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Total sulphate vs. sulphuric acid monomer in nucleation studies

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Abstract

Sulphuric acid is known to be a key component for atmospheric nucleation. Precise determination of sulphuric acid concentration is crucial factor for prediction of nucleation rates and subsequent growth. In our study, we have noticed a substantial discrepancy between sulphuric acid monomer and total sulphate concentrations measured from the same source of sulphuric acid vapour. The discrepancy of about one to two orders of magnitude was found with similar formation rates. To investigate this discrepancy and its effect on nucleation, a method of thermally controlled saturator filled with pure sulphuric acid (97 % wt.) for production of sulphuric acid vapour is introduced and tested. Sulphuric acid-water nucleation experiment was done using a laminar flow tube. Two independent methods of mass spectrometry and online ion chromatography were used for detecting sulphuric acid concentrations. The results are compared to our previous results, where a method of furnace was used to produce sulphuric acid vapour (Brus et al., 2010, 2011). Measured sulphuric acid concentrations are compared to theoretical prediction calculated using vapour pressure and a mixing law. The calculated prediction of sulphuric acid concentrations agrees very well with the measured values when total sulphate is considered. Sulphuric acid monomer concentration was found to be about two orders of magnitude lower than the prediction, but with similar temperature dependency as the prediction and the results obtained with ion chromatograph method. Formation rates agree well when compared to our previous results with both sulphuric acid detection and sulphuric acid production methods separately.

1 Introduction

Secondary particle formation by gas to liquid conversion is widely recognized as an important source of aerosol particles in the atmosphere worldwide (Weber et al., 1996; Kulmala et al., 2004; Spracklen et al., 2006). These particles affect the radiative balance of the earth by scattering and absorbing the incoming radiation (Feingold and

Siebert, 2009). Aerosols can seriously reduce visibility and have also potential health effects (Davidson et al., 2005). Model calculations and observations suggest that new particle formation events can contribute a significant amount to Cloud Condensation Nuclei (CCN) which can alter the lifetime and albedo of clouds (Lihavainen et al., 2003, 2009; Merikanto et al., 2009).

Significant effort has been done by field measurements and laboratory studies together with computer simulations to understand the particle formation mechanism itself and the atmospheric conditions involved in the gas to liquid conversion. Despite the effort and numerous results, the underlying mechanism is not yet solved.

It is widely accepted that sulphuric acid plays a key role in atmospheric nucleation (Kulmala et al., 2006; Sipilä et al., 2010; Brus et al., 2011; Kirkby et al., 2011). Binary nucleation of sulphuric acid and water (Vehkamäki et al., 2002; Yu, 2006; Kirkby et al., 2011), ternary nucleation involving also ammonia and/or amines (Ball et al., 1999; Korhonen et al., 1999; Napari et al., 2002; Benson et al., 2009; Berndt et al., 2010; Kirkby et al., 2011; Zollner at al., 2012) and ion-induced nucleation (Lee et al., 2003; Lovejoy et al., 2004; Yu et al., 2008, 2010; Nieminen et al., 2011) have been suggested as possible mechanisms for the nucleation to occur in the atmosphere. Ions have been shown to lower the thermodynamic potential of nucleation (Arnold, 1980; Winkler et al., 2008; Kirkby et al., 2011) but the role of ions in boundary layer nucleation have been shown to be minor (Manninen et al., 2010; Paasonen et al., 2010; Kerminen et al., 2010; Hirsikko et al., 2011).

Recently several laboratory studies have been conducted concerning the role of sulphuric acid in atmospheric nucleation (e.g. Benson et al., 2008, 2011; Young et al., 2008; Berndt et al., 2008, 2010; Brus et al., 2010, 2011; Sipilä et al., 2010; Kirkby et al., 2011; Zollner et al., 2012) with different methods of producing the gas phase sulphuric acid with their own advantages and drawbacks. For example, evaporation method of weak sulphuric acid solution used by Viisanen et al. (1997) and Brus et al. (2010, 2011) introduces a thermal gradient into the beginning of the flow tube. Production of the sulphuric acid with SO_2 + OH reaction is used in most of the experiments since it is similar to that observed in atmosphere (e.g. Benson et al., 2008; Berndt et al., 2008, 2010; Sipilä et al., 2010; Kirkby et al., 2011). SO_2 oxidation method involves usage of UV light to produce OH radicals. The excess OH must be removed so that it would not disturb the nucleation process itself (Berndt et al., 2010). Other way is to have excess of SO_2, so all OH reacts rapidly with SO_2 but for the calculation of produced H_2SO_4 concentration, the exact concentration of OH produced must be known (Benson et al., 2008). Ball et al. (1999) and Zollner et al. (2012) produced sulphuric acid vapour by saturating N_2 flow in a glass saturator containing pure (~ 96 and ~ 98 %, respectively) sulphuric acid. Ball et al. (1999) varied the temperature of the saturator as Zollner et al. (2012) kept the saturator at constant temperature (303 K) and varied the carrier gas flow rate to change the sulphuric acid concentration.

As stated by others in literature (e.g. Benson et al., 2011; Brus et al., 2011; Kirkby et al., 2011) contaminants are most probably present in all the laboratory nucleation studies. These contaminants arise from different sources like water used for humidifying the carrier gas or the carrier gas itself contains some trace levels of contaminants. It is almost impossible to get rid of these contaminants which most probably affect the nucleation process itself.

Here we present a way to produce sulphuric acid vapour from thermally controlled saturator in a wide range of sulphuric acid concentration. The method is described, formation rates, size of the particles and produced sulphuric acid vapour concentrations of H_2SO_4-H_2O nucleation experiment are presented and compared to the results measured with previous setup where furnace was used to produce sulphuric acid vapour (Brus et al., 2010, 2011). The experimental setup, where saturator is used, was tested with two independent analytical methods to measure sulphuric acid concentration based on different principles. Total losses of sulphuric acid within the flow tube were determined and both analytical methods of detecting sulphuric acid compared. The level of ammonia contaminant in the setup was also determined.

Introducing saturator as the source of sulphuric acid vapour reduces disadvantages associated with other methods, like a temperature gradient arising from usage of furnace, or calculations of OH concentration produced with UV light and removal of excess OH associated with the oxidation of SO_2. The major disadvantage using this method is the handling of pure sulphuric acid when filling the saturator. Luckily, the saturation vapour pressure of sulphuric acid is very low and therefore, the sulphuric acid is consumed very slowly. Due to the high hygroscopicity of sulphuric acid, the saturator should not be exposed to humid flow as the pure liquid sulphuric acid would draw water vapour from the flow contaminating the sulphuric acid. This would lead to a significant error in the predicted concentration due to a much higher vapour pressure of water compared to sulphuric acid.

2 Experimental

The measurement setup presented here is partially introduced in Brus et al. (2010) and only the main principle of the method and the most significant changes are described here. The setup for testing the output of the saturator with two independent sulphuric acid detection methods is described. The instrumentation for sulphuric acid and freshly formed particles detection is shortly presented.

2.1 Saturator

The saturator was a horizontally placed cylinder made of iron with Teflon insert inside the cylinder (I.D. 5 cm). It was thermally controlled with a liquid circulating bath (LAUDA RC 6) and the temperature was measured just above the liquid surface with a calibrated PT100 probe (±0.05 K) inserted from the outlet side of the saturator (Fig. 1). The saturator was filled with 150–200 mL pure sulphuric acid (~ 97 % wt., Baker analyzed). H_2SO_4 vapour was produced by flowing purified, dry, particle free carrier gas through the saturator in the range of 0.05 to 1 L min^{-1} (lpm) saturating the flow with vapour according to the temperature of the saturator. The saturator flow was thermally controlled to the same temperature as the saturator before entering it to ensure temperature stability inside the saturator.

The theoretical prediction of sulphuric acid vapour concentration was calculated using equation for vapour pressure from Kulmala and Laaksonen (1990) which uses the measurements by Ayers et al. (1980) and theoretically extrapolates the vapour pressure to lower range of temperatures used in this study:

$$\ln p = \ln p_0 + \frac{\Delta H_\mathrm{v}(T_0)}{R} \times \left[-\frac{1}{T} + \frac{1}{T_0} + \frac{0.38}{T_\mathrm{c} - T_0} \times \left(1 + \ln \frac{T_0}{T} - \frac{T_0}{T} \right) \right] \qquad (1)$$

Where p is the vapour pressure (atm), $p_0 = -(10156/T_0) + 16.259$ atm (Ayers et al., 1980), T_c is critical temperature, 905 K and T_0 is chosen to be 360 K so $\Delta H_\mathrm{v}(T_0)/R = 10156$. See Kulmala and Laaksonen (1990) for more details. Here the predicted sulphuric acid concentration depends only on saturator temperature and flow rate through the saturator and mixing flow. Measured sulphuric acid concentration was compared also to empirical fit by Richardson et al. (1986):

$$\ln p = 20.70 - \frac{9360}{T} \qquad (2)$$

The fit is made to their measurement data in the temperature range of 263.15–303.15 K which fit well in to the temperature range of this study.

2.2 Setup for testing saturator with mass spectrometers and online ion chromatograph

The saturator was tested in two different tests. First with mass spectrometers: Chemical Ionization Mass Spectrometer (CIMS) (Eisele and Tanner, 1993; Mauldin et al., 1998; Petäjä et al., 2009) and Atmospheric Pressure interface Time Of Flight mass spectrometer, (CI-APi-TOF, Tofwerk AG, Thun, Switzerland and Aerodyne Research Inc., USA; Junninen et al., 2010) with similar Chemical Ionization inlet as the CIMS (Jokinen et al., 2012). Second test was done with the instrument for Measuring AeRosols and GAses (MARGA, Metrohm Applikon Analytical BV, Netherlands; ten Brink et al., 2007). Both measurements were performed with the same setup. The setup is presented in Fig. 1. The flow from the saturator (0.5 lpm) was mixed with dilution flow of carrier gas (20 or 40 lpm) after the saturator to meet the inlet flows of the instruments. The relative humidity (RH) was set by 2 or 3 Nafion humidifiers (MD-series, Perma pure, USA) and monitored from the excess flow. The design of the inlet system for mixing the different flows and flow schematics to the instruments can be found in the Supplement (Fig. S2). The temperature of the saturator was increased in 5° steps from approximately 273 to 303 K (MARGA) and 313 K (CIMS and CI-APi-TOF) in order to increase the sulphuric acid concentration. The temperature was kept constant from 2 to 8 h in order to achieve a steady state. The measured sulphuric acid monomer and total sulphate concentrations were compared to theoretical values calculated from the vapour pressure of sulphuric acid using Eqs. (1) and (2).

2.3 Flow tube setup for nucleation measurements

The flow tube setup consists of four main parts: a saturator, a mixing unit, a flow nucleation chamber, sulphuric acid and particle detection (Fig. 2). The sulphuric acid vapour is produced in the saturator and turbulently mixed with clean, particle free carrier gas in the mixing unit. Particles formed before the mixing unit are lost in the 1 m long Teflon tube (I.D. 4 mm) before the mixer by diffusion or by the turbulent mixing in the mixer. After the mixing unit, nucleation and subsequent growth take place in the 2 × 100 cm-long laminar flow chamber. The flow chamber is a stainless steel cylinder (I.D. 6 cm) positioned vertically and it is thermally controlled with a liquid circulating bath (LAUDA RC 6). One of the 100 cm long parts of the chamber has four holes on the sides every 20 cm from the beginning of the chamber with one hole in 5 cm Teflon connector between the 100 cm pieces. These holes are used to continuously measure temperature in the flow tube with PT100 probes to ensure constant desired nucleation temperature. The RH of the mixing flow is controlled by 2 or 3 Nafion humidifiers. RH and temperature are measured also at the end of the tube with Vaisala HMP37E and humidity data processor Vaisala HMI38. Both saturator and mixing flow of the tube are controlled by a mass flow rate controller (MKS type 250) with an accuracy of ±3 %. Flow rates through saturator for nucleation measurements were kept between 0.13 and 0.27 lpm. The mixing flow was kept at approximately 11 lpm. The line from the saturator to the mixing unit was kept at the same temperature as the saturator to prevent condensation of sulphuric acid.

2.4 H_2SO_4 monomer, sulphate and particle detection

Gas phase sulphuric acid monomers were measured with CIMS or CI-APi-TOF. The CI-inlet used in both instruments works as follows: the sulphuric acid molecules are ionized in ambient pressure via proton transfer between nitrate ions (NO_3^-) and sulphuric acid molecule (H_2SO_4). The nitrate ions are produced from nitric acid with radioactive ^{241}Am-source and mixed in a controlled manner in a drift tube utilizing concentric sheath and sample flows together with electrostatic lenses.

After the ionization in the inlet, the instruments differ from each other. In the CIMS sample flow is dried using a nitrogen flow to dehydrate the molecules before entering the vacuum system. In the CI-APi-TOF a flow rate of 0.8 lpm is guided through a critical orifice. The ions are guided through the differentially pumped APi and finally to the TOF for detection according to the ions' m/z ratio.

The monomer concentration is determined by the ratio of the resulting ion signals (HSO_4^- and $HSO_4^- \cdot HNO_3$) and the reagent ion signals (NO_3^-, $HNO_3 \cdot NO_3^-$ and $(HNO_3)_2 \cdot NO_3^-$). This ratio is then multiplied with the instrument dependent calibration factor in both instruments. Calibration factor used here was 5×10^9 for both instruments. CIMS or CI-APi-TOF was not calibrated using the saturator setup, but before the experiments using the standard calibration procedure of oxidation of SO_2 with OH (Kürten et al., 2012). For more information about the calibration of CIMS, see Berresheim et al. (2000), Petäjä et al. (2009), Zheng et al. (2010) and Kürten et al., (2012). The nominal sample flow rate of these instruments is ~ 10 lpm. We considered only the monomer concentration, although detection of dimers and even larger clusters of pure sulphuric acid is possible with CI-APi-TOF. This is due to following reasons: the dimer concentration was always in the magnitude of ∼ 1 % of monomer concentration and larger (trimer and tetramer) cluster concentrations were even lower (e.g. Jokinen et al., 2012). The charging efficiency might not be the same for these clusters as it is for monomer. This would cause the calibration factor to change and the calculated concentration to be erroneous. The uncertainty in the resulting monomer concentration is estimated to be a factor of ∼ 2. The nominal lower detection limit of CIMS and CI-APi-TOF is estimated to be $5 \times 10^4\,\mathrm{cm^{-3}}$, and the upper limit is approximately $10^9\,\mathrm{cm^{-3}}$ for both instruments. At this high concentration the primary ion concentration start to deplete causing the calibration constant to change.

The total sulphate concentration was measured with an online ion chromatograph MARGA 2S ADI 2080. MARGA is able to detect 5 gases from the gas phase (HCl, HNO_3, HONO, NH_3, SO_2) and 8 major inorganic species from aerosol phase (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}). The sample flow is ∼ 16.7 lpm. From the sample flow all (more than 99.7 %) of water soluble gases are absorbed in to a wetted rotating denuder (WRD). Based on different diffusion velocities, aerosols pass WRD and enter Steam-jet-aerosol-collector (SJAC) (Slanina et al., 2001). In the SJAC conditions are supersaturated with water vapour, which condenses on particles and the particles are collected to the bottom of the SJAC. Sample solutions are drawn from the WRD and the SJAC into syringes (25 mL) and are analysed one after another once an hour. Samples are injected in cation and anion chromatographs with an internal standard (LiBr). Components are detected by conductivity measurements. The detection limits are $0.1\,\mathrm{\mu g\,m^{-3}}$ or better. For more information about the instrument, see Makkonen et al. (2012).

In our previous study (Brus et al., 2010) the total sulphate concentration was measured using method of bubblers, where a known flow rate from the flow tube was bubbled through alkaline solution thus trapping sulphate. This solution was then analysed using offline ion chromatography. See Brus et al. (2010) for details. The method of bub-

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bler is analogous to the MARGA and the main difference is that MARGA is an online as bubbler is an offline method.

The total particle number concentration was measured with a Particle Size Magnifier (PSM, Airmodus Oy, Finland; Vanhanen et al., 2011 coupled with CPC TSI model 3772) and with Ultra-Fine CPC's (UFCPC, TSI models 3776, 3025A) with cut-off mobility diameters of ∼ 1.5 and ∼ 3 nm, respectively. Differential Mobility Particle Sizer (DMPS) was used to measure particle number size distribution from 3 to ∼ 250 nm in closed loop arrangement (Jokinen and Mäkelä, 1997) using a blower to measure the wet size of the particles. The DMPS was run with a sheath flow of ∼ 11 lpm and sample flow of 1.5 lpm in the short HAUKE-type Differential Mobility Analyzer (DMA). The DMA was coupled with UCPC (TSI model 3025A) and with a bipolar radioactive (^{63}Ni) neutralizer. The charging efficiencies were calculated following the parameterization of Wiedensohler (1991). The RH of the sheath flow was monitored to ensure that it is same as the RH in the chamber.

3 Results and discussion

To quantify the sulphuric acid input for flow tube nucleation measurements, the saturator output was tested in two experiments, first with CIMS and CI-APi-TOF and latter with MARGA. After the tests, nucleation measurements of sulphuric acid-water system were conducted. This enabled direct comparison to the sulphuric acid production method used in our previous studies (Brus et al., 2010, 2011). Presented values from CIMS, CI-APi-TOF and MARGA measurements are residual, i.e. measured values at the end of the flow tube accounting for dilutions, if not mentioned to be different.

3.1 Test of the saturator

Results of the saturator test are presented in Fig. 3 as measured sulphuric acid concentrations and predicted values by Eqs. (1) and (2) as a function of temperature of the saturator. The mixing flows were 40 (dry and RH 15 %) or 20 lpm (for RH 29 %) for CIMS and APi-TOF and 20 lpm (only dry conditions) for MARGA measurements. Saturator flow rate was 0.5 lpm. Mass spectrometers were tested at dry and humid conditions. Dry experiments were run with two mass spectrometer inlet flow rates (6 and 10 lpm) and with extra 1 m (I.D. 4 mm) Teflon tubing between the saturator and the mixing unit to test the effect of wall losses. Humidified experiments were done with two inlet flow rates (6 lpm for RH 29 % and 10 lpm for RH 15 %). MARGA experiments were conducted at dry conditions.

The total sulphate concentration measured with MARGA (black squares) fit the prediction by Eq. (2) (dashed line) very well and the prediction by Eq. (1) (solid line) underestimates the total sulphate concentration slightly. MARGA has relatively high inlet flow rate (~16.7 lpm) so inlet losses are low, but with increased temperature of the saturator diffusional losses are visible.

Sulphuric acid monomer concentration measured with CIMS and CI-APi-TOF fit each other very well but they show one to two orders of magnitude lower concentrations than predicted by Eqs. (1) and (2) and measured with MARGA. The slope is similar as the predictions and as the points measured with MARGA. The dimer concentrations were always approximately 1 to 10 % of the monomer concentration and trimer approximately 1 % of the dimer concentration (see Supplement, Fig. S5).

Relative humidity does not have any significant effect on the measured values by CIMS and CI-APi-TOF. RH can affect the wall losses by preventing the sulphuric acid to evaporate from the inlet walls as the vapour pressure of water is several orders of magnitude higher than sulphuric acid. The predictions by Eqs. (1) and (2) do not consider relative humidity as the flow through the saturator is always dry. The relative humidity of the mixing flow causes the sulphuric acid molecules to get hydrated as sulphuric acid is very hygroscopic but because the results from humid and dry measurements are very similar, CIMS and CI-APi-TOF can be considered measuring well in humid conditions also. The effect of RH is discussed in Eisele and Tanner (1995) and our results agree with the discussion there.

Change of the nominal inlet flow rate of CIMS and CI-APi-TOF do not have large effect either. The inlet lines were short (~ 20 cm) in the saturator tests so the wall losses due to lower inlet flow rate does not play a big role. Using the instruments with lower flow rate may alter the calibration factor as it is acquired with inlet flow rate of 10 lpm.

Tests with different saturator flow rates (0.05–1 lpm) were conducted to estimate the limits of the saturator flow (not shown in Fig. 3). With 0.05 lpm saturator flow rate diffusional losses to the walls dominated causing the measured sulphuric acid concentrations decrease as a function of the saturator temperature. In the saturator flow rate range from 0.2 up to at least 1 lpm, sulphuric acid concentrations behaved as expected. Results of different flow rate tests, as well as results from tests with carrier gases with different purity, can be found in the Supplement (Sects. 3 and 4).

3.2 Losses of sulphate and sulphuric acid in the flow tube

Total losses were not directly measured but they were determined by comparing results from saturator tests to the results from nucleation measurements. The setup of the measurements was similar in both experiments except for the flow tube that was used in nucleation measurements. By accounting for the different mixing ratios of saturator flow rate and mixing flow rate, these measurements become comparable and the total losses in the flow tube can be determined. Total Loss Factor (TLF) includes wall losses and losses to the particle phase (nucleation and condensational losses).

Figure 4 presents the measured sulphuric acid monomer and total sulphate concentration from the saturator tests (squares) and nucleation measurements (stars) as a function of the saturator temperature. Saturator tests are done in dry conditions and nucleation measurements in RH 30 %. Inlet pipe is used to connect a mass spectrometer to the flow tube. Brus et al. (2011) state that the Wall Loss Factor (WLF) in the inlet pipe of length 100 + 22 cm is $\mathrm{WLF}_{\mathrm{inlet}} = \sim 4$. This factor, together with the mixing ratios, was used to account for the data so that they would be directly comparable.

A linear fit was applied to the data and TLF were determined from the fits. The TLF were determined for a saturator temperature range of 286–300 K for CIMS and 284–297 K for MARGA depending on the measurement range of the data. The average TLF are 14.2 ± 4.2 for CIMS and 10.0 ± 1.2 for MARGA. The R^2 values for the fits are 0.96, 0.87, 0.90 and 0.61 for CIMS saturator test, CIMS nucleation measurement, MARGA saturator test and MARGA nucleation measurement, respectively.

From Fig. 4 it is evident that wall losses are not the only losses affecting the measured concentrations as the trends in the fits for nucleation measurements are less steep than the ones from saturator tests. The losses to the particle phase also affect the situation. The maximum losses of sulphuric acid to particle phase are calculated using the DMPS data measured at the end of the nucleation chamber only. The total volume of the particles is calculated within the size distribution assuming that the particles are composed only of pure sulphuric acid with density of 1.84 g cm^{-3}. The losses of sulphuric acid to particles range from 0 % (dry conditions, $T_{\text{sat}} = 273$ K) up to maximum of 1.4 % (RH = 30 %, $T_{\text{sat}} = 292$ K) of the total sulphate concentration. Higher saturator temperature increases the number and the diameter of the particles and relative humidity increases the diameter of the particles. The losses to the particle phase are significant at highest values of saturator temperature but this estimate is the maximum limit as the particles are not composed only of pure sulphuric acid molecules. Contaminants from the flow condense to the particle phase or get bond with sulphuric acid. Also, when using humid conditions sulphuric acid particles uptake water as sulphuric acid is very hygroscopic. At the highest temperature of the saturator the size distribution unfortunately extends out of the DMPS range (3–250 nm) and particles larger than 250 nm are not accounted for the losses to the particle phase, thus on the other hand underestimating the losses. Losses to the clusters smaller than the cut-off size of the particle counters are probably significant. For more details about the losses to the particle phase see Supplement (Sect. 1).

3.3 Nucleation measurements

Formation rates J of sulphuric acid-water were measured in the range from 0.1 to ~ 300 $\text{cm}^{-3}\,\text{s}^{-1}$ with sulphuric acid monomer concentration approximately from 5×10^5 to $10^7\,\text{cm}^{-3}$ or in total sulphate concentration approximately from 4×10^8 to $3 \times 10^9\,\text{cm}^{-3}$. Formation rates are usually reported as $J_{1.5}$ or J_3 (cut-off sizes of the particle counters are 1.5 nm for PSM and 3 nm for TSI models 3776 and 3025) as discussed in Kulmala et al. (2012). However, particles measured at the end of our flow tube were almost always in the range of 8–20 nm, so we report formation rates as they were determined with our particle counters. The results are discussed below.

Figure 5 presents DMPS and CIMS data for one cycle of saturator temperatures. The upper most panel presents the number size distribution as a function of time, 2nd panel from top the total particle number concentration, 3rd panel from top shows the hourly averaged sulphuric acid monomer concentration with SD as the error bars and the lower most panel shows hourly averaged saturator temperature. One can see from Fig. 5, 1st and 2nd panels from the top that when the temperature of the saturator changes, the number concentration and the number size distribution are not stable immediately. The sulphuric acid concentration overshoots a bit at the beginning as system is stabilizing to steady state. First hour from averages from each of the saturator temperatures were excluded to ensure only stable state data ($\text{SD}(T) = \pm 0.05\,\text{K}$) were included in the averages. When a new cycle started, the T_{sat} dropped from the maximum value (~ 315 K) to the minimum (273 K) causing a long period of unstable data, and first two hours were excluded from the beginning of the cycle. In the upper most panel in Fig. 5, nucleation is the main process below temperature of ~ 290 K and growth takes over at higher temperatures. This can be seen as the bimodal distribution at highest saturator temperatures.

Figures 6 and 7 present the number concentration N_{exp} (upper left panel), geometric mean diameter D_{p} (upper right panel) and formation rate J (lower left panel) of freshly nucleated particles with sulphuric acid monomer concentration [H_2SO_4 monomer] or total sulphate [SO_4^{2-}] (lower right panel) as a function of saturator temperature T_{sat} for nucleation temperature of 298 K with several different relative humidity (Fig. 6) and saturator flow rates (Fig. 7).

From Fig. 6 one can see that in the flow tube measurements with CIMS and CI-APi-TOF all the variables behave as expected to the increasing saturator temperature. Increasing saturator temperature increases number concentration and diameter of freshly nucleated particles. The number concentration and formation rate seems to saturate at the highest temperatures but this apparent saturation is due to the limits of the PSM (coupled with CPC, TSI model 3772). The upper limit of particle concentration for CPC 3772 is 10^4 cm^{-3}, so higher concentrations were still measured as 10^4 cm^{-3}. This is also supported by DMPS data which shows higher total particle concentration than PSM. Coagulation has a minor effect on the particle number due to a short residence time ($\tau = 30$ s) and relatively low particle concentration. The relative humidity affects mostly the diameter of the particles but also decreasing RH decreases the formation rate if similar sulphuric acid concentration is considered. Lower formation rate with decreased RH might be caused by the diminishing of the particle diameter below the detection limit of UCPC (TSI model 3776).

In Fig. 7, squares present measurements at dry conditions and stars with RH 30 %. The lower right panel shows also the detection limit of MARGA for total sulphate concentration. Detection limit was determined from 20 h of measurements with saturator flow rate set to zero and averaged over the time period. Detection limit was 1.35×10^9 cm^{-3}. All the total sulphate concentrations measured below this detection limit were considered as erroneous and rejected from further analysis, even though these values are presented in Fig. 7. MARGA can be used with concentration columns to measure lower concentrations of species but it was not available in this study.

From Fig. 7 one can see that all the variables responded in a similar manner as CIMS and CI-APi-TOF experiment (Fig. 6). As the temperature of the saturator approaches to the temperature of the mixing unit (laboratory temperature, ~ 294 K) the number concentration of particles drops and starts to increase again when saturator temperature is higher than the mixing unit. This is an artefact of the setup.

Main difference between Figs. 6 and 7 can be found in the mean diameter of the particles. In the experiment with CIMS and CI-APi-TOF, the diameter ranges all the way up to ~ 130 nm (Fig. 6, right upper panel) as in the experiment with MARGA, maximum diameter is only approximately ~ 23 nm (Fig. 7 right upper panel). The main reason is that in the CIMS and CI-APi-TOF experiment the saturator temperature was increased 15 K higher than in the MARGA experiment. This increases sulphuric acid vapour concentration approximately order of magnitude which condenses on the surface of the particles growing their diameter. At lower saturator temperatures (< 290 K) the mean diameters are closer to each other at similar saturator temperatures and relative humidity. The residence times in the flow tube are same in both experiments (~ 30 s).

3.4 Formation rates and comparison to our previous results

Figure 8 presents formation rates J of H_2SO_4-H_2O system as a function of sulphuric acid monomer concentration measured with CIMS at nucleation temperature of $T = 298$ K and relative humidity of RH ~ 30 %. Sulphuric acid was produced with method of furnace (red squares, Brus et al., 2011) and with saturator (the black squares, this study). Sulphuric acid concentration for data from Brus et al. (2011) is presented here as residual concentration (i.e. at the end of the flow tube) so that these two measurements would be comparable. Brus et al. (2011) present their data as the initial concentration. Both data sets have almost identical slopes (1.3 and 1.2) and the data sets have a difference of a factor of 2. For the data set measured with production method of furnace, the residence time ($\tau = 15$ s) is defined as the time the particles spend in the flow tube after the nucleation zone. Nucleation zone was experimentally determined (Brus et al., 2010) and confirmed with CFD model (Herrmann et al., 2010) to be at the middle of the flow tube in the measurements with the furnace, where a thermal gradient was present. For the saturator measurements (this work), the residence time ($\tau = 30$ s) was defined as the whole time the particles spend in the flow tube. The difference of the residence time is exactly factor of 2. Formation rate is defined as the number concentration divided by the residence time, so these two sets of data lie on top of each other if the same residence time would have been used for formation rate determination.

Figure 9 presents formation rates J of H_2SO_4-H_2O as a function of residual total sulphate concentration $[SO_4^{2-}]$ at relative humidity of RH ~ 30 % and at nucleation temperature of $T = 298$ K. Stars presents the data from measurements where sulphuric acid vapour was produced with furnace and total sulphate measured with bubbler method (Brus et al., 2010). The residence time used in there was $\tau = 15$ s. Squares presents total sulphate measured with MARGA in this study with different flow rates through the saturator, and the residence time was $\tau = 30$ s. All the points have SD as error bars. The detection limit of MARGA is also marked as a dashed vertical line. Formation rates are similar with both production methods. As in previously, the factor of two difference in the residence time increases the scattering between the two data sets.

Figures 8 and 9 show that formation rate data is reproducible with both sulphuric acid production methods. The data is more scattered in Fig. 9 due to the larger integration times used in MARGA and bubbler measurements. During several hours of integration time, a small change in flow rates can cause a significant difference in the resulting concentration. MARGA data is close to the detection limit of the instrument which also causes larger scattering.

Figure 10 shows comparison of formation rates J as a function of residual sulphuric acid monomer $[H_2SO_4$ monomer$]$ or total sulphate concentration $[SO_4^{2-}]$ from this study to our previous studies with SD as error bars. Note the factor of two difference between the residence times. Squares show values measured using mass spectrometers (PSM, red and black squares; TSI 3776, green squares). Stars presents data measured using ion chromatograph (i.e. total sulphate) methods with two different UCPC's (TSI 3025A, black stars and TSI 3776, red stars). Figure 10 shows that the production method does not have significant effect as the results lie on same line when comparing results obtained with mass spectrometers or MARGA and bubbler method. The conditions for all the measurements were similar ($T = 298$ K, RH ~ 30 %).

The slope of the data measured using MARGA or bubblers is steeper than the slope of the results measured with mass spectrometers. There is a discrepancy of one to two orders of magnitude between sulphuric acid monomer and total sulphate concentration for similar formation rates. The CPC 3776 (green squares) was probably undercounting at the lowest sulphuric acid concentrations. This can be seen in Fig. 10 as the green squares are not on line with the other squares. This is probably caused by the small size of the particles at so low sulphuric acid concentration ($1\text{–}2 \times 10^6\,\mathrm{cm}^{-3}$) (Sipilä et al., 2010).

3.5 Contaminants

In our previous study (Brus et al., 2011) an ion chromatograph was used to determine the background levels of ammonia and it was found that the background concentration was below the detection limit of the IC (500 pptv), accounting for the flow rates in the nucleation chamber. The concentration of background ammonia was measured with the MARGA system in this study. An average concentration of ammonia was 60 pptv for dry conditions and 126 pptv for RH 30 % supporting our previous results. The concentration did not change as a function of saturator temperature and thus, it is assumed to originate from the purified, particle free air used as carrier gas in all measurements and the ultrapure water (Milli-Q, Millipore) used for humidification. The concentration for dry conditions is in the same order of magnitude as the concentration of total sulphate at the lowest (273 K) temperature of the saturator. With increasing the saturator temperature, ammonia to total sulphate-ratio decreases from ~ 1 : 1 to ~ 1 : 10 or less for dry conditions and from ~ 3 : 1 to ~ 1 : 5 for humid conditions. Results of extensive measurements and discussion of the influence of several different carrier gases on measured sulphuric acid concentration by mass spectrometers can be found in the Supplement (Sect. 3).

4 Conclusions

A method of saturator to produce sulphuric acid vapour from neat liquid sulphuric acid for laboratory studies is presented. The sulphuric acid concentration was measured with two independent methods and it was shown to produce exact concentrations as prediction from Richardson et al. (1986) and slightly higher than prediction from Kulmala and Laaksonen (1990) when measured with MARGA (Fig. 3). Concentration of sulphuric acid monomer measured with CIMS and CI-APi-TOF was one to two orders of magnitude lower than the total sulphate values measured with MARGA and the prediction by Eqs. (1) and (2). The only source of sulphuric acid (sulphate measured by MARGA) is the liquid sulphuric acid inside the saturator as seen in Fig. 3. Possible reason for the discrepancy is that the sulphuric acid is in particle phase as the saturator is a significant source of particles. However, these particles are lost in the way from the saturator to the nucleation chamber due to two main reasons; the flow rate in the tube (length: 1 m, I.D. 4 mm) from the saturator to the nucleation chamber is relatively low (0.5 lpm) increasing diffusional losses and the highly turbulent mixing of the saturator flow with the mixing flow ($Q_{\mathrm{sat}} : Q_{\mathrm{mix}} \approx 1:30$ or more) in the mixer which is an effective trap for the particles. The loss of the particles is confirmed with DMPS measurements which cannot explain the discrepancy (Supplement, Fig. S1). Maximum losses to the particle phase range from 0 up to 1.4 % with an average below 1 % of the total sulphuric acid. The discrepancy cannot be explained by the formation of larger clusters containing solely sulphuric acid (dimer, trimer, etc.) either, because the concentration of these clusters are in the order of few percents or lower than the monomer concentration (Supplement, Fig. S5).

The saturator has been used in combination with a flow tube described earlier (Brus et al., 2010) to measure characteristics of H_2SO_4-H_2O nucleation. It takes about 1 h to stabilize the sulphuric acid vapour concentration after changing the saturator temperature. The characteristics of the freshly nucleated particles together with the conditions used for the nucleation has been identified and presented (Figs. 4–7). Total losses of sulphuric acid to the whole flow tube setup have been determined for both methods to detect the concentration of sulphuric acid.

The average Total Loss Factors determined are TLF = 10.0 ± 1.2 (T_{sat} = 284–297 K) for MARGA and TLF = 14.2 ± 4.2 (T_{sat} = 286–300 K) for CIMS both having a slight increasing deviation from the first order losses as a function of saturator temperature (Fig. 4). The second order losses are caused by losses to the particles (minor) and losses to the clusters (major) which are too small to be detected by particle counters.

Formation rates of sulphuric acid-water system were compared to our previous studies (Brus et al., 2010, 2011), where a method of furnace was used (Figs. 8–10). Results obtained using mass spectrometers lie on the same line independent of the sulphuric acid vapour production method (furnace vs. saturator). At a lower sulphuric acid monomer concentration ($1–2 \times 10^6$ cm^{-3}) the UCPC used (TSI model 3776) was probably undercounting compared to more efficient counter (PSM), which is caused by the small size of the particles. The slopes of the fits to the formation rate data as a function of sulphuric acid monomer concentration are very similar (1.3 and 1.2 for using furnace and saturator, respectively) as obtained in Brus et al. (2011). The discussion and interpretation of the slopes (Sect. 3.1) and comparison to the atmospheric data (Sect. 3.5) can be found in Brus et al. (2011). Nucleation results obtained using bubblers or MARGA agree well when compared to each other. Conditions for these studies were similar (T = 298 K, RH ~ 30 %) but at similar formation rates, the sulphuric acid monomer concentration is one to two orders of magnitude lower than the total sulphate.

Other possible reasons for this difference between sulphuric acid monomer and total sulphate is that sulphuric acid molecules are most probably bond to some molecule(s) (e.g. amines, ammonia, organics) and not been detected by CIMS or identified from the CI-APi-TOF spectra (Kulmala et al., 2013). As Kurten et al. (2011) state, base molecules can be only in minor importance due to the fact that nitrate ion (NO_3^-) will most probably substitute the base out in the CIMS charging process. Nevertheless, there is expected to be a substantial pool of clusters formed of sulphuric acid-base molecules in our system, which are too small to be detected by current state-of-art particle counters such as PSM. These clusters are the main reason for the discrepancy between measured total sulphate and the monomer concentrations. Same or similar clusters are most probably forming in all laboratory nucleation experiments involving sulphuric acid, as there are always contaminants present in the carrier gases (see Supplement, Sect. 6 and Figs. S6–S11). Average ammonia concentration of 60 pptv was found in the system for dry conditions and 126 pptv for RH 30 % as a contaminant and it was independent of the saturator temperature. It is assumed to originate from the purified, dry, particle free air used as carrier gas and from the ultrapure water used for humidifying the mixing flow. Ammonia concentration is enough to affect the nucleation process itself significantly but the magnitude of this effect was not studied in this work. Ammonia can bind sulphuric acid by forming clusters which might reduce the monomer concentration measured with CIMS and CI-APi-TOF slightly but as the contaminant level was constant and saturator temperature was increased, reducing the contaminant to total sulphate-ratio from $\sim 1:1$ to $\sim 1:10$ for dry conditions and from $\sim 3:1$ to $\sim 1:5$ for humid conditions, it does not explain the discrepancy between the two sulphuric acid detection methods.

The total sulphate (originally total sulphuric acid) is responsible for the particle growth as demonstrated in Skrabalova et al. (2014). The contribution of the total sulphate to the nucleation process itself is not yet fully understood. However, recent results suggest that sulphuric acid monomer is the main component in nucleation (Brus et al., 2014) and not the overall sulphuric acid. The clusters where the sulphuric acid is bond must be identified from the CI-APi-TOF spectra to understand the possible other molecules involved in the nucleation process.

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References

Arnold., F.: Ion-induced nucleation of atmospheric water vapor at the mesopause, Planet. Space Sci., 28, 1003–1009, doi:10.1016/0032-0633(80)90061-6, 1980.

Ayers, G. P., Gillett, R. W., and Gras, J. L.: On the vapor pressure of sulphuric acid, Geophys. Res. Lett., 7, 433–436, 1980.

Ball, S. M., Hanson, D. R., and Eisele, F. L.: Laboratory studies of particle nucleation: initial results for H_2SO_4, H_2O, and NH_3 vapors, J. Geophys. Res., 104, 23709–23718, doi:10.1029/1999JD900411, 1999.

Benson, D., Young, L.-H., Kameel, F., 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.

Benson, D. R., Erupe, M. E., and Lee, S.-H.: Laboratory-measured H_2SO_4-H_2O-NH_3 ternary homogeneous nucleation rates: initial observations, Geophys. Res. Lett., 36, L15818, doi:10.1029/2009GL038728, 2009.

Benson, D. R., Yu, J. H., Markovich, A., and Lee, S.-H.: Ternary homogeneous nucleation of H_2SO_4, NH_3, and H_2O under conditions relevant to the lower troposphere, Atmos. Chem. Phys., 11, 4755–4766, doi:10.5194/acp-11-4755-2011, 2011.

Berndt, T., Stratmann, F., Bräsel, S., Heintzenberg, J., Laaksonen, A., and Kulmala, M.: SO_2 oxidation products other than H_2SO_4 as a trigger of new particle formation. Part 1: Laboratory investigations, Atmos. Chem. Phys., 8, 6365–6374, doi:10.5194/acp-8-6365-2008, 2008.

Berndt, T., Stratmann, F., Sipilä, M., Vanhanen, J., Petäjä, T., Mikkilä, J., Grüner, A., Spindler, G., Lee Mauldin III, R., Curtius, J., Kulmala, M., and Heintzenberg, J.: Laboratory study on new particle formation from the reaction OH + SO_2: influence of experimental conditions, H_2O vapour, NH_3 and the amine tert-butylamine on the overall process, Atmos. Chem. Phys., 10, 7101–7116, doi:10.5194/acp-10-7101-2010, 2010.

Berresheim, H., Elste, T., Plass-Dülmer, C., Eisele, F. L., and Tanner, D. J.: Chemical ionization mass spectrometer for long-term measurements of atmospheric OH and H_2SO_4, Int. J. Mass Spectrom., 202, 91–109, 2000.

Brus, D., Hyvärinen, A.-P., Viisanen, Y., Kulmala, M., and Lihavainen, H.: Homogeneous nucleation of sulfuric acid and water mixture: experimental setup and first results, Atmos. Chem. Phys., 10, 2631–2641, doi:10.5194/acp-10-2631-2010, 2010.

Brus, D., Neitola, K., Hyvärinen, A.-P., Petäjä, T., Vanhanen, J., Sipilä, M., Paasonen, P., Kulmala, M., and Lihavainen, H.: Homogenous nucleation of sulfuric acid and water at close to atmospherically relevant conditions, Atmos. Chem. Phys., 11, 5277–5287, doi:10.5194/acp-11-5277-2011, 2011.

Brus, D., Hyvärinen, A.-P., Anttila, T., Neitola, K., Koskinen, J., Makkonen, U., Hellén, H., Hemmilä, M., Sipilä, M., Mauldin III, R. L., Jokinen, T., Petäjä, T., Kurtén, T., Vehkamäki, H., Kulmala, M., Viisanen, Y., Lihavainen, H., and Laaksonen, A.: Reconsidering the sulphuric acid saturation vapour pressure: classical Nucleation Theory revived, Phys. Rev. Lett., in review, 2014.

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

Eisele, F. and Tanner, D.: Measurement of the gas phase concentration of H_2SO_4 and methane sulfonic acid and estimates of H_2SO_4 production and loss in the atmosphere, J. Geophys. Res., 98, 9001–9010, doi:10.1029/93JD00031, 1993.

Feingold, G. and Siebert, H.: Cloud-aerosol interactions from the micro to the cloud scale, Chapt. 14, in: Clouds in the Perturbed Climate System, edited by: Heintzenberg, J. and Charlson, R. J., The MIT Press, Cambridge, 576 pp., 2009.

Herrmann, E., Brus, D., Hyvärinen, A.-P., Stratmann, F., Wilck, M., Lihavainen, H., and Kulmala, M.: A computational fluid dynamics approach to nucleation in the water-sulfuric acid system, J. Phys. Chem. A, 114, 8033–8042, 2010.

Hirsikko, A., Nieminen, T., Gagné, S., Lehtipalo, K., Manninen, H. E., Ehn, M., Hõrrak, U., Kerminen, V.-M., Laakso, L., McMurry, P. H., Mirme, A., Mirme, S., Petäjä, T., Tammet, H., Vakkari, V., Vana, M., and Kulmala, M.: Atmospheric ions and nucleation: a review of observations, Atmos. Chem. Phys., 11, 767–798, doi:10.5194/acp-11-767-2011, 2011.

Jokinen, T., Sipilä, M., Junninen, H., Ehn, M., Lönn, G., Hakala, J., Petäjä, T., Mauldin III, R. L., Kulmala, M., and Worsnop, D. R.: Atmospheric sulphuric acid and neutral cluster measurements using CI-APi-TOF, Atmos. Chem. Phys., 12, 4117–4125, doi:10.5194/acp-12-4117-2012, 2012.

Jokinen, V. and Mäkelä, J. M.: Closed-loop arrangement with critical orifice for DMA sheath/excess flow system, J. Aerosol Sci., 28, 643–648, 1997.

Junninen, H., Ehn, M., Petäjä, T., Luosujärvi, L., Kotiaho, T., Kostiainen, R., Rohner, U., Gonin, M., Fuhrer, K., Kulmala, M., and Worsnop, D. R.: A high-resolution mass spectrometer to measure atmospheric ion composition, Atmos. Meas. Tech., 3, 1039–1053, doi:10.5194/amt-3-1039-2010, 2010.

Kerminen, V.-M., Petäjä, T., Manninen, H. E., Paasonen, P., Nieminen, T., Sipilä, M., Junninen, H., Ehn, M., Gagné, S., Laakso, L., Riipinen, I., Vehkamäki, H., Kurten, T., Ortega, I. K., Dal Maso, M., Brus, D., Hyvärinen, A., Lihavainen, H., Leppä, J., Lehtinen, K. E. J., Mirme, A., Mirme, S., Hõrrak, U., Berndt, T., Stratmann, F., Birmili, W., Wiedensohler, A., Metzger, A., Dommen, J., Baltensperger, U., Kiendler-Scharr, A., Mentel, T. F., Wildt, J., Winkler, P. M., Wagner, P. E., Petzold, A., Minikin, A., Plass-Dülmer, C., Pöschl, U., Laaksonen, A., and Kulmala, M.: Atmospheric nucleation: highlights of the EUCAARI project and future directions, Atmos. Chem. Phys., 10, 10829–10848, doi:10.5194/acp-10-10829-2010, 2010.

Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagné, S., Ickes, L., Kürten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S., Tsagkogeorgas, G., Wimmer, D., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Downard, A., Ehn, M., Flagan, R., Haider, S., Hansel, A., Hauser, D., Jud, W., Junninen, H., Kreissl, F., Kvashin, A., Laaksonen, A., Lehtipalo, K., Lima, J., Lovejoy, E., Makhmutov, V., Mathot, S., Mikkilä, J., Minginette, P., Mogo, S., Nieminen, T., Onnela, A., Pereira, P., Petäjä, T., Schnitzhofer, R., Seinfeld, J., Sipilä, M., Stozhkov, Y., Stratmann, F., Tomé, A., Vanhanen, J., Viisanen, Y., Aron Vrtala, A., Wagner, P., Walther, H., Weingartner, E., Wex, H., Winkler, P., Carslaw, K., Worsnop, D., Baltensperger, U., and Kulmala, M.: Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation, Nature, 476, 429–433, doi:10.1038/nature10343, 2011.

Korhonen, P., Kulmala, M., Laaksonen, A., Viisanen, Y., McGraw, R., and Seinfeld, J. H.: Ternary nucleation of H_2SO_4, NH_3 and H_2O in the atmosphere, J. Geophys. Res., 104, 26349–26353, doi:10.1029/1999JD900784, 1999.

Kulmala, M. and Laaksonen, A.: Binary nucleation of water-sulfuric acid system: comparison of classical theories with different H_2SO_4 saturation vapor pressures, J. Chem. Phys., 93, 696, doi:10.1063/1.459519, 1990.

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, doi:10.1016/j.jaerosci.2003.10.003, 2004.

Kulmala, M., Lehtinen, K. E. J., and Laaksonen, A.: Cluster activation theory as an explanation of the linear dependence between formation rate of 3 nm particles and sulphuric acid concentration, Atmos. Chem. Phys., 6, 787–793, doi:10.5194/acp-6-787-2006, 2006.

Kulmala, M., Petäjä, T., Nieminen, T., Sipilä, M., Manninen, H. E., Lehtipalo, K., Dal Maso, M., Aalto, P. P., Junninen, H., Paasonen, P., Riipinen, I., Lehtinen, K. E. J., Laaksonen, A., and Kerminen, V.-M.: Measurement of the nucleation of atmospheric aerosol particles, Nat. Protoc., 7, 1651–1667, doi:10.1038/nprot.2012.091, 2012.

Kulmala, M., Kontkanen, J., Junninen, H., Lehtipalo, K., Manninen, H. E., Nieminen, T., Petäjä, T., Sipilä, M., Schobesberger, S., Rantala, P., Franchin, A., Jokinen, T., Järvinen, E., Äijälä, M., Kangasluoma, J., Hakala, J., Aalto, P. P., Paasonen, P., Mikkilä, J., Vanhanen, J., Aalto, J., Hakola, H., Makkonen, U., Ruuskanen, T., Mauldin III, R. L., Duplissy, J., Vehkamäki, H., Bäck, J., Kortelainen, A., Riipinen, I., Kurten, T., Johnston, M. V., Smith, J. N., Ehn, M., Mentel, T. F., Lehtinen, K. E. J., Laaksonen, A., Kerminen, V.-M., and Worsnop, D. R.: Direct observations of atmospheric aerosol nucleation, Science, 339, 943–946, 2013.

Kürten, A., Rondo, L., Ehrhart, S., and Curtius, J.: Calibration of a chemical ionization mass spectrometer for the measurement of gaseous sulfuric acid, J. Phys. Chem. A, 116, 6375–6386, 2012.

Lee, S.-H., Reeves, J. M., Wilson, J. C., Hunton, D. E., Viggiano, A. A., Miller, T. M., Ballenthin, J. O., and Lait, L. R.: Particle formation by ion nucleation in the upper troposphere and lower stratosphere, Science, 301, 1886–1889, doi:10.1126/science.1087236, 2003.

Lovejoy, E. R., Curtius, J., and Froyd, K. D.: Atmospheric ion-induced nucleation of sulphuric acid and water, J. Geophys. Res., 109, D08204, doi:10.1029/2003JD004460, 2004.

Lihavainen, H., Kerminen, V.-M., Komppula, M., Hatakka, J., Aaltonen, V., Kulmala, M., and Viisanen, Y.: Production of "potential" cloud condensation nuclei associated with atmospheric new-particle formation in northern Finland, J. Geophys. Res., 108, 4782, doi:10.1029/2003JD003887, 2003.

Makkonen, U., Virkkula, A., Mäntykenttä, J., Hakola, H., Keronen, P., Vakkari, V., and Aalto, P. P.: Semi-continuous gas and inorganic aerosol measurements at a Finnish urban site: comparisons with filters, nitrogen in aerosol and gas phases, and aerosol acidity, Atmos. Chem. Phys., 12, 5617–5631, doi:10.5194/acp-12-5617-2012, 2012.

Manninen, H. E., Nieminen, T., Asmi, E., Gagné, S., Häkkinen, S., Lehtipalo, K., Aalto, P., Vana, M., Mirme, A., Mirme, S., Hõrrak, U., Plass-Dülmer, C., Stange, G., Kiss, G., Hoffer, A., Törő, N., Moerman, M., Henzing, B., de Leeuw, G., Brinkenberg, M., Kouvarakis, G. N., Bougiatioti, A., Mihalopoulos, N., O'Dowd, C., Ceburnis, D., Arneth, A., Svenningsson, B., Swietlicki, E., Tarozzi, L., Decesari, S., Facchini, M. C., Birmili, W., Sonntag, A., Wiedensohler, A., Boulon, J., Sellegri, K., Laj, P., Gysel, M., Bukowiecki, N., Weingartner, E., Wehrle, G., Laaksonen, A., Hamed, A., Joutsensaari, J., Petäjä, T., Kerminen, V.-M., and Kulmala, M.: EUCAARI ion spectrometer measurements at 12 European sites – analysis of new particle formation events, Atmos. Chem. Phys., 10, 7907–7927, doi:10.5194/acp-10-7907-2010, 2010.

Mauldin III, R. L., Frost, G., Chen, G., Tanner, D., Prevot, A., Davis, D., and Eisele, F.: OH measurements during the First Aerosol Characterization Experiment (ACE 1): observations and model comparisons, J. Geophys. Res., 103, 16713–16729, doi:10.1029/98JD00882, 1998.

Merikanto, J., Spracklen, D. V., Mann, G. W., Pickering, S. J., and Carslaw, K. S.: Impact of nucleation on global CCN, Atmos. Chem. Phys., 9, 8601–8616, doi:10.5194/acp-9-8601-2009, 2009.

Napari, I., Noppel, M., Vehkamäki, H., and Kulmala, M.: Parametrization of ternary nucleation rates for H_2SO_4-NH_3-H_2O vapors, J. Geophys. Res., 107, 4381, doi:10.1029/2002JD002132, 2002.

Nieminen, T., Paasonen, P., Manninen, H. E., Sellegri, K., Kerminen, V.-M., and Kulmala, M.: Parameterization of ion-induced nucleation rates based on ambient observations, Atmos. Chem. Phys., 11, 3393–3402, doi:10.5194/acp-11-3393-2011, 2011.

Paasonen, P., Nieminen, T., Asmi, E., Manninen, H. E., Petäjä, T., Plass-Dülmer, C., Flentje, H., Birmili, W., Wiedensohler, A., Hõrrak, U., Metzger, A., Hamed, A., Laaksonen, A., Facchini, M. C., Kerminen, V.-M., and Kulmala, M.: On the roles of sulphuric acid and low-volatility organic vapours in the initial steps of atmospheric new particle formation, Atmos. Chem. Phys., 10, 11223–11242, doi:10.5194/acp-10-11223-2010, 2010.

Petäjä, T., Mauldin, III, R. L., Kosciuch, E., McGrath, J., Nieminen, T., Paasonen, P., Boy, M., Adamov, A., Kotiaho, T., and Kulmala, M.: Sulfuric acid and OH concentrations in a boreal forest site, Atmos. Chem. Phys., 9, 7435–7448, doi:10.5194/acp-9-7435-2009, 2009.

Richardson, C. B., Hightower, R. L., and Pigg, A. L.: Optical measurements of evaporation of sulphuric acid droplets, Appl. Optics, 25, 1226–1229, 1986.

Sipilä, M., Berndt, T., Petäjä, T., Brus, D., Vanhanen, J., Stratmann, F., Patokoski, J., Mauldin III, Roy, L., Hyvärinen, A.-P., Lihavainen, H., and Kulmala, M.: The role of sulphuric acid in atmospheric nucleation, Science, 327, 1243–1246, doi:10.1126/science.1180315, 2010.

Škrabalová, L., Brus, D., Anttila, T., Ždímal, V., and Lihavainen, H.: Growth of sulphuric acid nanoparticles under wet and dry conditions, Atmos. Chem. Phys., 14, 6461–6475, doi:10.5194/acp-14-6461-2014, 2014.

Slanina, J., ten Brink, H. M., Otjes, R. P., Even, A., Jongejan, P., Khlystov, S., Waijers-Ijpelaan, A., Hu, M., and Lu, Y.: The continuous analysis of nitrate and ammonium in aerosols by the steam jet aerosol collector (SJAC): extension and validation of the methodology, Atmos. Environ., 35, 2319–2330, doi:10.1016/S1352-2310(00)00556-2, 2001.

Spracklen, D. V., Carslaw, K. S., Kulmala, M., Kerminen, V.-M., Mann, G. W., and Sihto, S.-L.: The contribution of boundary layer nucleation events to total particle concentrations on regional and global scales, Atmos. Chem. Phys., 6, 5631–5648, doi:10.5194/acp-6-5631-2006, 2006.

ten Brink, H., Otjes, R., Jongejan, P., and Slanina, S.: An instrument for semi-continuous monitoring of the size-distribution of nitrate, ammonium, sulphate and chloride in aerosol, Atmos. Environ., 41, 2768–2779, doi:10.1016/j.atmosenv.2006.11.041, 2007.

Vanhanen, J., Mikkilä, J., Lehtipalo, K., Sipilä, M. M., Manninen, H., Siivola, E., Petäjä, T., and Kulmala, M.: Particle size magnifier for nano-CN detection, Aerosol Sci. Tech., 45, 533–542, doi:10.1080/02786826.2010.547889, 2011.

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, 4622, doi:10.1029/2002JD002184, 2002.

Viisanen, Y., Kulmala, M., and Laaksonen, A.: Experiments on gas–liquid nucleation of sulfuric acid and water, J. Chem. Phys., 107, 920, doi:10.1063/1.474445, 1997.

Weber, R. J., Marti, J. J., McMurry, P. H., Eisele, F. L., Tanner, D. J., and Jefferson, A.: Measured atmospheric new particle formation rates: implications for nucleation mechanisms, Chem. Eng. Commun., 151, 53–64, doi:10.1080/00986449608936541, 1996.

Wiedensohler, A. and Fissan, H. J.: Bipolar charge distributions of aerosol particles in high-purity argon and nitrogen, Aerosol Sci. Tech., 14, 358–364, doi:10.1080/02786829108959498, 1991.

Winkler, P. M., Steiner, G., Vrtala, A., Vehkamäki, H., Noppel, M., Lehtinen, K. E. J., Reischl, G. P., Wagner, P. E., and Kulmala, M.: Heterogeneous nucleation experiments bridging the scale from molecular ion clusters to nanoparticles, Science, 319, 1374–1377, doi:10.1126/science.1149034, 2008.

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, doi:10.5194/acp-8-4997-2008, 2008.

Yu, F.: From molecular clusters to nanoparticles: second-generation ion-mediated nucleation model, Atmos. Chem. Phys., 6, 5193–5211, doi:10.5194/acp-6-5193-2006, 2006.

Yu, F.: Ion-mediated nucleation in the atmosphere: key controlling parameters, implications, and look-up table, J. Geophys. Res., 115, D03206, doi:10.1029/2009JD012630, 2010.

Yu, F., Wang, Z., Luo, G., and Turco, R.: Ion-mediated nucleation as an important global source of tropospheric aerosols, Atmos. Chem. Phys., 8, 2537–2554, doi:10.5194/acp-8-2537-2008, 2008.

Zheng, J., Khalizov, A.,Wang, L., and Zhang, R.: Atmospheric pressure-ion drift chemical ionization mass spectrometry for detection of trace gas species, Anal. Chem., 82, 7302–7308, doi:10.1021/ac101253n, 2010.

Zollner, J. H., Glasoe, W. A., Panta, B., Carlson, K. K., McMurry, P. H., and Hanson, D. R.: Sulfuric acid nucleation: power dependencies, variation with relative humidity, and effect of bases, Atmos. Chem. Phys., 12, 4399–4411, doi:10.5194/acp-12-4399-2012, 2012.

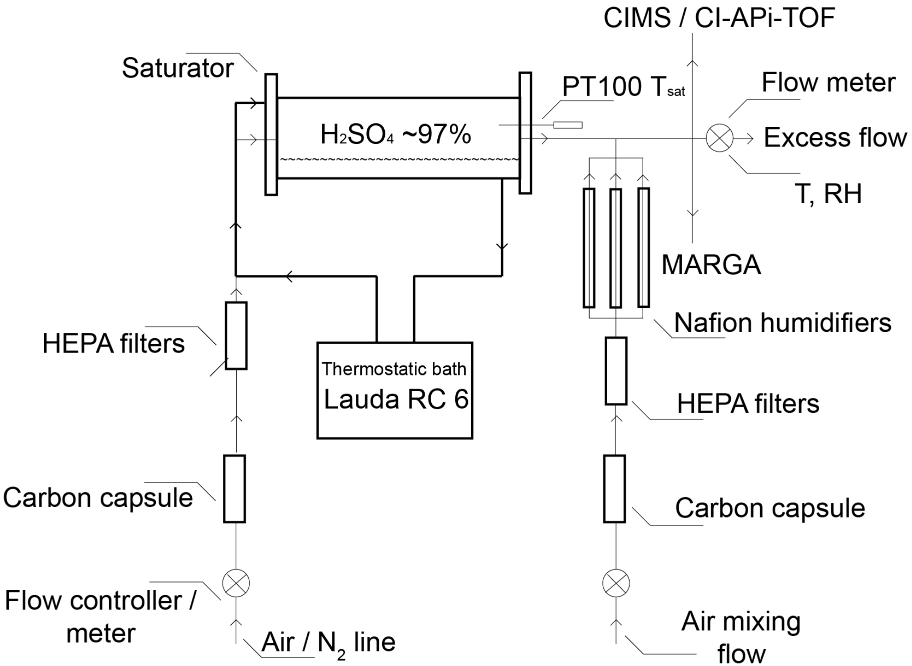

Figure 1. Sechematic figure of the setup for testing the saturator.

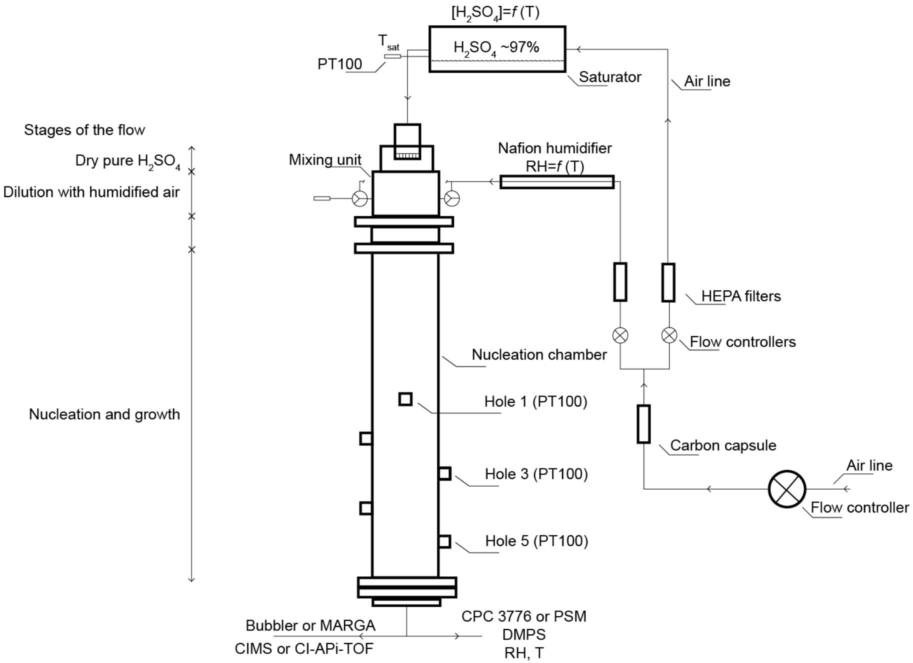

Figure 2. Flow tube setup.

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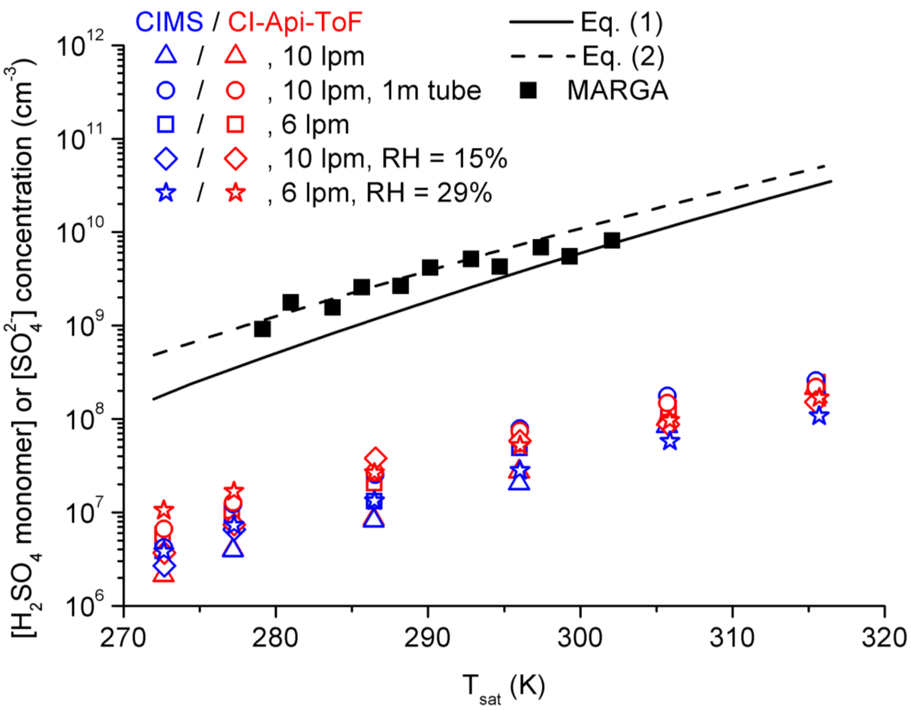

Figure 3. Measured sulphuric acid monomer $[H_2SO_4$ monomer] and total sulphate $[SO_4^{2-}]$ (black squares) concentrations together with predicted values by Eqs. (1) and (2) as a function of saturator temperature T_{sat}. Saturator flow rate is $Q_{sat} = 0.5$ lpm and mixing flow rates were 40 lpm (dry for CIMS and CI-APi-TOF and RH 15 %) and 20 lpm (MARGA and RH 29 %). CIMS (blue markers) and CI-APi-TOF (red markers) have been tested with 6 lpm and 10 lpm (nominal) inlet flow rates and also with an extra 1 m Teflon tubing after saturator.

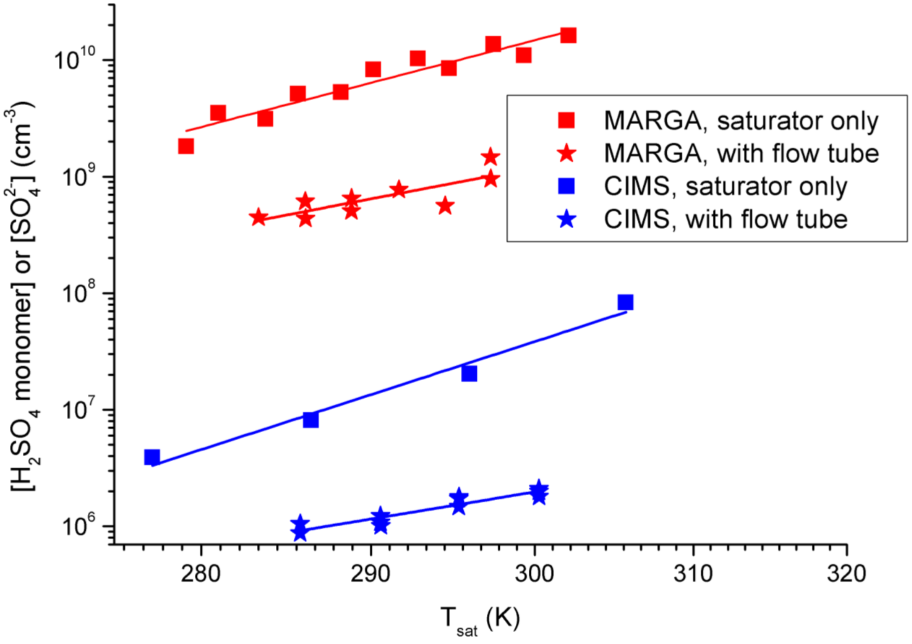

Figure 4. Comparison of MARGA and CIMS data between test with only saturator (dry conditions, squares) and with saturator and flow tube (RH ∼ 30 %, stars). Different flow rates through saturator have been accounted for. Average total loss factors are $TLF_{MARGA} = 10.0 \pm 1.2$ and $TLF_{CIMS} = 14.2 \pm 4.2$. See text for details.

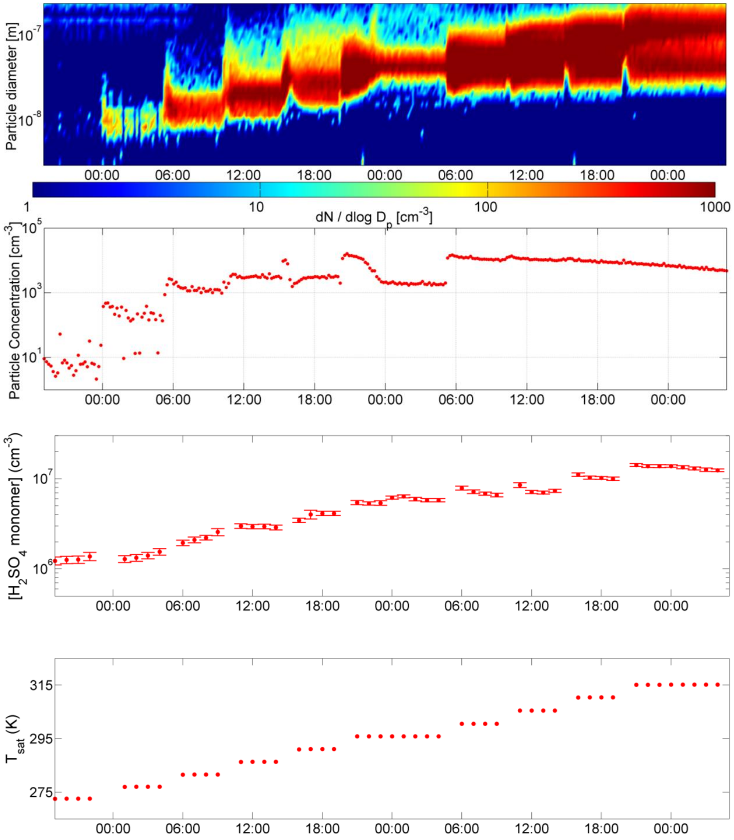

Figure 5. DMPS and CIMS data from one T_{sat} cycle. Upper most panel shows the number size distribution, 2nd panel from top shows the total number concentration from DMPS, 3rd panel presents the CIMS measured sulphuric acid monomer concentration averaged over one hour with SD as error bars and the last panel shows hourly averaged temperature of the saturator.

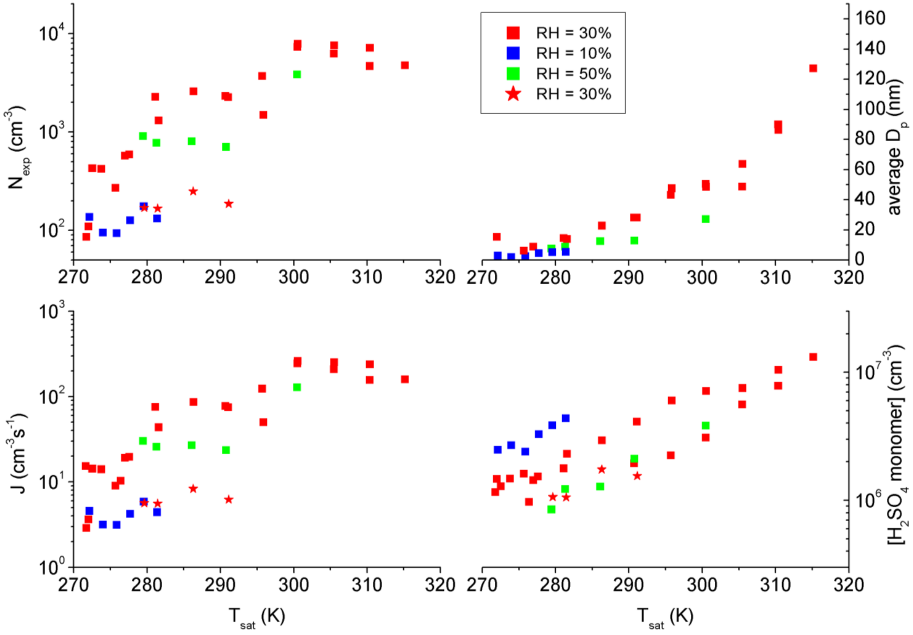

Figure 6. Number concentration N_{exp} (left upper panel) measured with PSM and TSI 3776, geometric mean diameter D_p (right upper panel), formation rate J (left lower panel) of the freshly nucleated particles and sulphuric acid monomer concentration measured with CIMS (squares) or CI-APi-TOF (stars) with several relative humidities as a function of saturator temperature with saturator flow of 0.1 lpm. All data is averaged over time period of constant saturator temperature extracting first hour. Stars are measured with CI-APi-TOF and squares with CIMS. All data is averaged over time period of constant saturator temperature (±0.05 K) extracting first hour.

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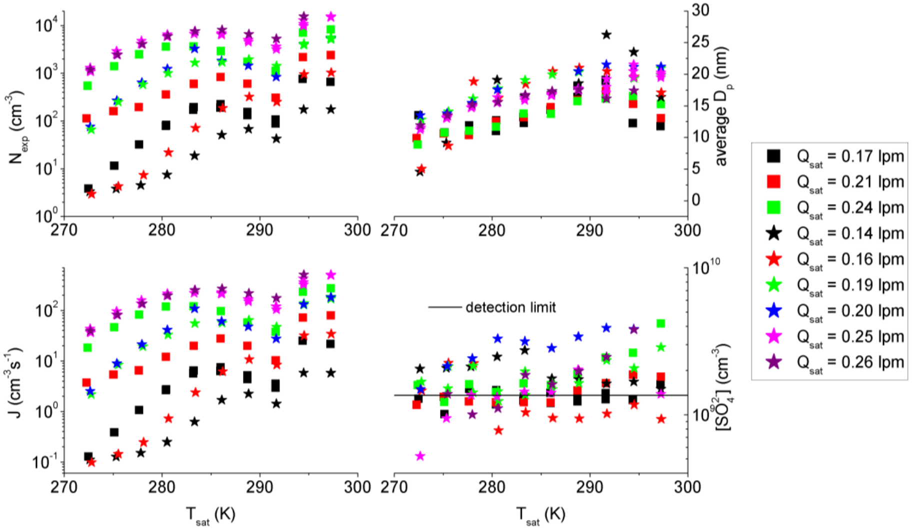

Figure 7. Number concentration N_{exp} (left upper panel) measured with TSI 3776, geometric mean diameter D_p (right upper panel), formation rate J (left lower panel) of the freshly nucleated particles and total sulphate concentration from MARGA (right lower panel) with detection limit of MARGA with several different saturator flow rates as a function of saturator temperature. Squares represents measurements at dry conditions, stars are measured with RH of ∼ 30 %. All data is averaged over time period of constant saturator temperature (±0.05 K) extracting first hour.

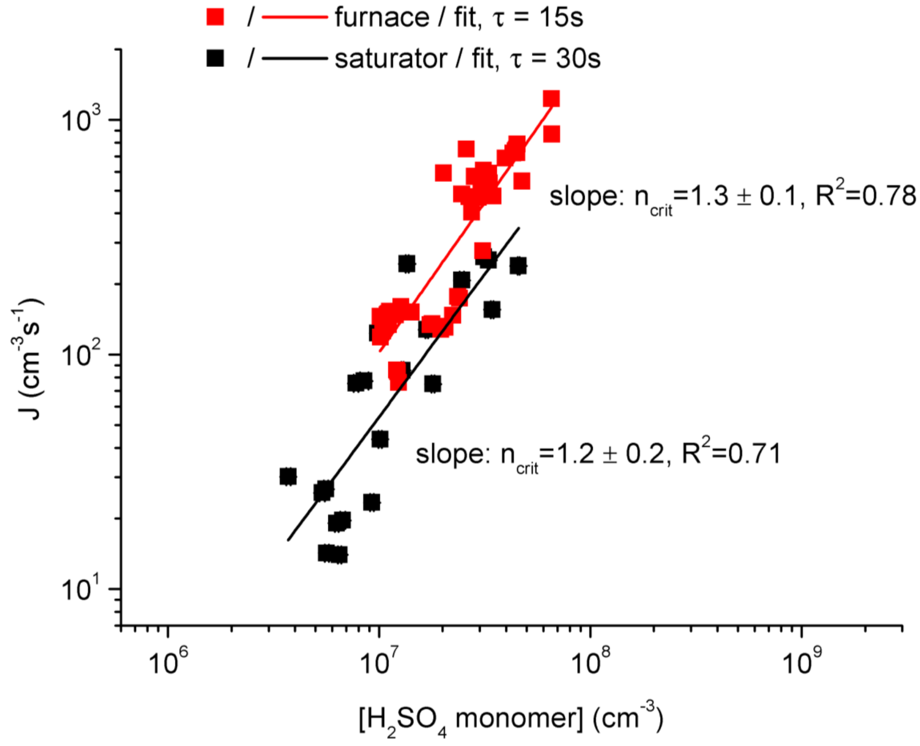

Figure 8. Formation rates J as a function of residual sulphuric acid monomer concentration [H_2SO_4 monomer] at $T = 298$ K and RH ~ 30 % measured using CIMS. In the first data set (red squares) sulphuric acid vapour was produced with furnace method and residence time was defined to be 15 s (Brus et al., 2011).

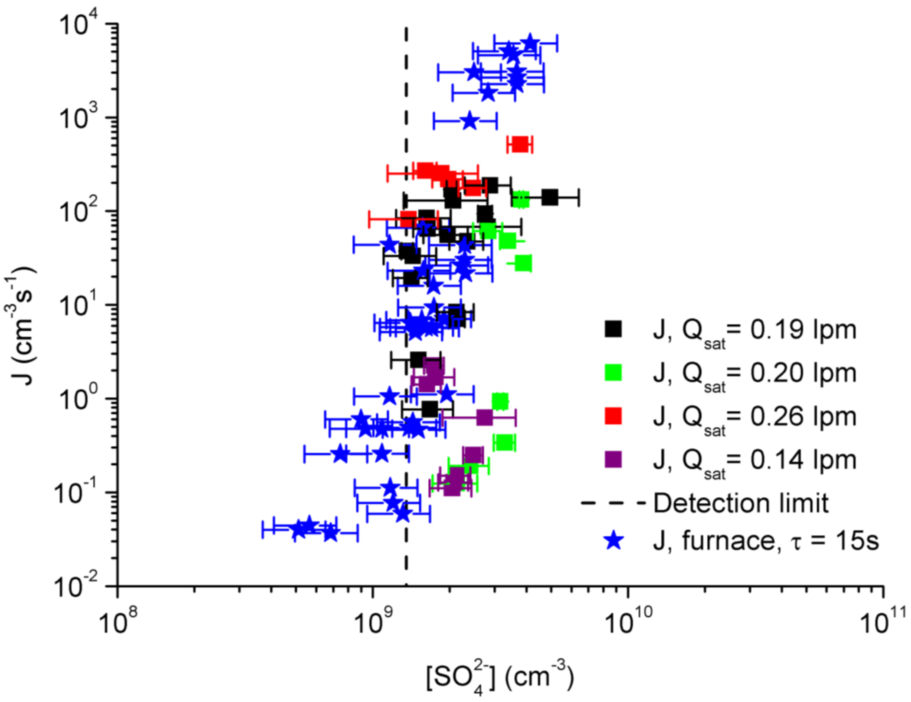

Figure 9. Formation rates J as a function of total sulphate concentration [SO_4^{2-}] measured with MARGA or bubbler with different saturator flow rates. MARGA's detection limit is marked with the dashed line. Relative humidity RH ~ 30 % and nucleation temperature T = 298 K. Sulphuric acid vapour was produced with furnace method (Brus et al., 2010) for bubbler measurements and with saturator method for MARGA.

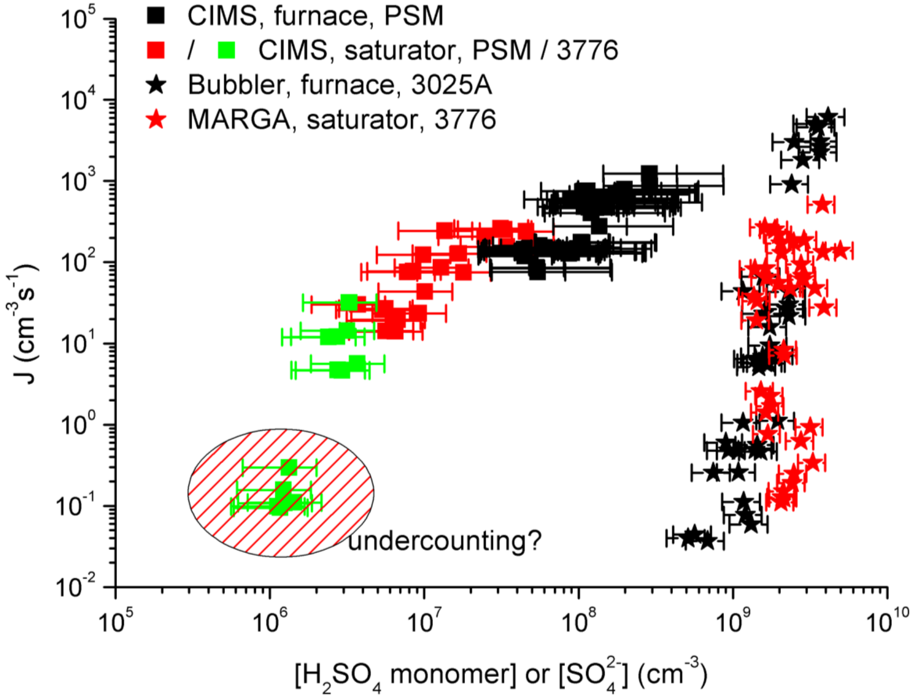

Figure 10. Comparison of formation rates *J* as a function of residual sulphuric acid monomer concentration $[H_2SO_4]$ or total sulphate concentration $[SO_4^{2-}]$ to our previous results. Conditions are similar ($T = 298$ K, RH ~ 30 %). Note the factor of two difference between the residence times between furnace and saturator measurements. Sulphuric acid vapour was previously produced with furnace method and total sulphate concentration measured with bubbler method (Brus et al., 2010).