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Homogeneous nucleation of sulfuric acid and water mixture: experimental setup and first results

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Abstract

In this study we introduce a new laminar flow tube suitable for binary and ternary homogeneous nucleation studies. The production of sulfuric acid and water vapor mixture, the experimental setup and the method of sulfuric acid concentration determination are discussed in details. Wall losses were estimated from the measured sulfuric acid concentration profile along the laminar flow tube and compared to a theoretical prediction. In this investigation the experimental evidence of new particle formation was observed at concentration of 10^9 molecules of sulfuric acid in cm^3 and nucleation rates measured at three relative humidities (RH) 10, 30 and 50% cover six orders of magnitudes from 10^{-3} to 10^3 particles in cm^3. Particle free air was used as a carrier gas. Our first results are compared to theoretical prediction of binary homogeneous nucleation, to results obtained by other investigators and to atmospheric nucleation.

1 Introduction

Aerosol particles in the atmosphere affect the radiative balance of the globe both directly and indirectly (Twomey, 1991, 1974); thus affecting the global temperature. Aerosols may also cause negative health effects (Davidson et al., 2005) and they can seriously affect visibility. New particle formation in the atmosphere has received considerable attention lately both from atmospheric scientists and aerosol researchers. Atmospheric new particles have been observed to form by self-condensing, or nucleating homogeneously in events lasting few hours nearly all around the world (Kulmala et al., 2004). This pathway can dramatically increase the local aerosol number concentrations (Spracklen et al., 2006).

To understand the mechanism of new particle formation events, considerable work has been done involving direct field and laboratory measurements, as well as computer simulations both on nucleation itself and the aerosol dynamics observed during

the events. Despite coming closer to drawing conclusions of all available data, exact knowledge of the nucleation event mechanism remains unclear.

The first step of new particle formation or any first order phase transition is nucleation. Vapor to liquid nucleation may occur if the partial pressure of the vapor exceeds its equilibrium vapor pressure in the surrounding conditions. It has been calculated that in the atmosphere the equilibrium vapor pressure of sulfuric acid is low enough for it to be a likely candidate to nucleate homogeneously (Seinfeld and Pandis, 1998). While binary nucleation of sulfuric acid and water may explain nucleation in stratospheric or upper tropospheric temperatures (Clarke et al., 1998; Weber et al., 1999; Vehkamäki et al., 2002), some other substances enhancing nucleation may be needed in the lower troposphere. These compounds are yet to be identified, although ammonia has been suggested as a favorite candidate (Korhonen et al., 1999).

Laboratory experiments on nucleation of binary sulfuric acid and water date back to 1976 when Reiss et al. (1976) measured nucleation rates in a piston cloud chamber. Similar experiments were conducted by Boulaud et al. (1977) in a reactor study, Mirabel and Clavelin (1978) in a thermal diffusion cloud chamber, and Friend et al. (1980) in laminar flow reactor. More recent experiments include those made by Wyslouzil et al. (1991), Viisanen et al. (1997), Ball et al. (1999), Zhang et al. (2004), Berndt et al. (2006), Benson et al. (2008), and Young et al. (2008). All the latter experiments relied on a flow-based measurement technique. Some experimentalists (Friend et al., 1980; Berndt et al., 2006; Benson et al., 2008; Young et al., 2008) employ photo-oxidation of SO_2, some produce gaseous mixture from liquid H_2SO_4, using saturators (Wyslouzil et al., 1991; Ball et al., 1999) or liquid samples (Viisanen et al., 1997). However, it has to be pointed out that laboratory measurements are widely conducted at 10–30°C higher temperatures than nucleation occurring in the atmosphere. Only a narrow temperature range of 20–30°C was utilized in measurements by Wyslouzil et al. (1991) showing that 5°C decrease in nucleation temperature leads to an increase in nucleation rate from two to four orders in magnitude.

In this work we present a new laminar flow tube (LFT) based on design suggested by Viisanen et al. (1997). The LFT is very simple in construction and easy to operate, it is also capable to perform long-lasting experiments with a stable particle production. We show how the concentration of sulfuric acid is measured, and its losses to wall in the nucleation chamber are estimated. The obtained nucleation rate data are then compared to the binary homogenous nucleation parameterization of Vehkamäki et al. (2002) and experimental data published by others.

2 Experimental setup

The laminar flow tube built recently at Finnish Meteorological Institute in Helsinki, Finland is capable of both binary and ternary homogeneous nucleation measurements. The laminar flow tube is positioned vertically and its whole length is about three meters. The experimental setup consists of five main parts: an atomizer, a furnace, a mixing unit, a nucleation chamber and a particle detector unit, see Fig. 1. A liquid solution of known concentration and amount (0.22 ml/min) is introduced by HPLC Pump (Waters 515) through a ruby micro-orifice (Bird Precision – 20 μm) together with sheath particle free air (about 4 l/min) into the furnace. The dispersion is vaporized in a furnace (Pyrex glass tube) which is 60 cm long and has I.D. of 2.5 cm. The tube is wrapped with resistant heating wires. The temperature inside the furnace is kept approximately at 470 K and controlled by PID controller within ±0.1 K (DigiTrace, TCONTROL-CONT-02). After the furnace, the vapor is filtered with Teflon filter (MITEX^{TM} Millipore 5.0 μm LS) to remove any liquid residue or particulate impurities. The filtered vapor is then introduced into mixing unit made of Teflon and cooled by turbulent mixing with room temperature particle free air to about 320 K. The flow rate of mixing air is about 8 l/min. Both lines of particle free air (furnace sheath air and mixing air) are controlled by flow rate controller within ±3% (MKS type 250). The vapor gas mixture is then cooled to a wanted nucleation temperature in nucleation chamber which is kept at a constant temperature (298 K) with two liquid circulating baths (Lauda RK-20). The nucleation

chamber is made of stainless steel, its I.D. is 6 cm and whole length is 200 cm. Concentration of water vapor is measured in the middle and at the end of nucleation chamber (see Fig. 1) with two humidity and temperature probes Vaisala HMP37E of humidity data processor Vaisala HMI38 within ±3%. The aerosol number concentration is measured just after nucleation chamber with an ultrafine condensation particle counter (UCPC TSI 3025A).

A typical experiment is done in following way. First we run the experiment with pure water to clean the tube till particle concentration inside the nucleation chamber drops to 0.5 particles in cm^3, which is our background value for pure water. Then the Teflon filter is changed with a clean one and autoclaved with hot particle free air at temperature of 470 K. The autoclaving of the filter is accompanied with a huge particle production which drops down exponentially and takes about 12 h. In the next phase the pure water is used again to flush the tube wall, again the tube is flushed till particle concentration drops to 0.5 particles in cm^3. Consequently the solution of sulfuric acid and water is made. The series of experiments start at the lowest concentration of sulfuric acid and the highest RH (in our case RH∼50%) and ends at the highest concentration of sulfuric acid and the lowest RH (RH∼10%). The concentration of sulfuric acid and water solution in the tube is continuously increased in small steps, i.e. each step means new solution of sulfuric acid and water. The measurements cannot be conducted backwards with lower concentration of sulfuric acid and water than was the previous one, as this usually leads to overproduction of particles due to desorption of sulfuric acid from the walls, i.e. to change of the slope in J_{exp} vs. [H$_2$SO$_4$] plot.

2.1 Temperature measurements

Temperature of the vapor-gas mixture is registered along the laminar flow tube using five PT100 probes. All PT100 probes were calibrated against a standardized thermometer at Finnish Meteorological Institute within a standard error of ±0.05 K. First PT100 probe is immersed into mixer, other four are immersed into nucleation chamber with a distance of 20 cm from each other, see Fig. 1 for details. The temperature 298 K

is achieved at a distance of ~80 cm from the beginning of nucleation chamber; see the axial temperature profile in Fig. 2. The radial temperature profile in nucleation chamber was also measured. This was done by pushing the PT100 probes towards the axis of the chamber with a step of 5 mm to obtain good profile resolution. It can be seen on figure 3 that at distance 20 cm from the beginning of nucleation chamber we obtained parabolic temperature profile. The radial profile is almost flat at the distance of 80 cm. It has to be pointed out that the temperatures measured close to the axis of the nucleation chamber are slightly influenced by heat conduction along the surface of the PT100 probe. At normal experimental conditions the PT100 probes are immersed so that they create flat surface together with inner wall of nucleation chamber, the bodies of probes are not disturbing the laminar flow inside the chamber.

2.2 RH measurements

The concentration of water vapor in the system might be generally changed in to ways. First, the flow rate of liquid sample from HPLC pump might be changed. Second, the water vapor concentration might be changed by sucking the vapor mixture just after the furnace and before the vapor is introduced into mixer. Both of mentioned approaches have certain limitations.

The optimal value of HPLC liquid sample flow rate was found to be 0.22 ml/min, which produces a stable jet for long-running experiments. The lower HPLC flow rate usually led to creation of droplets at micro-orifice and the higher flow rate led to very high values of RH which puts significant demands on subsequent sucking section.

In Fig. 4 it can be seen how we can change the RH in the system if we keep the HPLC liquid sample flow rate (0.22 ml/min) and the two dilution air flow rates constant, and employ only sucking section in between furnace and mixer. Concentration of water vapor is measured in the middle and at the end of nucleation chamber (see Fig. 4) with a humidity data processor Vaisala HMI38 and two Vaisala HMP37E humidity and temperature probes. Both measured values of RH differ within 3%, which is the declared precision of the sensors by manufacturer. The applicable range of RH with this

experimental setup is from 10 to 65%. The value of RH becomes more stable when the sucking flow rate becomes higher.

2.3 Particle counting and stability

The aerosol number concentration is measured just after nucleation chamber with an
ultrafine condensation particle counter (UCPC TSI 3025A), which was calibrated with silver particles to a d_{50} cut off of 2.18 nm. Figure 5 shows the stability of particle production for three RH's (10, 30 and 50%) in long-running (more then 20 h) experiments. When the experiment is started the particle production starts to slowly increase, depending on RH, and reaches a certain plateau value in two to three hours. The stable
particle production then lasts for many hours with a maximum of ±20% change in total number concentration per hour.

The flow rate test on Fig. 6 describes what flow rate is the most suitable for our experiments. The flow rate in nucleation chamber can also be expressed as a residence time, t. The particle number concentration N_{exp} at 50% of RH is increasing with
increasing residence time in the nucleation chamber till about 60 s then the particle number concentration N_{exp} stays constant till 90 s. At RH of 30% we can see slight increase in particle number concentration till 40 s, and then it starts to decrease with longer residence time.

When we transfer the particle number concentration to nucleation rate J_{exp} with simple relationship $J_{exp}=N_{exp}/t$, we obtain a different perspective, the maxima of the dependency then shifts closer to lower resident times and nucleation rate starts to decrease earlier. The decrease is faster at lower RH. The flow in our LFT has an optimal residence time from 30 to 45 s, with residence time shorter than 30 s we face undercounting of UCPC because the most of the particles are not able to grow beyond the
detection limit of UCPC. With residence time longer than 45 s, on the other hand, we have to face particle losses on the nucleation chamber wall.

Complementary measurements of particle size distribution were also done to show how the particle mean diameter is changing with residence time, see Fig. 7. To

measure size distribution the Differential Mobility Particle Sizer (DMPS with a short HAUKE type DMA and UCPC TSI 3025A) system was used. The experiment was done at three resident times 30, 45 and 90 s at H_2SO_4 total concentration of 9.84×10^9 molecules in cm^3, and RH of 50%. The mean particle diameter is increas-
ing with longer residence time, but on the other hand the total particle concentration is decreasing, the same behavior was found in flow rate test experiment, see Fig. 6. Mean particle diameters of 2.2, 2.4 and 2.7 nm were estimated for resident times of 30, 45 and 90 s respectively. The mean particle diameter is larger than the cut-off of UCPC 3025A (2.18 nm) for all resident times.

Figure 8 shows comparison of integral particle count obtained from inversion of DMPS data and total particle count measured with UCPC 3025A. Due to inversion of DMPS data, the total concentrations are different from those measured with the stand-alone UCPC. The DMPS gives a higher total particle count with a factor of 2.8, 2.7 and 1.4 for resident times 30, 45 and 90 s compared to total particle count measured with UCPC 3025A (with counting efficiency and tube losses not taken into account), also particle losses due to diffusion seems to be higher at residence time of 90 s for inverted DMPS data. The stand-alone UCPC was used to give the particle count data in our measurements as we do not know the exact dependency of particle mean diameter as function of sulfuric acid concentration, D_p=f($[H_2SO_4]$) at all measurement conditions.

2.4 Nucleation zone determination

The nucleation zone is a region inside the nucleation chamber where the nucleation takes place. It is very important to determine the region where the nucleation is initiated. It ensures that the nucleation is a homogeneous process independent on any local changes in vapor-gas mixture composition and temperature, especially at the beginning of nucleation chamber where the particles might be spontaneously produced only because of rapid change in temperature. The cut-off of UCPC 3025A was found unsatisfactory for that purpose, the thermodynamically stable clusters (TSC; Kulmala et al., 2007) formed by binary homogeneous nucleation (BHN) of sulfuric acid and

water are neutral molecular clusters with mean mobility diameters about 1.5 nm. The Pulse High CPC, which is able to measure particles with mean diameter about 1.5 nm, was found to be the appropriate device for these measurements. Also special probe with 45 degrees cut tip was used for that purpose. It has to be pointed out here that PH-CPC is a unique device and it was used in these measurements for short period of time, only to determine the nucleation zone. The PH-CPC is a modified version of UCPC 3025A, where the laser is changed to a lamp that produces white light. The multi channel analyzer (MCA) is attached inside the PH-CPC; MCA is analyzing the amount of scattered light that is proportional to the size of the measured particles. The main disadvantage associated with the PH-CPC is that the particle concentration cannot be too high, i.e. the experiment has to be carried out at low concentrations of sulfuric acid. If more than one particle enters the optics at the same time the MCA might detect them as one particle and its size will be overestimated. Also if the detector has just detected a particle, it will be offline for certain time (orders of milliseconds) and cannot detect a new particle so the concentration might be underestimated. The detailed principle of operation and more technical details about PH-CPC can be found in Sipilä et al. (2008).

To obtain the position of nucleation zone the particle concentration was measured in a similar way as the temperature profile inside the nucleation chamber. The probe was pushed from the wall inner surface towards the axis of the chamber with a step of 1 cm to obtain the particle concentration profile in the nucleation chamber. The measurements were repeated for each hole at four different distances (20, 40, 60 and 80 cm) along the nucleation chamber and also one measurement was done at the end of the tube to obtain total particle concentration. Figure 9 shows the particle number concentration for two residence times (30 and 45 s) along the axis of nucleation chamber. Residence times of 30 and 45 s are calculated for the whole length of nucleation chamber. It is clear that only about one per cent of total count at the end of the nucleation chamber is already present at 20 cm from its beginning. It means that there is no significant particle production caused by rapid change in temperature in the mixing unit.

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Figure 10 shows the particle number concentration as a function of the radius and the distance from the beginning of the nucleation chamber for two resident times (30 and 45 s). It looks like there is some turbulent mixing for the residence time of 30 s (Fig. 10a) at the beginning of nucleation chamber compared to residence time of 45 s
5 (Fig. 10b) where the particle production seems to be much smoother. The nucleation zone is bit broader for residence time of 30 s than 45 s and starts around 60 cm and 70 cm respectively from the beginning of nucleation chamber. The nucleation zone peak starts around 80 cm for both residence times and we estimate that its maxima are located somewhere close to 1 m from the beginning of the nucleation chamber. The
10 estimated distance of 1 m at which maxima of nucleation zone takes place will be used hereafter for calculation of residence time and subsequent calculation of nucleation rate.

The nucleation time was then estimated as a distance from the nucleation zone maximum to the end of the tube where they were counted. We expect that we might
15 face undercounting of particles which are not able to grow to detectable size.

2.5 Preparation of solution, determination of H_2SO_4 concentration and wall loses

The liquid samples of sulfuric acid and water mixture are prepared from 0.01 M solution of H_2SO_4 (Reagecon, AVS purity) and ultrapure water (Millipore, TOC less than 10 ppb,
20 resistivity 18.2 MΩ cm at 25°C). The desired solution concentration is prepared in two steps of dilution. First, 1 l of primary solution of concentration (1.96×10^{-4} mol/l) is made by putting 20 ml of 0.01 mol of H_2SO_4 to 1 l of pure water. Then the desired final solution for particular measurement is made. To cover RH's from 50% to 10% we prepare 1 l of final solution from 0.5 ml to 70 ml of primary solution. The final solution concentration
25 is then checked by Ion Chromatography with a lower detection limit of 0.02 mg/l of $(SO_4)^{-2}$.

For the determination of sulfuric acid concentration in the nucleation chamber we employed the method of trapping $(SO_4)^{-2}$ ions into NaOH hydroxide solution using

bubblers. The hydroxide solution was prepared in similar way as the solution of sulfuric acid and water. First a primary solution was made and then was prepared hydroxide solution for each particular experiment. The only condition to obey was to keep hydroxide solution molar concentration in excess to double of the molar concentration of sulfuric acid and water solution which was injected into furnace.

The aim of this experiment was to obtain the concentration profile of sulfuric acid as a function of distance along the laminar flow tube, see Fig. 1 (yellow targets). Several samples were taken and subsequently analyzed by Ion Chromatography method in analytical laboratory at Finnish Meteorological Institute. First sample was taken from the prepared solution to obtain initial concentration for Mass Balance calculation; second one was obtained from the bubbler positioned at the sucking section just after furnace, two samples were obtained from two bubblers at the distance of 80 cm from beginning of nucleation chamber, and two last samples from two bubblers at the end of the nucleation chamber (200 cm). Each bubbler of the pair at distance of 80 and 200 cm was working at different flow rate (4 and 1.5 l/min) and held different volume of hydroxide solution (0.1 and 0.05 l) to crosscheck the obtained concentrations of $(SO_4)^{-2}$. The resulting concentration of sulfuric acid at which the nucleation occurs was then estimated as an averaged concentration between positions 3 and 4 (at distance of 140 cm), see Fig. 1. The necessary time for obtaining detectable amount of $(SO_4)^{-2}$ (more than 0.02 mg/l) was usually longer than 24 h, which demanded very stable production of particles throughout the whole experiment.

Figure 11 shows the concentration of sulfuric acid determined by Ion Chromatography (IC) as a function of sulfuric acid concentration calculated by Mass Balance (MB), both correspond to the position 2 on Fig. 1, after first dilution with particle free air and after furnace. The dashed line represents no losses along the furnace. The losses of sulfuric acid are higher at RH of 10%.

Figure 12 shows the ratios of H_2SO_4 concentration determined by Ion Chromatography and initial H_2SO_4 concentration calculated by Mass Balance as a function of initial H_2SO_4 concentration calculated by Mass Balance. The Mass Balance calculation

provides us concentration of sulfuric acid at the beginning of nucleation chamber and does not include any losses connected to diffusion to walls at any part (i.e. at furnace and mixing unite). The estimated wall losses for 10% RH are about 54%, for 30% RH about 27%, and for 50% RH about 28%. The overall error of the method of sulfuric acid concentration determination was estimated to ±17% including the inherent error of Ion Chromatography analysis.

The wall loss factor (WLF) of sulfuric acid can be defined as

$$\text{WLF} = \frac{[H_2SO_4]_0}{[H_2SO_4]_t} \tag{1}$$

Where $[H_2SO_4]_0$ is the initial concentration of sulfuric acid obtained from Mass Balance calculations, and $[H_2SO_4]_t$ is concentration of sulfuric acid at residence time, t, in the nucleation chamber. Figure 13 shows wall loss factor as function of residence time obtained from bubbler experiments. Also the calculated WLF is included in the figure; calculations are made in the same way as was shown in Young et al. (2008) using RH dependent diffusion coefficient of sulfuric acid in nitrogen published by Hanson and Eisele (2000). Calculated values of the WLF overestimate the WLF obtained from bubbler experiment by a factor of 2. The dependency of WLF on RH seems to be more pronounced for measured values, which inherently suggest stronger dependency of diffusion coefficient on RH or a different wall loss mechanism than a first order diffusion limited process.

3 Results and discussion

The homogeneous nucleation rates of sulfuric acid and water as a function of sulfuric acid concentration at three different RH's: 10, 30 and 50% were determined in this study. All experiments were carried out at nucleation temperature of 25°C. The particle number concentration was measured during whole experiment but evaluated only for steady state particle production (several hours) and subsequently averaged to obtain

only one experimental point. One experimental point also means one solution of sulfuric acid and water. The concentration of sulfuric acid was calculated by Mass Balance and the corresponding losses obtained via bubbler experiment and subsequent Ion Chromatography analyses were applied for each experimental point.

5   The obtained nucleation rates as a function of concentration of sulfuric acid at constant RH are shown on Fig. 14. The homogeneous nucleation rate data cover about six orders in magnitude from 10^{-3} to 10^3 particles in cm^3 and the total sulfuric acid concentration ranged from 10^9 to 2×10^{10} molecules in cm^3 (depending on RH). Nucleation rates presented on Fig. 14 should be rather taken as the lowest nucleation rate observ-

10   able in our system than the real nucleation rates. First, we definitely face undercounting of nucleated particles due to d_{50} cut-off of UCPC 3025A, especially at lower concentrations of each RH. Second, the counting efficiency was not implemented into resulting nucleation rates. From our DMPS measurements (Sect. 2.3, Fig. 8) we can see that the inverted DMPS data are about factor of three higher than total particle count of

15   UCPC 3025A. Third, we prefer some undercounting of nucleated particles against high losses of sulfuric acid on the wall of nucleation chamber due to long residence times necessary to let particles grow to detectable sizes. We believe that utilizing more efficient counters like PH-CPC will reduce this problem in future measurements.

    The results are accompanied with theoretical prediction of binary homogeneous

20   nucleation calculated according to parameterization suggested by Vehkamäki et al. (2003). This parameterization uses the model for the hydrate formation relying on ab-initio calculations of small sulfuric acid clusters and on experimental data for vapor pressures and equilibrium constants for hydrate formation. The experimental data are from about three to four orders of magnitude higher than suggested by theoretical

25   prediction. The slopes of experimental data are comparable to theoretical prediction at RH's of 30 and 50%, but shallower at 10%. The linear fit to experimental data suggests about 8, 6, and 4 sulfuric molecules in critical cluster for RH's 50, 30 and 10% respectively. This value is undoubtedly influenced by undercount of particles at low concentrations of sulfuric acid concentrations due to d_{50} cut-off of UCPC 3025A. It is

necessary to mention that for the experiments carried out at the RH of 10% it was very difficult to keep the particle production stable. The LFT was very sensitive for any small change of the input parameters (flow rates of sheath and mixing air, temperature of furnace) which lead to huge changes in particle production especially at higher nucleation rates; this might be the cause of shallower slope. The error bars stand for uncertainty of the estimated H_2SO_4 concentrations from the bubbler experiments ($\pm 17\%$).

3.1 Comparison to experimental data of others and atmospheric nucleation

The experimental data of this work are compared in Fig. 15 with data obtained by others and also to atmospheric nucleation data obtained in Quest 2 campaign in Hyytiälä, Finland (Sihto et al., 2006). In this investigation the experimental evidence of new particle formation was observed at about 10^9 molecules of sulfuric acid in cm^3, which is directly comparable to new particle formation observed in studies of Ball et al. (1999) and Young et al. (2008) even though RH in their studies are about factor 2 lower. Data of Viisanen et al. (1997) who used similar experimental setup were measured at comparable RH's but they lie at about one order of sulfuric acid concentration higher. The wall losses of 40% estimated in Viisanen et al. (1997) are comparable to wall losses estimated in this work by bubbler experiments. We expect that difference between data of Viisanen et al. (1997) and our results rises mostly from different counting efficiency of devices for particle concentration counting used. Similar conclusions might be stated for data of Wyslouzil et al. (1991). Data of Berndt et al. (2006) were originally published as $N_{exp}=f([H_2SO_4])$. To obtain nucleation rates, J_{exp}, we divided the original dataset with residence time of 290 s. Their data then show experimental evidence of new particle formation for in situ produced H_2SO_4 at about 10^7 molecules in cm^3. Atmospheric nucleation data are not directly comparable to any laboratory studies till present time. They are included just to provide a complex overview, the mean temperature of atmospheric nucleation data is about 0°C and the range of RH's is from 30 to 95%, also nucleation rate is determined for nucleated particles with a mean diameter of 1.5 nm.

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4 Conclusions

A new laminar flow tube capable of binary and ternary nucleation measurements, its experimental setup and basic functionality was presented in this work. The detailed axial and radial profiles of temperature and the way of regulation of RH were presented. The preparation procedure of sulfuric acid solution and the determination of sulfuric concentration in the nucleation chamber were discussed. The wall losses of 54%, 27%, and 28% were estimated from the bubbler experiments for three RH's 10, 30, and 50%, respectively, with the estimated error of 17%. The stability of particle production of long-lasting experiments was demonstrated and the optimal residence times for the nucleation experiments were found to be in range from 30 to 45 s (for whole nucleation chamber). The measurements of nucleation zone using PH-CPC showed that the peak of new particle production is located about 100 centimeters from the beginning of nucleation chamber.

Generally, the strategy of rather slight undercounting of nucleated particles due to insufficient growth times was preferred compared to higher losses of sulfuric acid to the nucleation chamber wall due to long resident times. The experimental evidence of new particle formation was observed at about 10^9 molecules of sulfuric acid in cm^3 which is in good agreement with previously published laboratory studies. The nucleation rates were obtained from total number particle count divided by the resident time from nucleation zone peak to end of the tube. The obtained nucleation rates cover six orders in magnitude and they range from 10^{-3} to 10^3 particles in cm^3. The experimental data are from about three to four orders of magnitude higher compared to parameterization of BHN (Vehkamäki et al., 2003). The agreement with previously published data of other investigators is good, but the concentration of sulfuric acid necessary for new particle formation is still several orders higher than observed in atmospheric measurements.

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Ball, S. M., Hanson, D. R., and Eisele, F. L., and McMurry, P. H.: Laboratory studies of particle nucleation: Initial results for H_2SO_4, H_2O, and NH_3 vapors, J. Geophys. Res., 104 (D19), 23709–23718, 1999.

Benson, D. R., Young, L. H., Kameel, F. R., and Lee, S.-H.: Laboratory-measured nucleation rates of sulfuric acid and water binary homogeneous nucleation from the SO_2+OH reaction, Geophys. Res. Lett., 35, L11801, doi:10.1029/2008GL033387, 2008.

Berndt, T., Böge, O., and Stratmann, F.: Formation of atmospheric H_2SO_4/H_2O particles in the absence of organics: A laboratory study, Geophys. Res. Lett., 33, L15817, doi:10.1029/2006GL026660, 2006.

Boulaud, D., Madelaine, G., Vigla, D., and Bricard, J.: Experimental study on the nucleation of water vapor sulphuric acid binary system, J. Chem. Phys., 66, 4854–4860, 1977.

Clarke, A. D., Varner, J. L., Eisele, F., Mauldin, R. L., Tanner, D., and Litchy, M.: Particle production in the remote marine atmosphere: Cloud outflow and subsidence during ACE 1, J. Geophys. Res., 103(D13), 16397–16409, 1998.

Davidson, C. I., Phalen, R. F., and Solomon, P. A.: Airborne particulate matter and human health: A review, Aerosol Sci. Tech., 39, 737–749, 2005.

Friend, J. P., Barnes, R. A., and Vasta, R. M.: Nucleation by free radicals from the photooxidation of sulfur dioxide in air, J. Phys. Chem., 84, 2423–2436, 1980.

Hanson, D. R. and Eisele, F.: Diffusion of H_2SO_4 in humidified nitrogen: Hydrated H_2SO_4, J. Phys. Chem. A, 104, 1715–1719, 2000.

Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., and McMurry, P. H.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, J. Aerosol Sci., 35, 143–176, 2004.

Kulmala, M., Riipinen, I., Sipilä, M., Manninen, H. E., Petäjä, T., Junninen, H., Dal Maso, M., Mordas, G., Mirme, A., Vana, M., Hirsikko, A., Laakso, L., Harrison, R. M., Hanson, I., Leung,

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C., Lehtinen, K. E. J. and Kerminen, V.-M.: Towards direct measurement of atmospheric nucleation, Science, 318, 89–92, doi:10.1126/science.1144124, 2007.

Mirabel, P. and Clavelin, J. L.: Experimental study of nucleation in binary mixtures: The nitric acid-water and sulphuric acid-water systems, J. Chem. Phys., 68, 5020–5027, 1978.

5   Reiss, H., Margolese, D. I., and Schelling, F. J.: Experimental study of nucleation in vapor mixtures of sulphuric acid and water, J. Colloid Interf. Sci., 56, 511–526, 1976.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: From air pollution to climate change, Wiley, New York, 1998.

Sihto, S.-L., Kulmala, M., Kerminen, V.-M., Dal Maso, M., Petäjä, T., Riipinen, I., Korhonen, H.,
10   Arnold, F., Janson, R., Boy, M., Laaksonen, A., and Lehtinen, K. E. J.: Atmospheric sulphuric acid and aerosol formation: implications from atmospheric measurements for nucleation and early growth mechanisms, Atmos. Chem. Phys., 6, 4079–4091, 2006, http://www.atmos-chem-phys.net/6/4079/2006/.

Sipilä, M., Lehtipalo, K., Kulmala, M., Petäjä, T., Junninen, H., Aalto, P. P., Manninen, H. E.,
15   Kyrö, E.-M., Asmi, E., Riipinen, I., Curtius, J., Kürten, A., Borrmann, S., and O'Dowd, C. D.: Applicability of condensation particle counters to measure atmospheric clusters, Atmos. Chem. Phys., 8, 4049–4060, 2008, http://www.atmos-chem-phys.net/8/4049/2008/.

Spracklen, D. V., Carslaw, K. S., Kulmala, M., Kerminen, V.-M., Mann, G. W., and Sihto, S.-
20   L.: The contribution of boundary layer nucleation events to total particle concentrations on regional and global scales, Atmos. Chem. Phys., 6, 5631–5648, 2006, http://www.atmos-chem-phys.net/6/5631/2006/.

Twomey, A.: Pollution and the planetary albedo, Atmos. Environ., 8, 1251–1256, 1974.

Twomey, S.: Aerosols, clouds and radiation, Atmos. Environ., 25A, 2435–2442, 1991.

25   Vehkamäki, H., Kulmala, M., Napari, I., Lehtinen, K. E. J., Timmreck, C., Noppel, M., and Laaksonen, A.: An improved parameterization for sulfuric acid-water nucleation rates for tropospheric and stratospheric conditions, J. Geophys. Res., 107(D22), 4622, doi:10.1029/2002JD002184, 2002.

Viisanen, Y., Kulmala, M., and Laaksonen, A.: Experiments on gas-liquid nucleation of sul-
30   phuric acid and water, J. Chem. Phys., 107, 920–926, 1997.

Weber, R. J., McMurry, P. H., Mauldin III, R. L., Tanner, D. J., Eisele, F. L., Clarke, A. D., and Kapustin, V. N.: New particle formation in the remote troposphere: A comparison of observations at various sites, Geophys. Res. Lett., 26(3), 307–310, 1999.

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Wyslouzil, B. E., Sienfeld, J. H., Flagan, R. C., and Okuyama, K.: Binary nucleation in acid-water systems, II. Sulphuric acid-water and a comparison with methanesulphonic acid-water, J. Chem. Phys., 94, 6842–6850, 1991.

Young, L. H., Benson, D. R., Kameel, F. R., Pierce, J. R., Junninen, H., Kulmala, M., and Lee, S.-H.: Laboratory studies of H_2SO_4/H_2O binary homogeneous nucleation from the SO_2+OH reaction: evaluation of the experimental setup and preliminary results, Atmos. Chem. Phys., 8, 4997–5016, 2008,
http://www.atmos-chem-phys.net/8/4997/2008/.

Zhang, R., Suh, I., Zhao, J., Zhang, D., Fortner, E. C., Tie, X., Molina, L. T., and Molina, M. J.: Atmospheric new particle formation enhanced by organic acids, Science, 304, 1487–1490, 2004.

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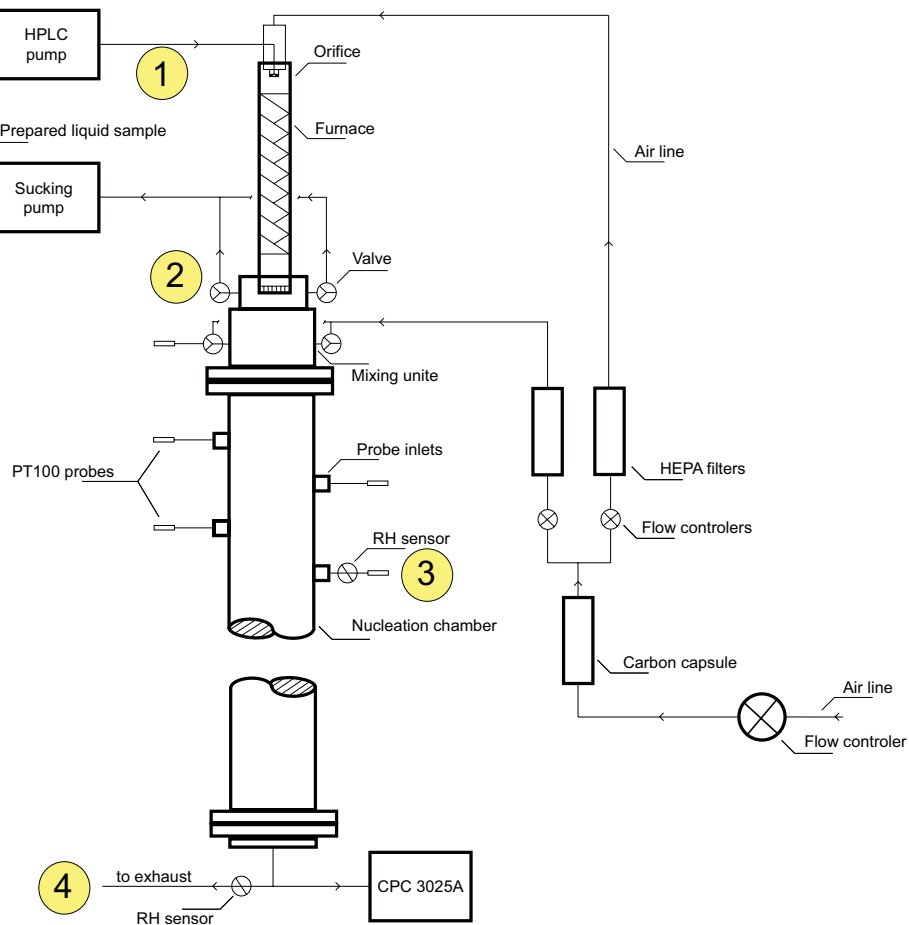
Fig. 1. The schematic picture of laminar flow tube. The yellow targets: **(1)** place where sulfuric acid was sampled from liquid solution. **(2)**, **(3)** and **(4)** are the places where sulfuric acid was sampled from vapor phase mixture by using bubblers.
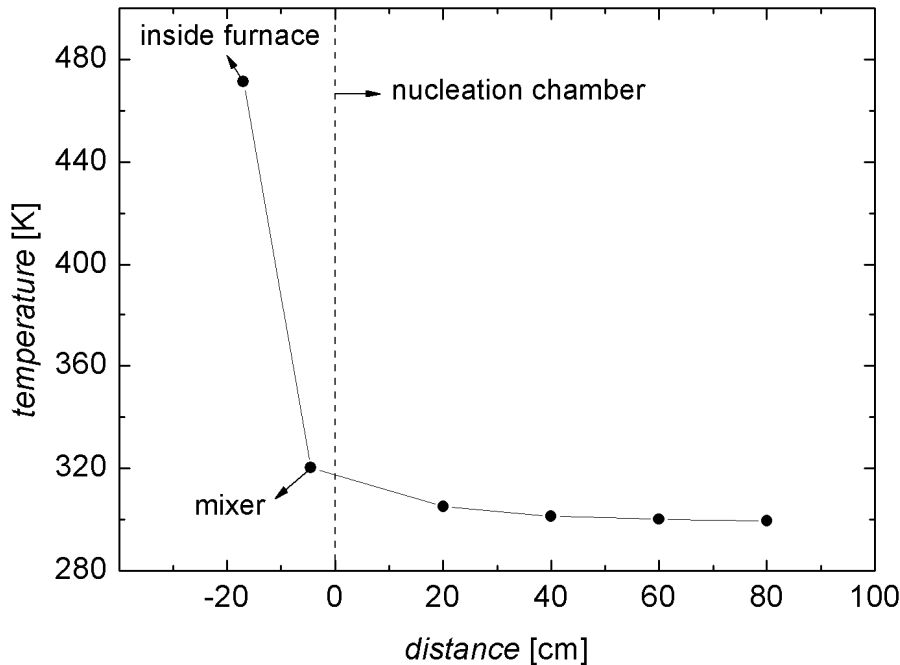
Fig. 2. Measured axial temperature profile inside the nucleation chamber.
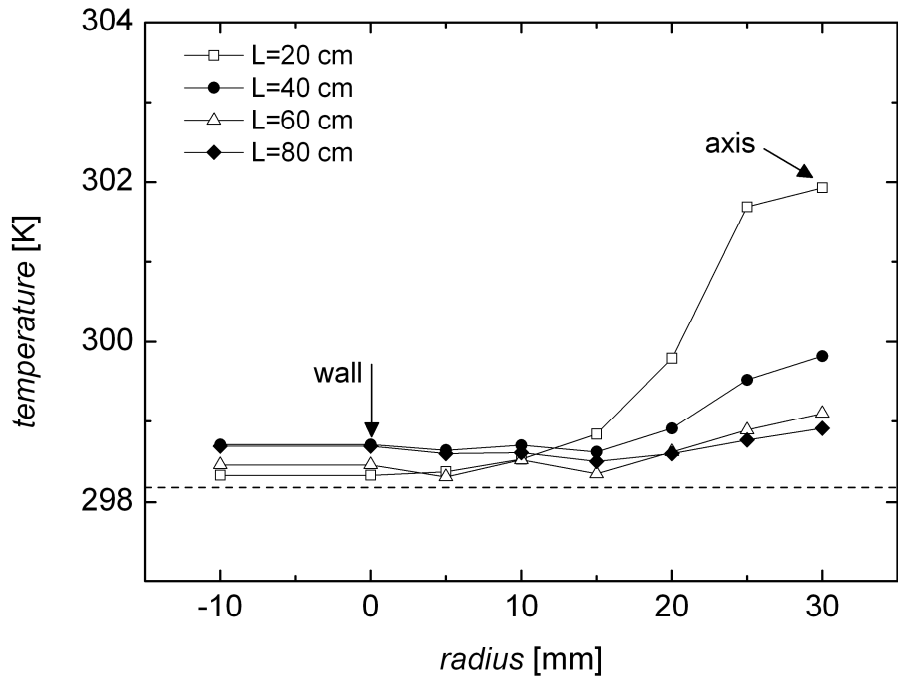
Fig. 3. Measured radial temperature profile inside the nucleation chamber.
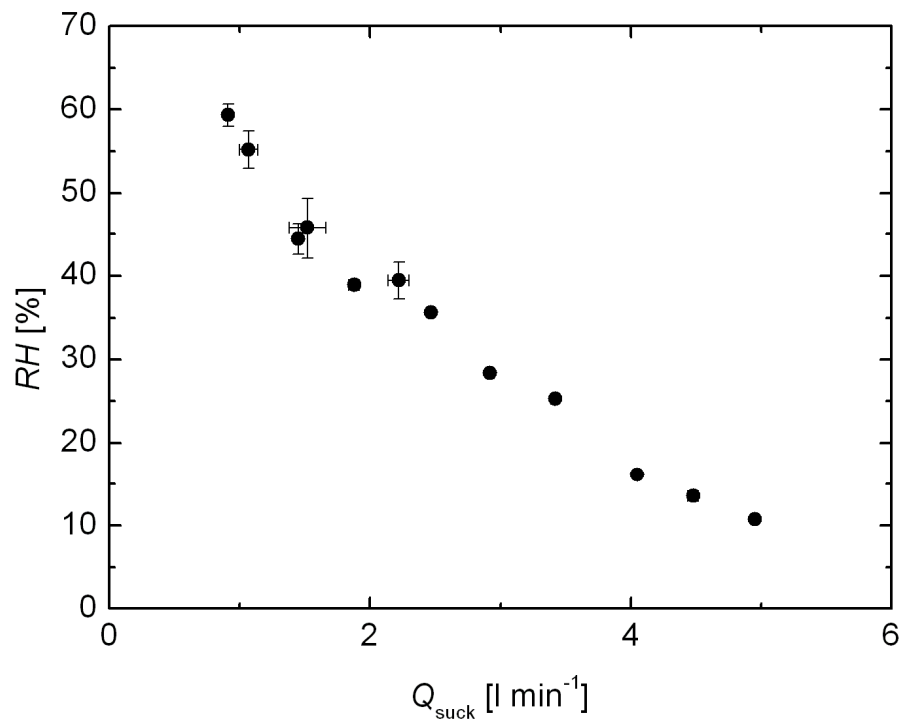
Fig. 4. Relative humidity as a function of flow sucked after furnace measured with pure water. HPLC liquid sample flow rate (0.22 ml/min) and two dilution air flow rates are kept constant.
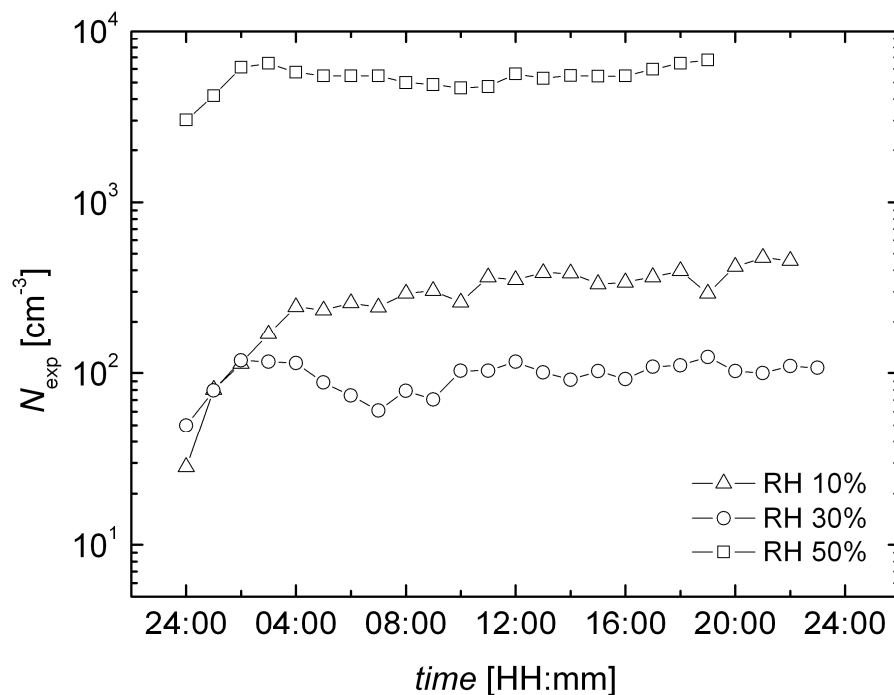
Fig. 5. Experimental particle number concentration (hourly averages) at three different RH's 10, 30 and 50% as a function of time.
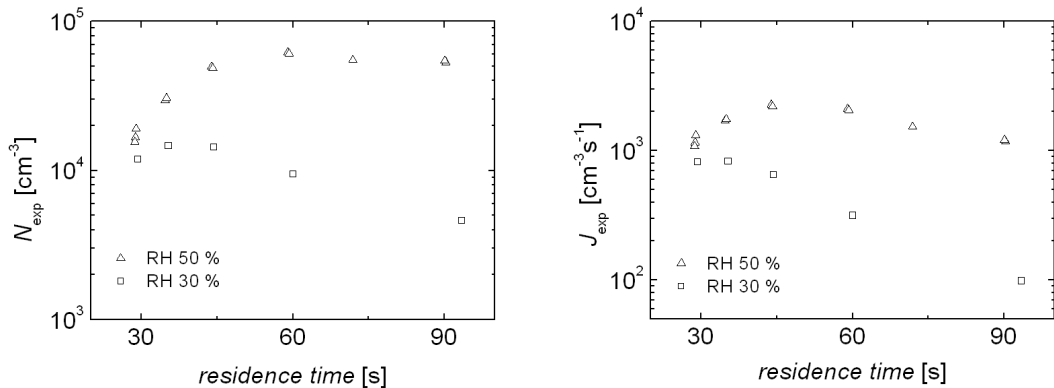
Fig. 6. Particle number concentration N_{exp} and nucleation rate J_{exp} as a function of residence time in the nucleation chamber.

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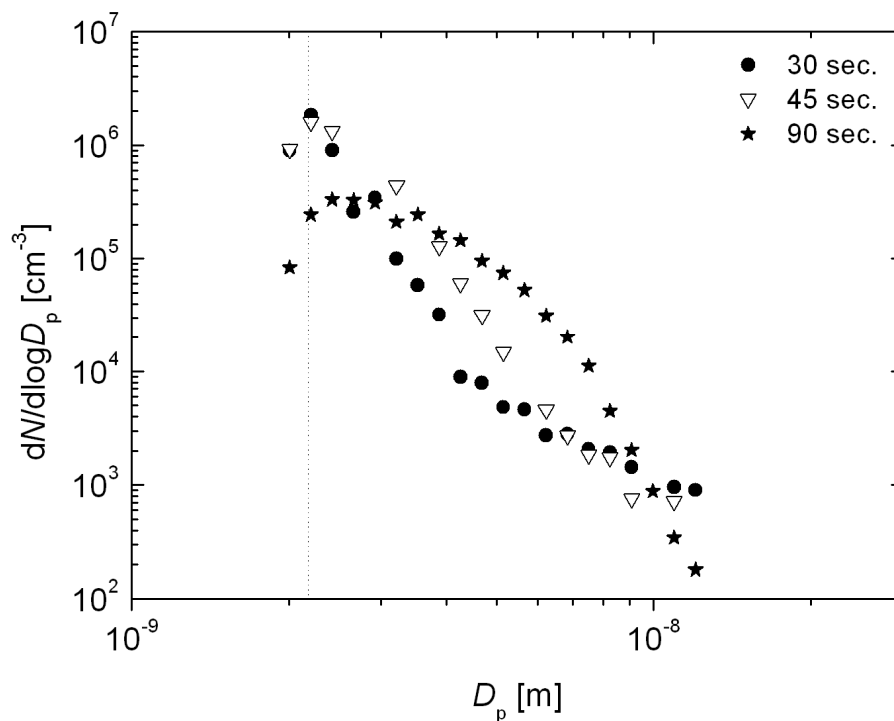
Fig. 7. Particle size distribution (DMPS with a short HAUKE DMA and UCPC TSI 3025A) measured at three resident times 30, 45 and 90 s, mean particle diameters were estimated to 2.2, 2.4 and 2.7 nm respectively. Measurements were done at H_2SO_4 concentration of 9.84×10^9 molecule per cubic centimeter and RH of 50%. Dotted line represents TSI 3025A d_{50} cut-off of 2.18 nm.
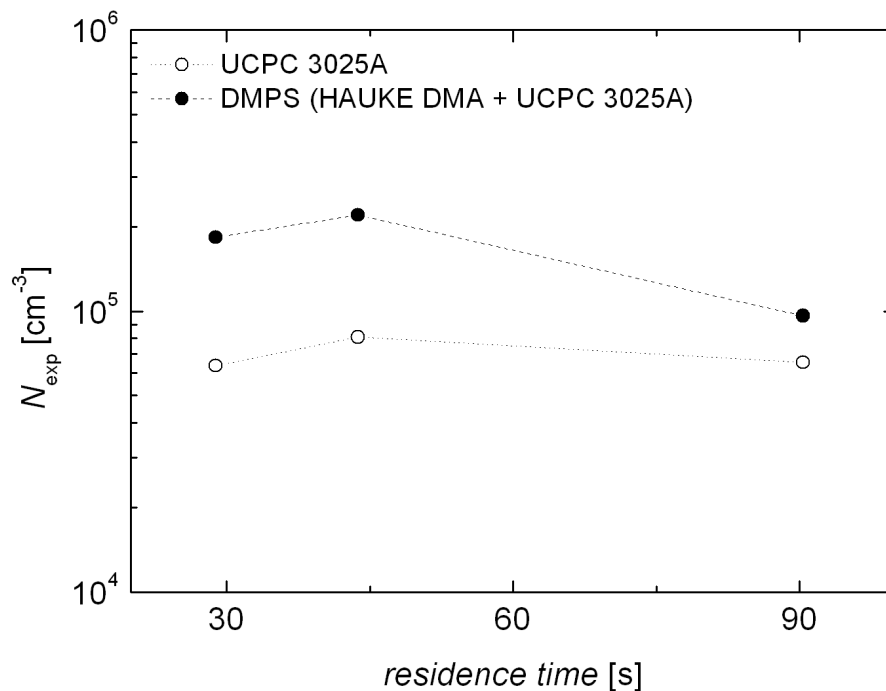
Fig. 8. Integral particle count obtained from inversion of DMPS measurements and total particle count measured with UCPC 3025A as a function of residence time.
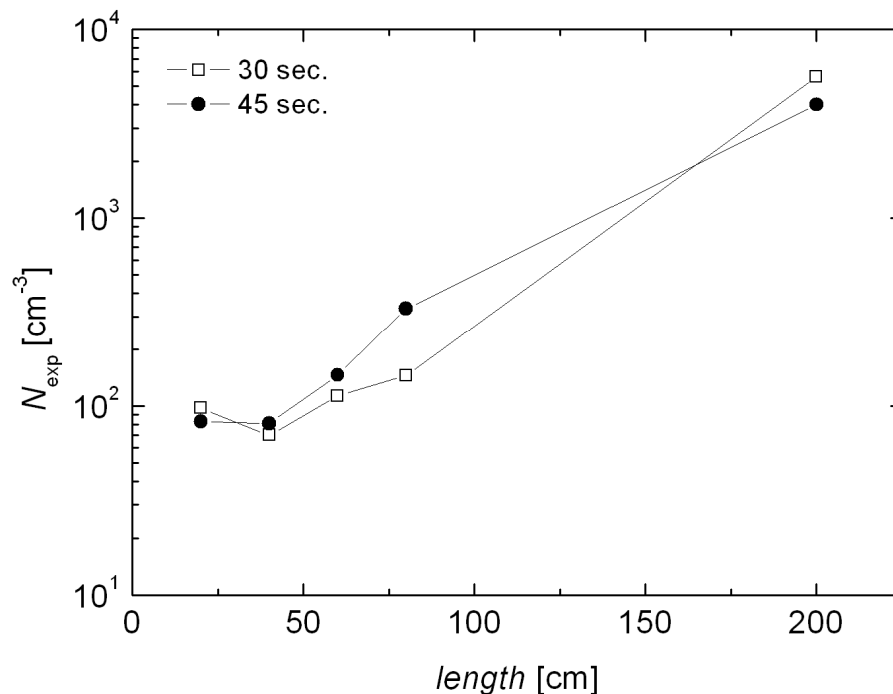
Fig. 9. Nucleation zone measured at the axes of the nucleation chamber, particle concentration measured with PHCPC at RH 30% and total concentration of 5.78×10^9 H_2SO_4 molecules in cm^3. The open symbols are measured at residence time of 30 s and solid symbols at residence time of 45 s.
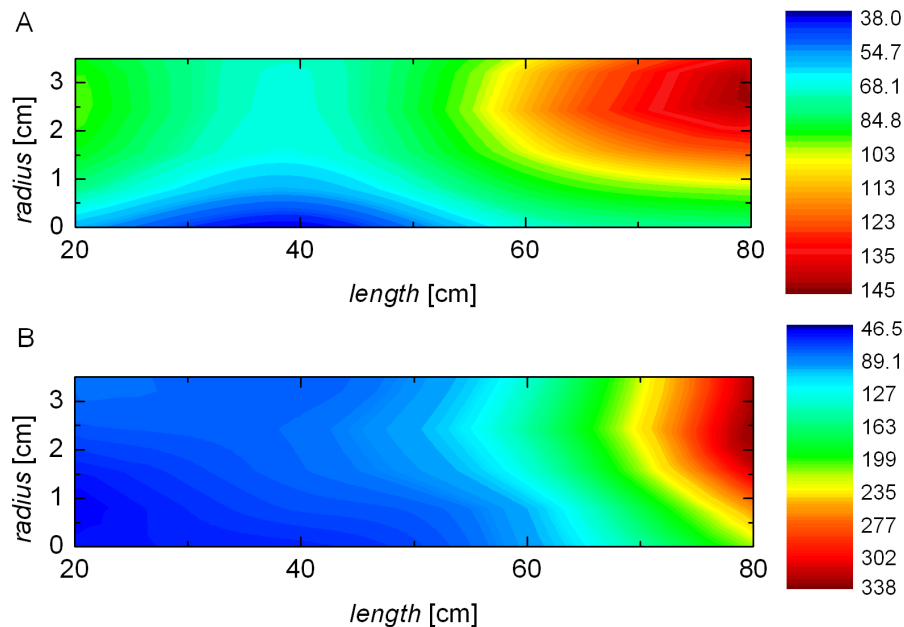
Fig. 10. Nucleation zone measured with PH-CPC at RH 30% and total concentration of 5.78×10^9 H_2SO_4 molecules in cm^3. **(A)** Residence time =30 s and **(B)** residence time =45 s. The radius =0 cm meaning wall, radius =3 cm meaning axis.
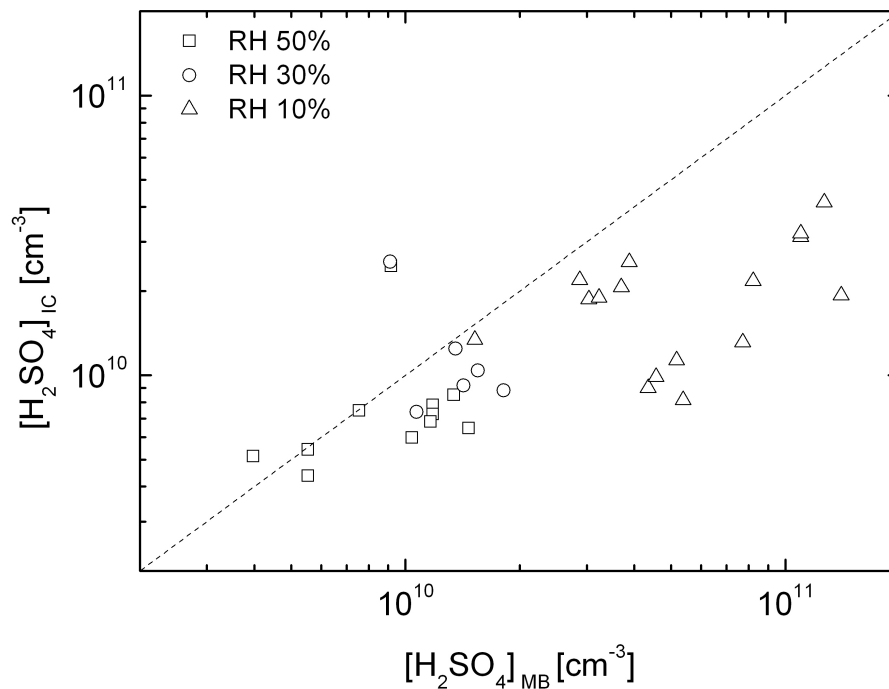
Fig. 11. Concentration of sulfuric acid at three RH's determined by Ion Chromatography as a function of sulfuric acid concentration calculated by Mass Balance, both correspond to the position 2 in Fig. 1, after the first dilution with particle free air and after furnace. The dashed line represents no losses along the furnace.
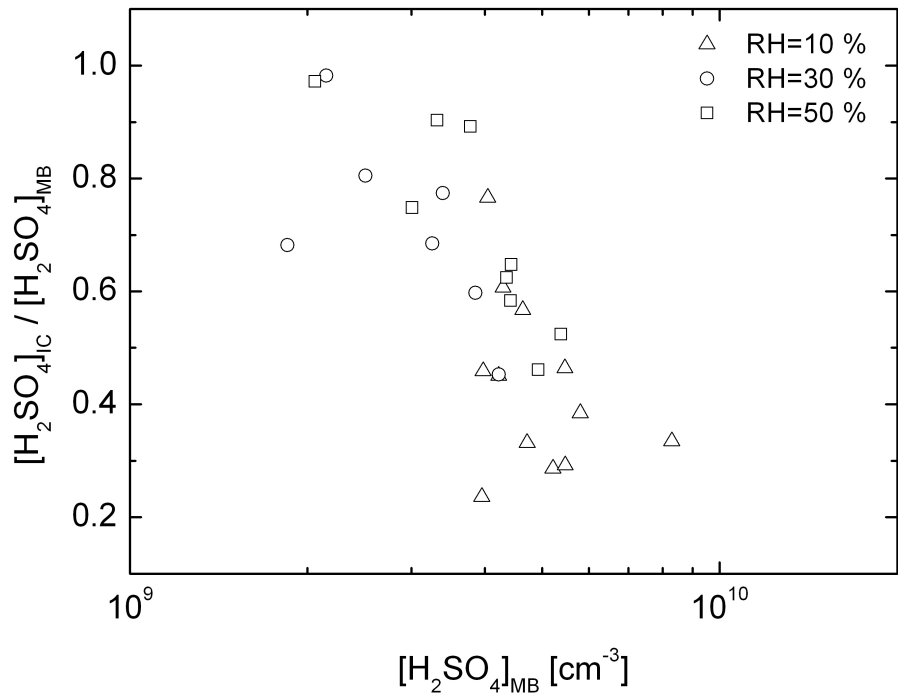
Fig. 12. The ratios of H_2SO_4 concentration determined by Ion Chromatography (IC) and initial H_2SO_4 concentration calculated by Mass Balance (MB) as a function of initial H_2SO_4 concentration calculated by Mass Balance (MB). **(A)** at RH=10% the average wall losses were estimated to be 54%, **(B)** at RH=30% the average wall losses were estimated to be 27%, and **(C)** at RH=50% the average wall losses were estimated to be 28%.

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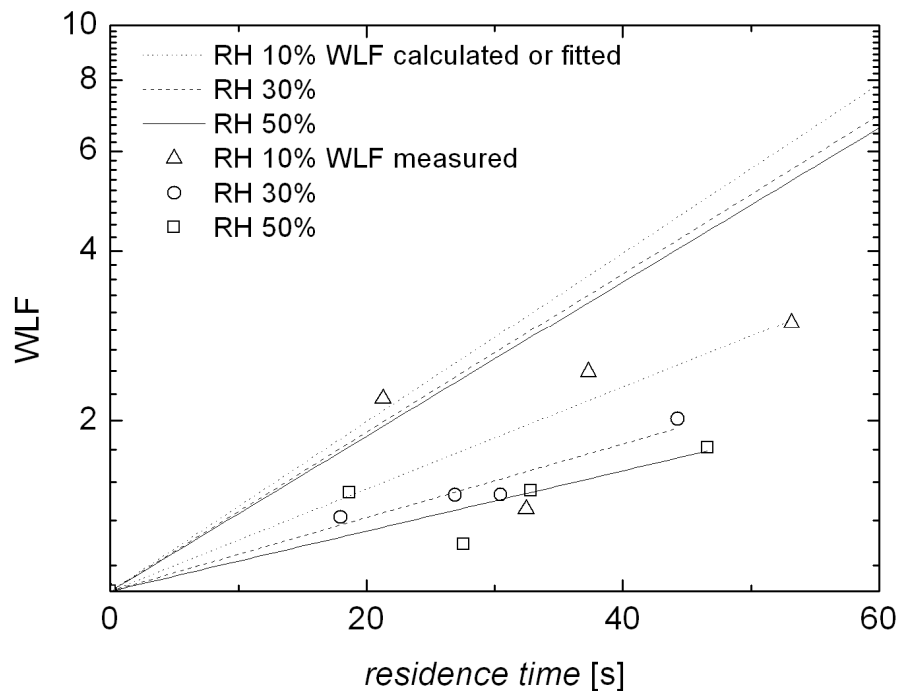
Fig. 13. Wall loss factor as a function of residence time, upper lines are calculated WLFs, points are measured WLFs, lower lines are linear fits to measured values and they correspond to same RH as calculated lines.
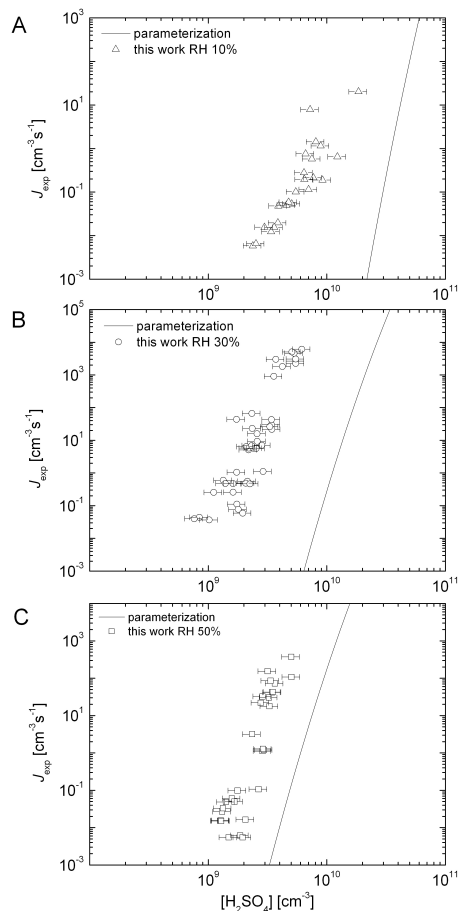
Fig. 14. Nucleation rate as a function of sulfuric acid concentration at three RH's 10, 30 and 50%. The error bars correspond to 17% uncertainty of bubbler experiment and subsequent Ion Chromatography analysis. The solid line is prediction of binary homogeneous nucleation of sulfuric acid and water calculated by using parameterization of Vehkamäki et al. (2003).
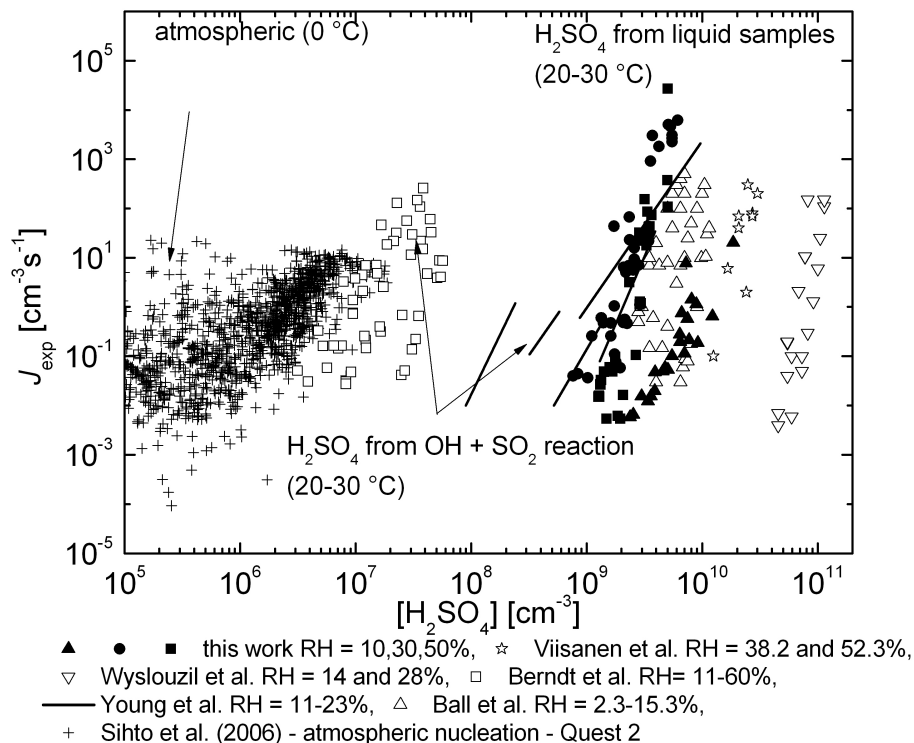
Fig. 15. The comparison of homogeneous nucleation rates as a function of sulfuric acid concentration obtained in this work to data published by others and atmospheric nucleation data obtained in Quest 2 campaign Hyytiälä, Finland.