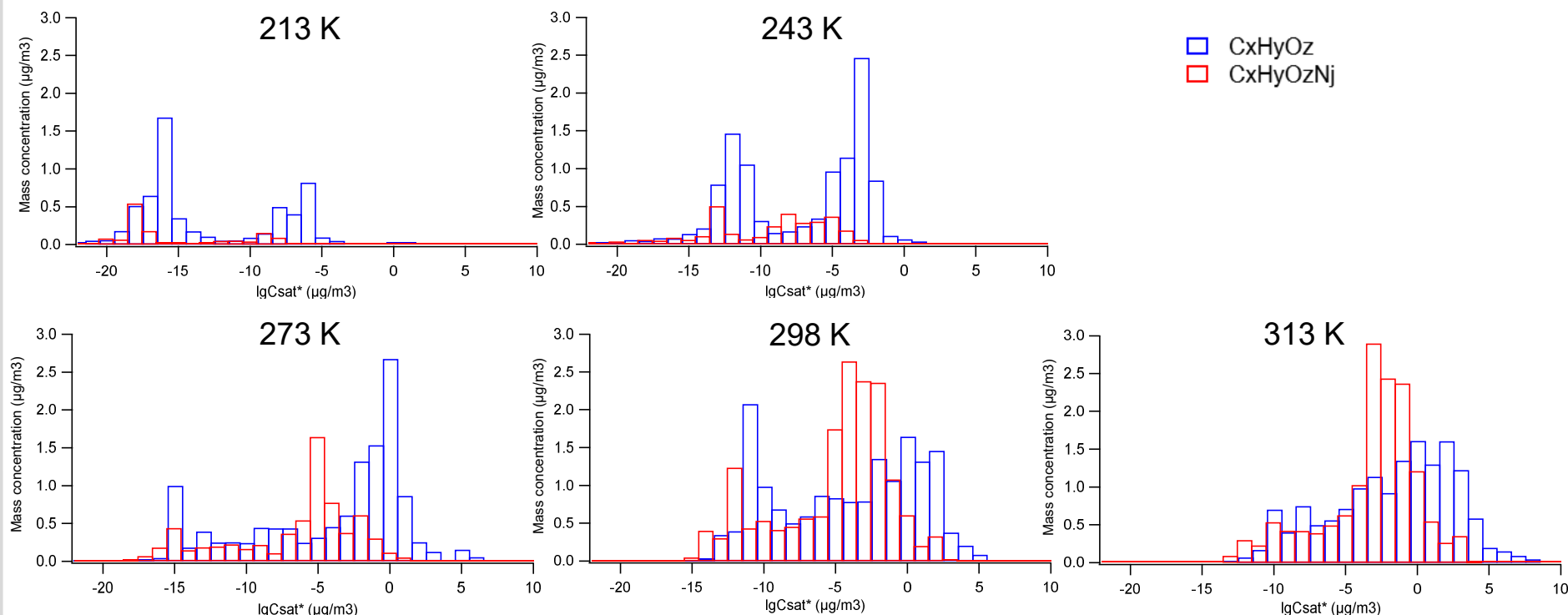
$$\Delta H_{vap} = (-5.7 \cdot \lg C_{sat}^*(298K) + 129) \cdot 1000;$$

Where ΔH_{vap} is the enthalpy of vaporization, kJ/mol;

Clausius – Clapeyron equation:

$$\lg C_{sat}^*(T) = \lg C_{sat}^*(298K) + (\Delta H_{vap} / (R \cdot \ln 10)) \cdot ((1/298) - (1/T));$$

Results: Volatility Distributions



- Particles formed at higher temperatures contain more volatile compounds.
- Nitrogen containing compounds $\text{C}_x\text{H}_y\text{O}_z\text{N}_j$ contribute mainly to LVOC and SVOC for particles formed at higher temperatures, while to ELVOC for lower temperatures.

Conclusion

- Particle phase analysis shows three groups of compound masses with m/z 200-400, (C_{5-16}), (m/z 400-540, (C_{20-34}), and m/z 540-700, (C_{35-40}) classified as monomers, dimers, and trimers, respectively.
- Trimeric compounds were observed preferentially in SOA formed at higher temperatures (273 K, 298 K, 313 K), while only monomeric and dimeric compounds were detected at lower temperatures (243 K and 213 K). Interestingly, dimeric compounds, including $C_xH_yO_z$ and $C_xH_yO_zN_j$, contribute more to SOA mass for the lower temperatures.
- Comparing volatility distributions for the five different temperatures and thermal desorption information from FIGAERO-CIMS (298-473 K), more compounds with lower volatilities are found for lower SOA formation temperatures.
- Nitrogen containing compounds $C_xH_yO_zN_j$ contribute mainly to LVOC and SVOC for particles formed at higher temperatures, while to ELVOC for lower temperatures.

Reference

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Thank you !

