

# Influence Of Particle Acidity To Secondary Organic Aerosol Yields And Products: Results From Aerosol Chamber Study Of The $\alpha$ -Pinene Ozonolysis

Yoshiteru Iinuma<sup>†</sup>, Olaf Böge<sup>†</sup>, Thomas Gnauk<sup>†</sup>, Berko Sierau<sup>†,‡</sup> and Hartmut Herrmann<sup>†</sup>

<sup>†</sup>Leibniz-Institut für Troposphärenforschung (IfT), Leipzig, D-04318 Germany

<sup>‡</sup>currently at University of Washington, Dept. of Atmospheric Sciences, Seattle, Washington 98195-1640

<http://www.tropos.de/>

yoshi@tropos.de

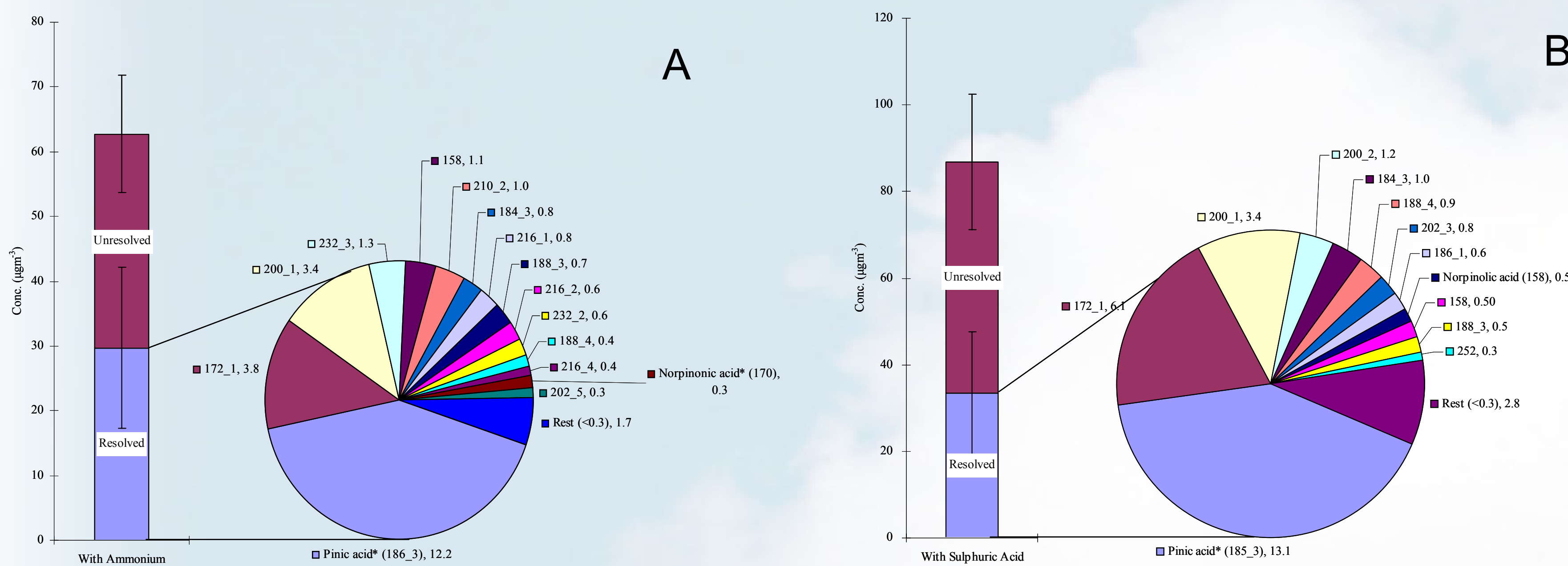


## Introduction

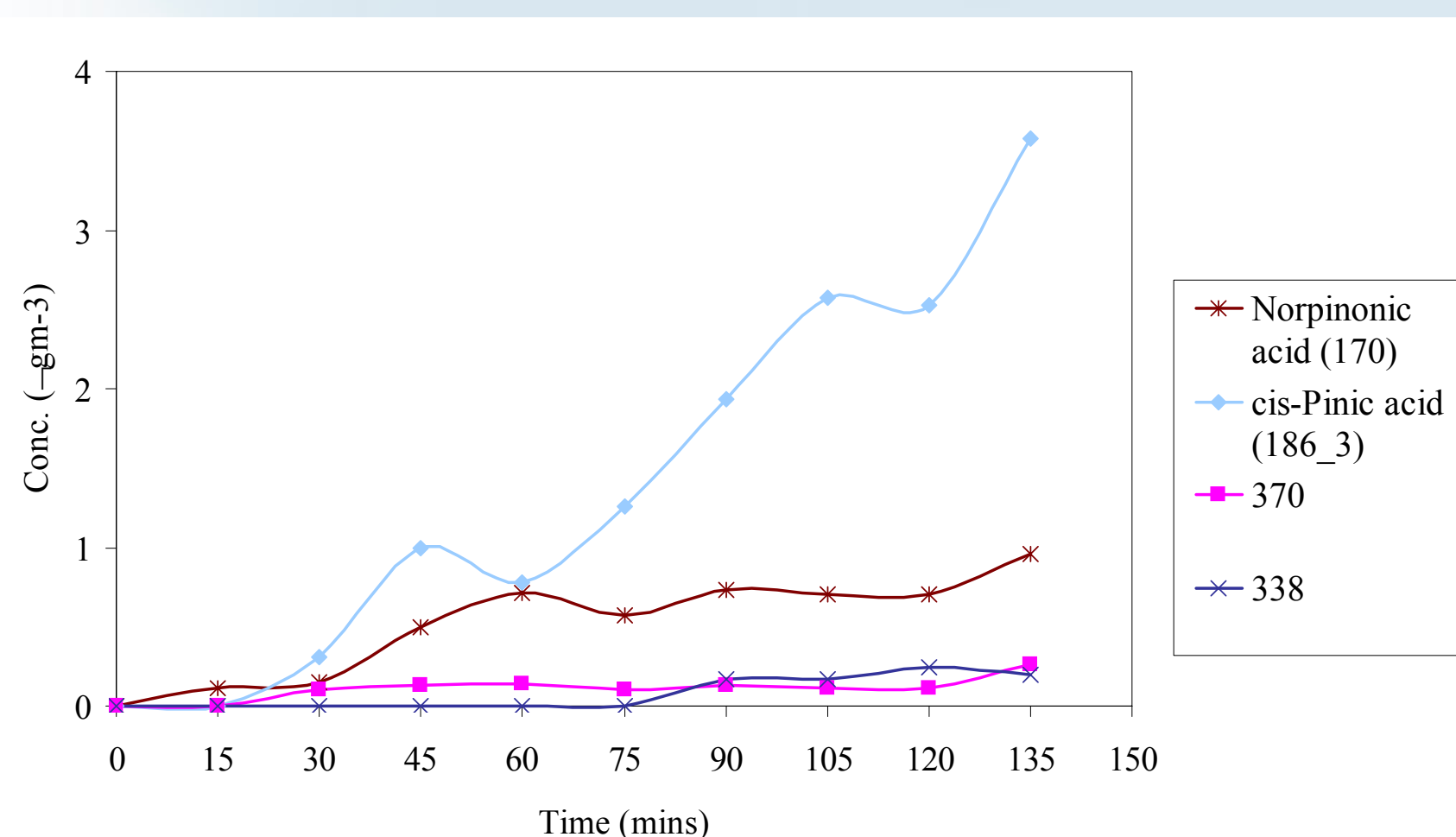
Secondary Organic Aerosol (SOA) is believed to contribute significantly to the atmospheric aerosols yet a large uncertainty remains to its extent of its contribution to measured concentration of organic aerosols in atmosphere and its formation mechanism is not fully understood. Recently, the evidences of second generation products from the acid-catalyzed reactions of primary oxidation compounds in the particle phase are found [Iinuma et al., 2004; Tolocka et al., 2004]. These evidences suggest that the formation of higher molecular weight compounds through heterogeneous reaction in the particle phase can play a significant role in the formation and growth of atmospheric particles.

Here we present the evidence of condensation of smaller organics in the acidic particle through polymerization or aldol condensation following the formation of aldehydes such as pinonaldehyde from the terpene ozonolysis.

## Results



**Figure 1.** Estimated particle phase concentration ( $\mu\text{g m}^{-3}$ ) of detected compounds for the experiment with (A) ammonium sulfate seed particles and (B) sulfuric acid seed particles. (\*: quantified with an authentic standard)

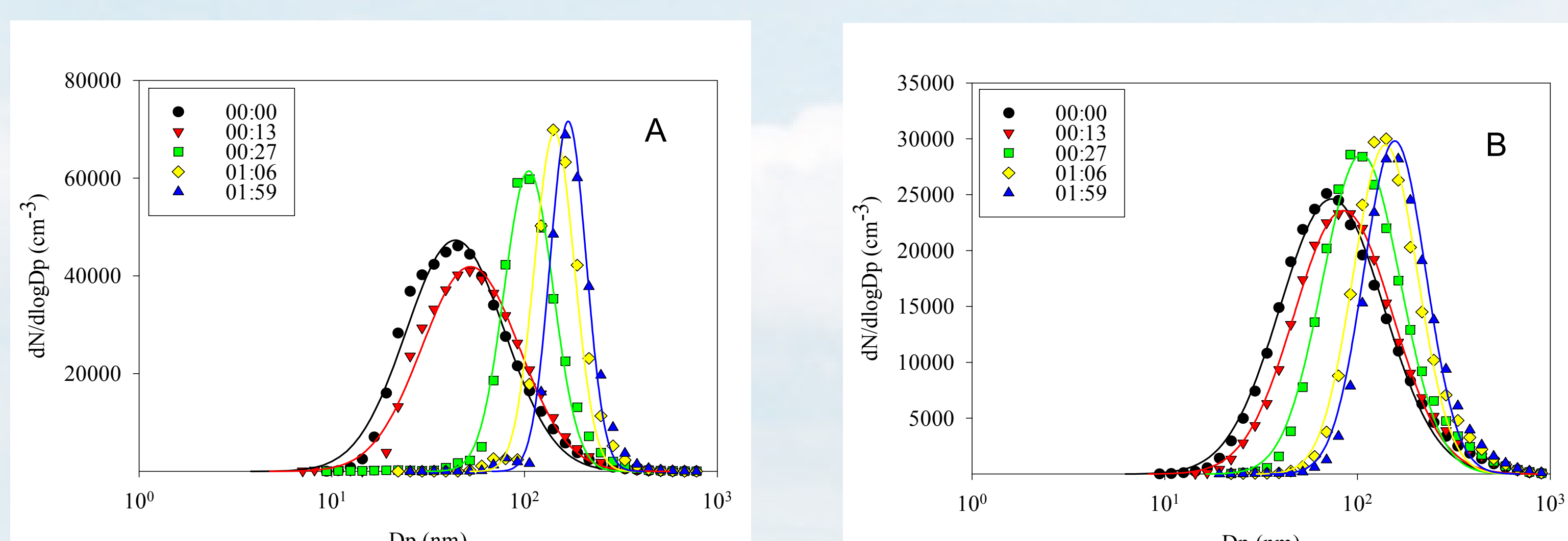


**Figure 2.** The evolution of selected  $\alpha$ -pinene oxidation products in the particle phase.

The coupling of CE-ESI-MS and C-GIS (Condensation-Growth and Impaction System) [Sierau et al. 2002] allows near online analysis of particle phase products. Figure 2 gives an example of such application for  $\alpha$ -pinene ozonolysis product study.

Size distribution data (Figure 3, bottom) confirms the result of time resolved chemical analysis (Figure 2) that the particle phase modification takes place after 15 minutes of  $\alpha$ -pinene ozonolysis in the gas phase.

After one hour, particle size distribution does not change dramatically though some of particle phase products still evolve after 2 hours (e.g. cis-pinonic acid).

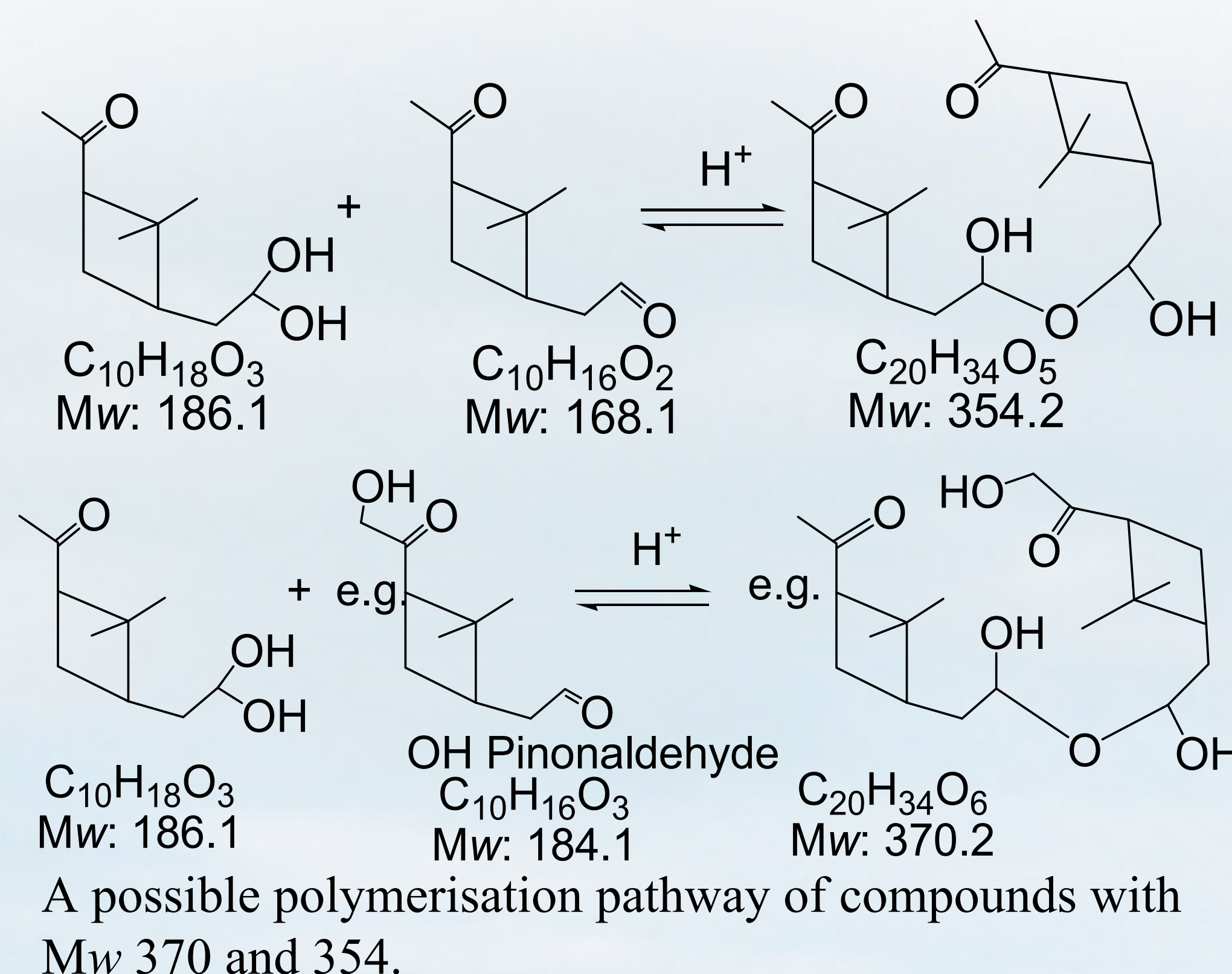


**Figure 3.** The particle number distributions as a function of time (A) with ammonium sulphate seed particles and (B) with sulphuric acid seed particles. The symbols represent the actual DMPS measurements and lines are the log-normal fittings.

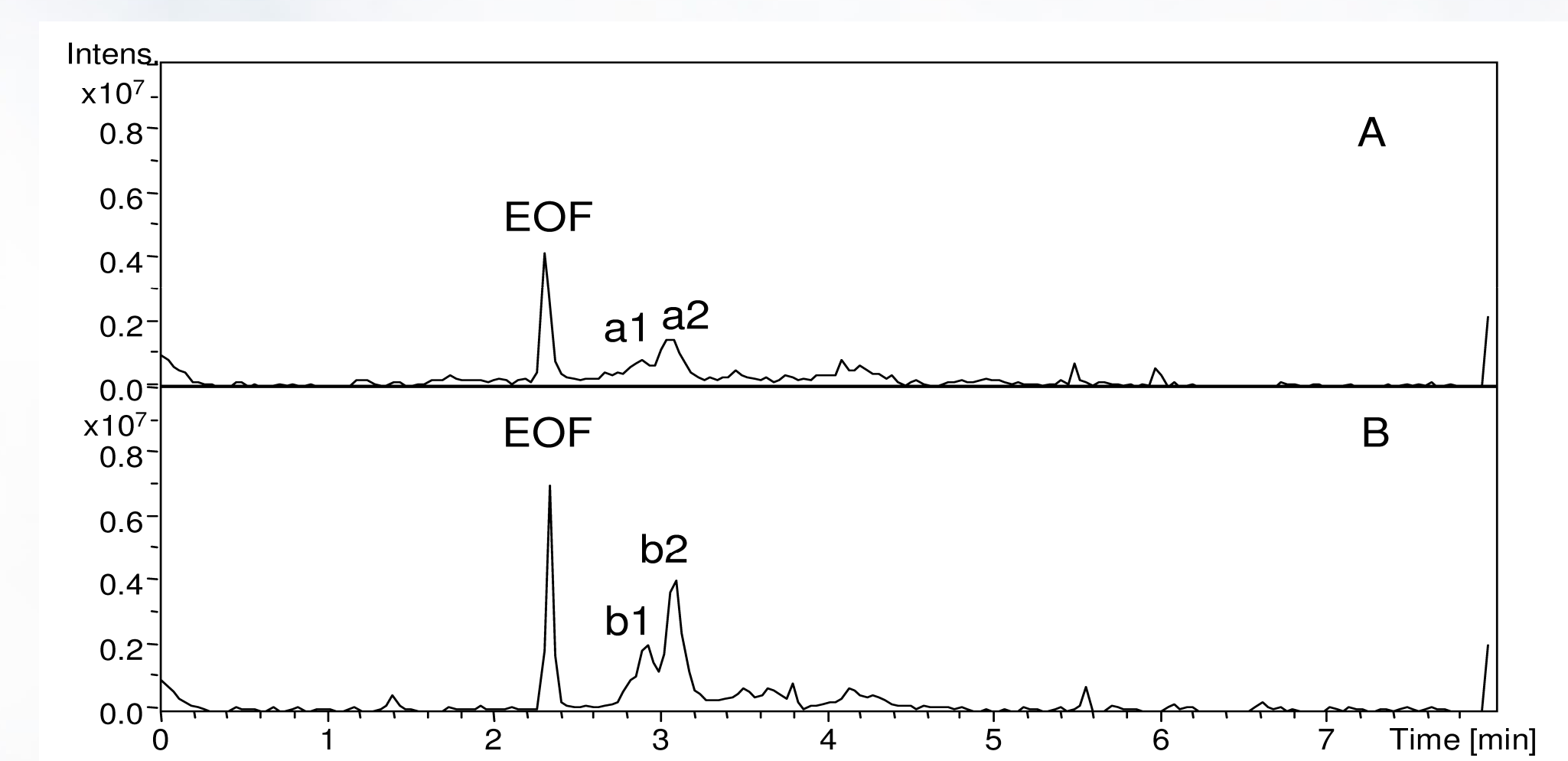
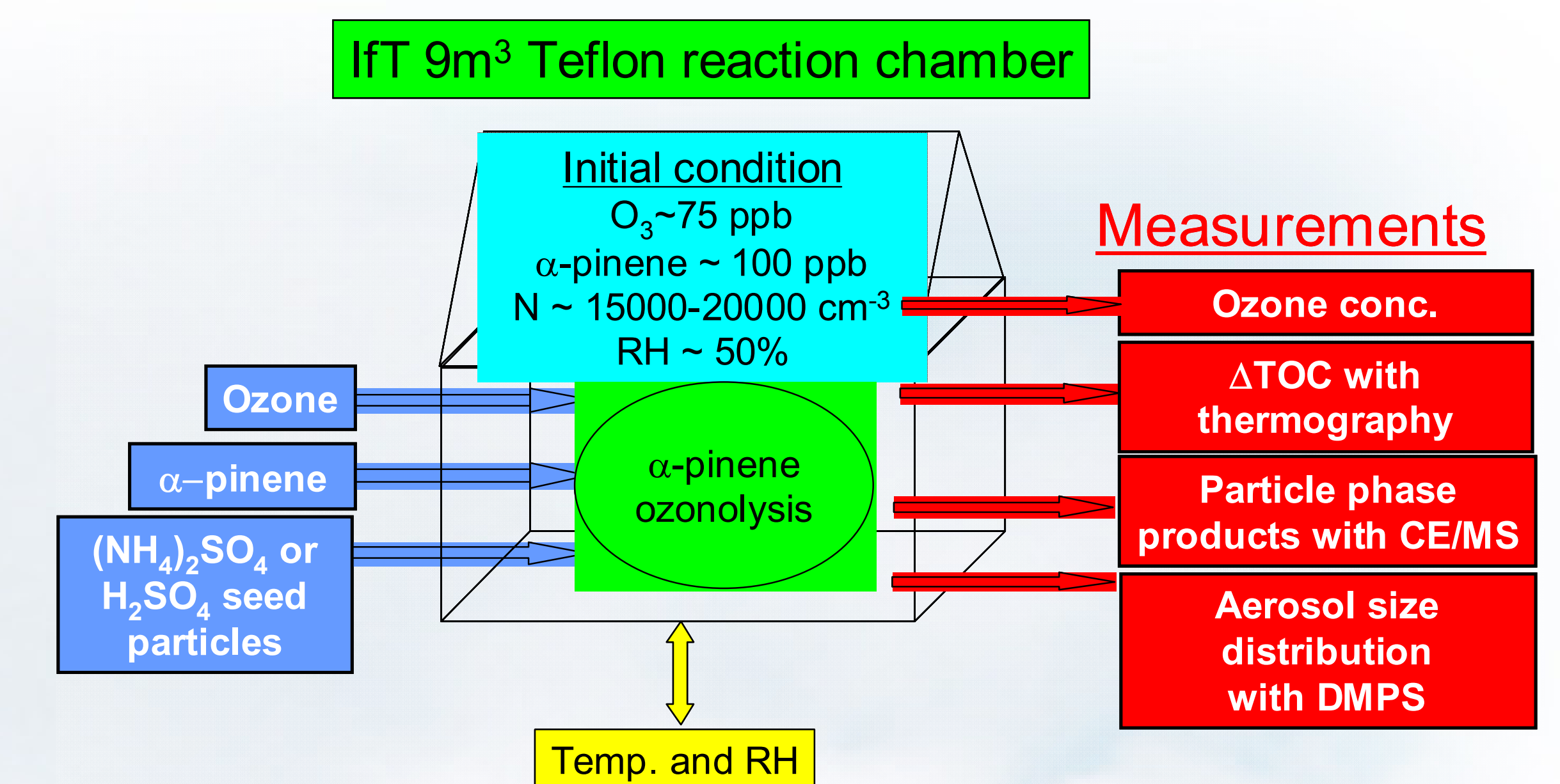
## TOC yields found in particles from the ozonolysis of $\alpha$ -pinene with $\text{H}_2\text{SO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ seed particles (from a thermographic method)

- A:  $\Delta\text{TOC}_{(\text{NH}_4)_2\text{SO}_4} = 52.4 \pm 8.5 \mu\text{g m}^{-3}$  (n=3)
- B:  $\Delta\text{TOC}_{\text{H}_2\text{SO}_4} = 72.3 \pm 14.2 \mu\text{g m}^{-3}$  (n=4)

• Sulphuric acid particles yielded nearly **40%** more OC compared with ammonium sulphate seed particles. The compounds with **molecular weight over 300 (possible dimers and oligomers)** are found from the CE/MS analysis of sulphuric acid particles samples.

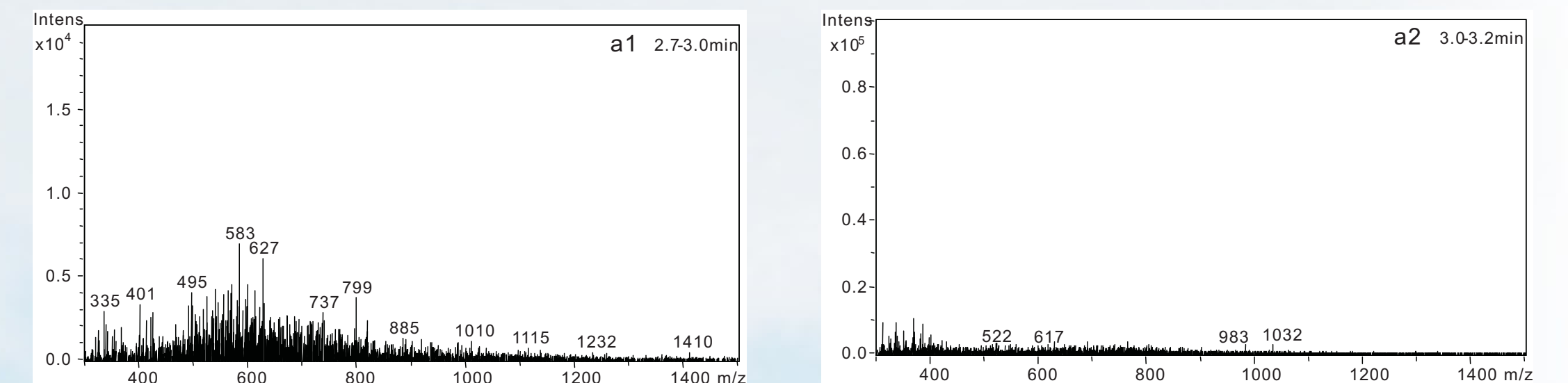


## Experimental Setup and Conditions



**Figure 4.** Extracted ion electropherograms for the experiments with (A) ammonium sulphate seed particles and (B) sulfuric acid seed particles (m/z 300-1500). EOF stands for electroosmotic flow

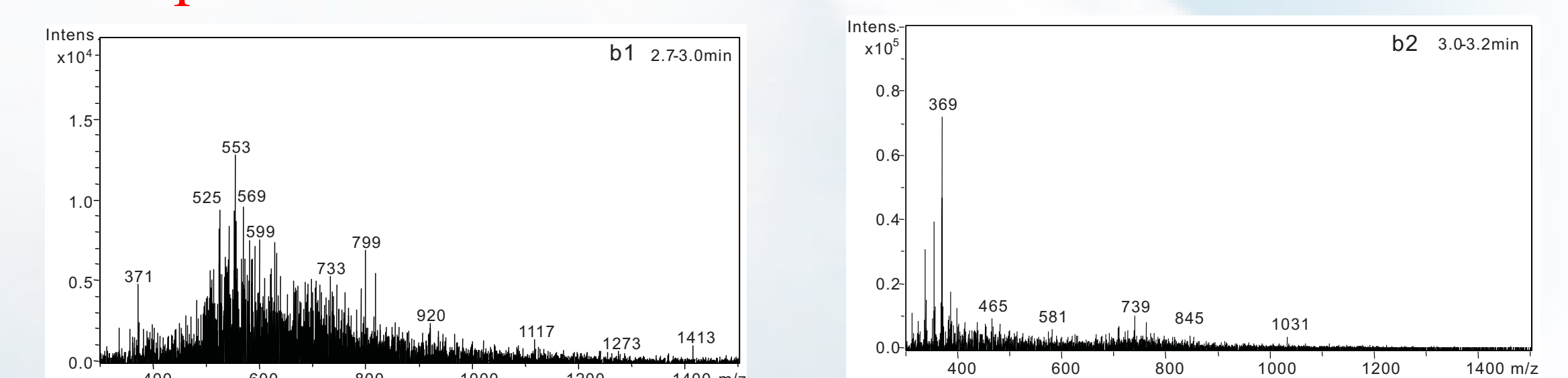
## Ammonium Sulphate



**Figure 5a1.** Background subtracted mass spectrum of peak a1 between 2.7-3.0 min in Figure 2A.

**Figure 5a2.** Background subtracted mass spectrum of peak a2 between 3.0-3.2 min in Figure 2A.

## Sulphuric Acid



**Figure 5b1.** Background subtracted mass spectrum of peak b1 between 2.7-3.0 min in Figure 2B.

**Figure 5b2.** Background subtracted mass spectrum of peak b2 between 3.0-3.2 min in Figure 2B.

## Summary

High molecular weight compounds observed by CE-ESI-MS analysis together with an increase in SOA yield measured by a thermographic method suggest sulfuric acid catalyzed the formation of larger molecules in the particle phase. This result indicates that particle acidity of atmospheric aerosols plays an important part in the heterogeneous reaction of SOA and may explain an unresolved fraction of organic aerosols in the atmosphere.

## References

- Iinuma, Y., Böge, O., Gnauk, T. and Herrmann, H., Atmos. Environ. 38, 761-773 (2004).  
 Tolocka, M., Jang, M., Ginter, J., Cox, F., Kamens, R., Johnston, M., Environ. Sci. Technol. 38, 1428-1434 (2004).  
 Sierau, B., Stratmann, F., Pelzing, M., Neusüß, C., Hofmann, D. and Wilck, M. J. Aero. Sci. 34, 225-242 (2002).

## Acknowledgements

Part of this project is supported by BMBF within AFO2000 in the projects BEWA2000 and EFEU under contract 07ATF25 and 07AFT47, respectively.