Growth of Sulfuric Acid Nanoparticles at Wet and Dry Conditions

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GROWTH OF SULFURIC ACID NANOPARTICLES AT WET AND DRY CONDITIONS

Lenka ŠKRABALOVÁ[1,2], David BRUS[3], Vladimír ŽDÍMAL[1] and Heikki LIHAVAINEN[3]

[1]Laboratory of Aerosol Chemistry and Physics, Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojová 135 Prague, 165 02, Czech Republic,
[2]Department of Physical Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8 Prague, 128 43, Czech Republic
[3]Finnish Meteorological Institute, Erik Palménin aukio 1, P.O. Box 503, FI-00101, Helsinki, Finland
skrabalova@icpf.cas.cz

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INTRODUCTION

Aerosol particles influence global radiative balance and climate directly through scattering and absorbing solar radiation and indirectly by acting as condensation cloud nuclei. The atmospheric nucleation is often followed by a rapid growth of freshly formed particles. The initial growth of aerosol is the crucial process determining the fraction of nucleated particles growing into cloud condensation nuclei sizes (~ 50 nm and larger). Many recent studies have suggested that the sulfuric acid plays a key role in the atmospheric nucleation and subsequent growth of newly formed particles. (Sipilä et al., 2010). The subject of this experimental study is growth behaviour of sulfuric acid nanoparticles produced by homogenous nucleation at wet and dry conditions.

EXPERIMENTAL SETUP

The nucleation experiments were carried out in a laminar flow tube at the Finnish Meteorological Institute. The measurements were performed at relative humidities ~1% and ~30%. The flow tube was kept at constant temperature and the nucleation temperatures investigated were 283, 293 and 303 K. The total gas flow inside the tube was maintained to provide 4 residence times in the tube - 30, 45, 60 and 90 s. Sulfuric acid was taken from a liquid reservoir by passing a stream of carrier gas through an acid saturator with high purity H_2SO_4 (97% w. t.) and the temperature of the acid saturator was increased stepwise in 7 consecutive increments of 5 K during each measurement resulting in gradually growing concentration of sulfuric acid in the flow tube. Due to presence of traces of NH_3 in the system, the nucleated sulfuric acid nanoparticles were partially neutralized to $(NH_4)_2SO_4$. At the outlet of the flow tube number concentration of produced particles was measured using an ultrafine condensation particle counter (UCPC TSI 3776) and particle size distributions using a differential mobility particle sizer (DMPS with a short HAUKE type DMA and UCPC TSI 3025A). The raw DMPS data were inverted to yield number size distributions of the formed particles. Obtained number size distributions were then fitted with log-normal distribution and median diameter of the nucleation mode was determined.

RESULTS

The increasing total particle concentrations and particle median diameters correspond with increasing H_2SO_4 concentration in the gaseous mixture due to gradually growing temperature of the acid saturator during the experiment (Fig. 1). The values of total number concentrations during all measurements ranged from $1{,}1\times10^3 \pm 0{,}17\times10^3$ to $47{,}3\times10^3 \pm 1{,}2\times10^3$ and were generally higher during experiments performed at relative humidity ~30% and higher temperatures. The values of median particle diameter ranged from 14,42 ± 0,08 nm to 39,84 ± 1,55 nm and particles grew bigger at relative humidity ~30% and at high H_2SO_4 concentrations. The repeatability of the performed

measurements is illustrated in Fig. 2, which shows the results of experiments at temperature 283 K and relative humidity ~1% taken 1 day apart. At the same temperature, H_2SO_4 concentrations, relative humidity and residence time, the maximum variance for the single median particle diameters determined from both experiments was 0,6 nm indicating that the measurements of the particle diameters were extremely reproducible. The determined curves of particle number concentration as a function of H_2SO_4 concentration measured by both DMPS and UCPC (Fig. 3) were found to be strongly dependent on the residence time of the gaseous mixture in the flow tube. The results clearly show that the observed total number concentration is influenced by the growth process and the longer the residence time, the larger fraction of nucleated particles is allowed to grow beyond the detection limit of the instruments. Absolutely no particles were detected during experiments performed at residence time of 30 s indicating that the nucleated particles were not able to grow to detectable sizes during the first 30 seconds of the experiments. Hygroscopic growth behaviour can be described using growth factors GF:

$$GF = \frac{D_p(wet)}{D_p(dry)}$$

In this study, dry diameter D_p(dry) corresponds to median particle diameters obtained from measurements performed at relative humidity ~1% and wet diameters D_p(wet) to median particle diameters obtained from measurements at relative humidity ~30%. Growth factors as a function of H_2SO_4 concentration obtained from measurements performed at T = 293 and 3 residence times is presented in Fig. 4. Our findings are compared with results from Biskos et al. (2010), who measured hygroscopic growth of acidic sulfate nanoparticles in a wide range of relative humidities. Biskos et al. (2010) report at relative humidity ~30% for dry diameters from 14,1 to 36,1 nm, which are comparable with this study, growth factors from 1,25 to 1,3. In this study, the growth factors for residence time 45s range from 1,06 to 1,22, for residence time 60s from 1,06 to 1,2 and for residence time 90s from 1,11 to 1,49. The best agreement for all residence times was found for H_2SO_4 concentrations from 2×10^8 to 8×10^8 corresponding to dry diameters from 21,3 nm to 26,1 nm.

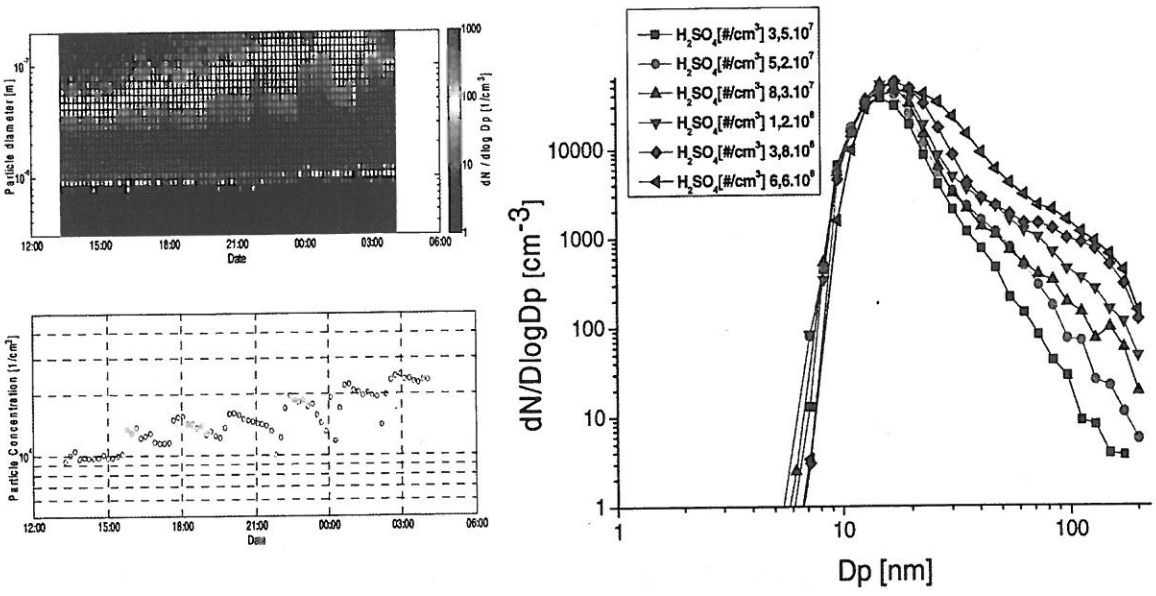

Fig. 1: The observed variation in particle size distribution and particle number concentration with time obtained from inversion process of raw DMPS data from a single experiment

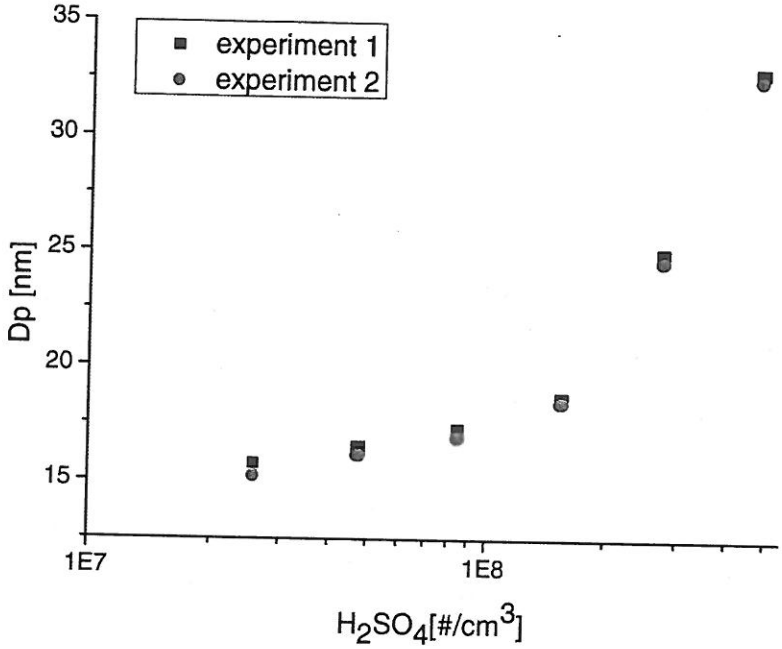

Fig. 2: The median particle diameters determined from measurements performed at the same conditions taken 1 day apart

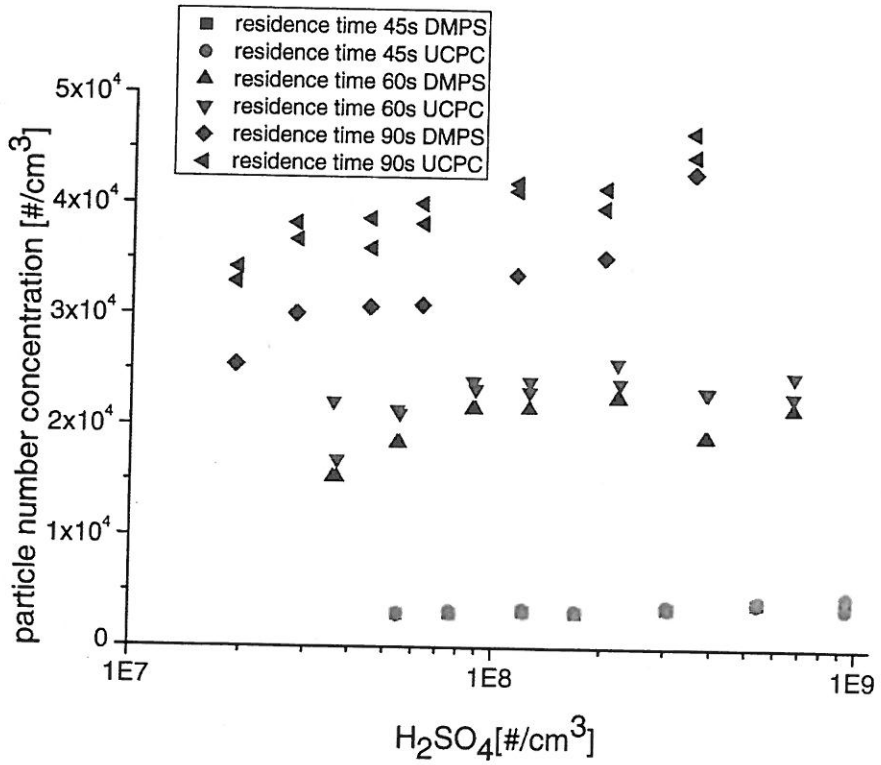

Fig. 3: The observed particle number concentration as a function of residence time at T = 293K and relative humidity ~30%

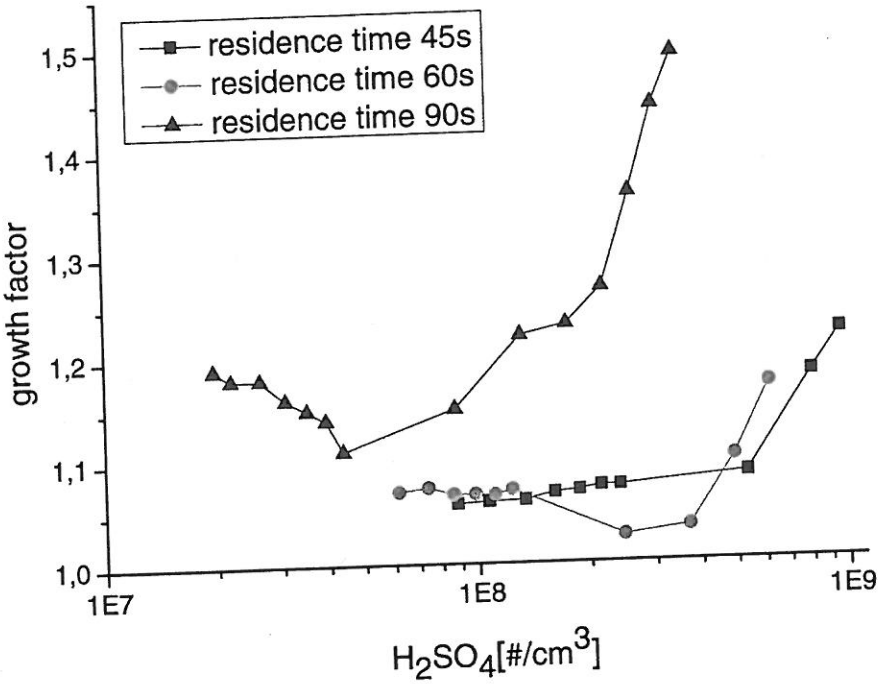

Fig.4: The growth factors as a function of H_2SO_4 concentration at T = 293K and 3 residence times

CONCLUSIONS

In this work the growth behaviour of sulfuric acid nanoparticles at wet and dry conditions was studied. The increasing total particle concentration and particle median diameters during experiments correspond with increasing H_2SO_4 concentration in the gaseous mixture. The comparison of median particle diameters obtained from measurements performed at the same conditions shows that the experiments were well reproducible. The determined curves of particle number concentration as a function of H_2SO_4 concentration were found to be strongly dependent on the residence time and the longer the residence time, the higher the total particle concentration. The hygroscopic growth behaviour, described using growth factors, was found to be in a good agreement with previously published results (Biskos et al., 2009).

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